



UNIVERSIDAD DE CÓRDOBA



FACULTAD DE CIENCIAS

Departamento de Química Orgánica

Grupo FQM 346: Catálisis Orgánica y Materiales Nanoestructurados

Instituto Químico para la Energía y el Medioambiente

**SÍNTESIS, CARACTERIZACIÓN Y APLICACIONES DE
MATERIALES DE NATURALEZA HÍBRIDA**

***SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF
MATERIALS WITH HYBRID NATURE***

Doctorado en Química Fina

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Memoria de Tesis Doctoral presentada por:

JUAN AMARO GAHETE

Para aspirar al grado de “Doctor por la Universidad de Córdoba”

Córdoba, DICIEMBRE de 2022

TITULO: *Síntesis, caracterización y aplicaciones de materiales de naturaleza híbrida*

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TÍTULO DE LA TESIS:

SÍNTESIS, CARACTERIZACIÓN Y APLICACIONES DE MATERIALES DE NATURALEZA HÍBRIDA

“SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF MATERIALS WITH HYBRID NATURE”

DOCTORANDO/A: Juan Amaro Gahete

INFORME RAZONADO DEL/DE LOS DIRECTOR/ES DE LA TESIS

La presente Memoria de Tesis Doctoral es el resultado del trabajo realizado por D. Juan Amaro Gahete en el grupo de investigación “Catálisis Orgánica y Materiales Nanoestructurados” (FQM-346), perteneciente al Departamento de Química Orgánica de la Universidad de Córdoba.

El doctorando ha llevado a cabo una intensa labor experimental que le ha permitido culminar con éxito los objetivos trazados en su plan de investigación. Para ello ha desarrollado una amplia variedad de destrezas, ha aprendido el manejo de diferentes técnicas e instrumentos científicos y la interpretación de la información suministrada por éstos, ha desarrollado capacidades relacionadas con la observación, la elaboración de hipótesis y conclusiones, la síntesis y el análisis de los resultados, y ha adquirido amplios conocimientos, incluso más allá de los temas relacionados directamente con los contenidos de su Tesis Doctoral. Todo ello, junto a su gran implicación, dedicación, iniciativa y autonomía, se reflejan en esta memoria de Tesis.

Los objetivos establecidos para esta Tesis Doctoral fueron enormemente ambiciosos y el doctorando ha aportado lo mejor de sí para cumplirlos de manera satisfactoria. El campo de los materiales híbridos es

extraordinariamente amplio. Incluso aquéllos de naturaleza orgánico-inorgánica son muy abundantes. En esta Tesis se han estudiado tres familias de estos materiales, todos ellos de gran trascendencia en la actualidad: polímeros de coordinación, incluyendo redes metal-orgánicas, organosílices periódicas mesoporosas, y materiales basados en grafeno.

Los polímeros de coordinación desarrollados en esta Tesis a partir de compuestos quirales procedentes de productos naturales y derivados han sido aplicados como catalizadores ácidos de Lewis para un proceso interesante en Química Fina, como es la cianosililación de diferentes benzaldehídos, destacando la enantioselectividad obtenida hacia las cianohidrininas correspondientes. Con relación a las redes metal-orgánicas, en esta Tesis se han descrito procedimientos de síntesis mejorados y el uso de los materiales resultantes en dos ámbitos muy diferentes. Por un lado, se emplearon diversos tipos de redes a la adsorción de etileno, gas esencial en la maduración de frutas. Por otro lado, se usaron como matrices para la incorporación de azufre con vistas a su integración en el cátodo de baterías Li-S.

Las organosílices periódicas mesoporosas han sido aplicadas como catalizadores biomiméticos en fotosíntesis artificial. Previamente, el doctorando realizó la síntesis de un precursor organosilícico, que contenía un análogo del centro activo de la enzima [FeFe]-hidrogenasa, y lo incorporó en la matriz. Con antelación, se realizó un exhaustivo trabajo de investigación bibliográfico para comprender, contextualizar y sentar las bases del futuro de este apasionante campo.

El tercer bloque de esta Tesis ha consistido en la preparación de materiales híbridos basados en grafeno. En primer lugar, se realizó un trabajo de preparación de grafenos y su caracterización mediante un gran número de técnicas físicas y químicas, con el que el doctorando adquirió experiencia previa en el estudio de estos materiales, lo que le serviría de base para los trabajos posteriores. En segundo lugar, se funcionalizó el borde de las láminas grafénicas con un complejo organometálico, lo que permitió realizar un estudio sobre las propiedades luminiscentes del material híbrido. El interés de los resultados quedó reflejado en que la publicación resultante fue calificada por la revista como *Hot Paper*. En tercer lugar, partiendo de una metodología basada en el trabajo anterior, pero con etapas adicionales, se obtuvo un material grafénico con centros activos aislados de tipo FeN₄, que se estudió con excelentes resultados en procesos electrocatalíticos.

Fruto de las investigaciones señaladas de forma somera anteriormente, el doctorando ha publicado numerosos trabajos en revistas científicas de prestigio, amén de otras publicaciones como capítulos de libro y actas de congresos, lo que le ha permitido desarrollar una excelente

producción científica. Además, son dignas de destacar las estrechas colaboraciones científicas que se han establecido durante el desarrollo de esta Tesis, no sólo con grupos de investigación españoles sino también con importantes grupos de otros países, todos ellos gozando de un amplio reconocimiento internacional. Junto a ello, las estancias internacionales realizadas por el doctorando, que exceden en mucho los requisitos establecidos para conseguir la mención internacional, destacan la internacionalización de sus estudios de doctorado.

La extraordinaria formación del doctorando en sus estudios de Grado y Máster se ha completado durante su etapa doctoral. Las actividades formativas han sido fundamentales en este sentido y cabe destacar su participación en numerosas jornadas, cursos y congresos nacionales e internacionales, así como en actividades de divulgación científica, destacando las presentaciones orales realizadas en diversas ocasiones.

La integración del doctorando en el mundo académico ha sido completa, por cuanto ha participado en la impartición de clases a estudiantes de Grado, siempre que su contrato se lo ha permitido, como el del Programa de Formación del Profesorado Universitario. Así mismo, ha intervenido en enseñanza a estudiantes de Bachillerato en jornadas de divulgación orientadas a despertar vocaciones científicas.

En definitiva, consideramos que la calidad de la Tesis Doctoral presentada y la formación adquirida a lo largo de sus estudios de Doctorado en el programa de Química Fina por D. Juan Amaro Gahete son excelentes.

Por todo ello, autorizamos y respaldamos la presentación de la Tesis Doctoral.

Córdoba, 26 de Septiembre de 2022

Firma de los directores



Fdo.: Francisco José Romero Salguero Fdo.: César Jiménez Sanchidrián

D. Antonio Ángel Romero Reyes, Director del Departamento de Química Orgánica de la Universidad de Córdoba,

CERTIFICA:

Que el presente Trabajo de Investigación, titulado “**SÍNTESIS, CARACTERIZACIÓN Y APLICACIONES DE MATERIALES DE NATURALEZA HÍBRIDA**”, que constituye la Memoria presentada por D. Juan Amaro Gahete para optar al título de Doctor en Química, ha sido realizado en los laboratorios del Departamento de Química Orgánica de la Universidad de Córdoba, bajo la dirección de los profesores **D. Francisco José Romero Salguero** y **D. César Jiménez Sanchidrián**, así como en el Departamento de Química (Ångström Laboratory) de la Universidad de Uppsala (Suecia), durante la estancia de seis meses que realizó bajo la supervisión del profesor **Dr. Sascha Ott**.

Y para que conste, firmo el presente certificado en Córdoba, a 26 de Septiembre de 2022.



Fdo. D. Antonio Ángel Romero Reyes

“Lo más bello que podemos experimentar es el lado misterioso de la vida; es el sentimiento profundo que se encuentra en la cuna del arte y de la ciencia verdadera.”

Albert Einstein

“La ciencia y la vida cotidiana no pueden ni deben ser separadas.”

Rosalind Franklin

“Estoy entre aquellos que piensan que la ciencia tiene una gran belleza.”

Marie Curie

“El éxito no es la victoria, sino todo lo que has peleado por ganar.”

“Lo básico es creer en ti e intentar dar lo mejor de uno mismo cada día.”

Rafael Nadal

“Haz de tu vida un sueño, y de tu sueño una realidad.”

Antoine de Saint-Exupéry

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Capítulo 1

Resumen General

RESUMEN DE LA TESIS DOCTORAL “SÍNTESIS, CARACTERIZACIÓN Y APLICACIONES DE MATERIALES DE NATURALEZA HÍBRIDA”

1.1. Motivación de la Tesis Doctoral

La posibilidad de llevar a cabo una combinación sinérgica de las propiedades de compuestos orgánicos y sustratos inorgánicos en un único material con características mejoradas es un antiguo desafío científico en continuo auge que comenzó a principios del siglo XVII y se ha extendido hasta la actualidad. En general, los materiales híbridos orgánico-inorgánicos representan la interfaz natural entre dos mundos de la química, cada uno con contribuciones muy significativas al campo de la ciencia de los materiales. La integración de ambas unidades estructurales a escala nanométrica otorga al material resultante propiedades características adicionales a las que poseen los propios componentes individualmente, resultando en diversas ventajas muy relevantes para aplicaciones específicas de gran interés tecnológico e industrial. Específicamente, los materiales híbridos orgánico-inorgánicos presentan las principales ventajas de los óxidos inorgánicos, exhibiendo una alta estabilidad mecánica, térmica y estructural, sin perder las versátiles características de los polímeros orgánicos, como la flexibilidad y la variabilidad funcional.

Se han empleado diferentes metodologías de síntesis para preparar sólidos híbridos incluyendo desde los procedimientos mecanoquímicos más simples basados en mezclas físicas hasta estrategias de síntesis más atractivas como procesos específicos de tipo sol-gel o preparaciones determinadas bajo condiciones solvotermales, ultrasonidos o incluso radiación microondas. La gran versatilidad ofrecida en el diseño de

materiales híbridos orgánico-inorgánicos permite su empleo en una amplia gama de aplicaciones de gran trascendencia en procesos actuales vinculados a la Química Fina. La presente Tesis Doctoral se ha abordado en base a tres grandes bloques temáticos de materiales híbridos orgánico-inorgánicos: **1) *polímeros de coordinación***, **2) *materiales híbridos orgánico-inorgánicos basados en sílices*** y **3) *materiales híbridos basados en grafeno***.

Los polímeros de coordinación han recibido una gran atención en las últimas décadas. Estos materiales pueden mostrar una amplia variedad de propiedades relevantes que pueden ser moduladas mediante una selección adecuada de nodos metálicos y conectores orgánicos funcionales. Los llamados metal-organic frameworks (MOFs) o redes metal-orgánicas, han aparecido como una importante clase de polímeros de coordinación. Los MOFs son catalogados como materiales porosos cristalinos formados por la unión de centros metálicos a través de ligandos orgánicos para generar estructuras que se extienden en el espacio en varias dimensiones. Por tanto, estos materiales despiertan gran interés entre la comunidad científica pudiendo ser utilizados en un amplio rango de aplicaciones como el almacenamiento de gases, adsorción de contaminantes orgánicos emergentes, purificación y separación de gases, (foto)catálisis o energía.

Respecto a las arquitecturas híbridas orgánico-inorgánicas basadas en sílice, los materiales periódicos mesoporosos organosilícicos (PMOs) han supuesto un avance fundamental en el campo de nuevos materiales porosos ordenados con características únicas. La integración de grupos funcionales orgánicos en estructuras inorgánicas de sílice supone una estrategia particularmente atractiva desde el punto de vista científico y amplía el campo de aplicación de estos materiales. En cuanto a la metodología de síntesis, cabe destacar que la preparación de un PMO aún

las ventajas y solventa las limitaciones de los procedimientos de anclaje post-síntesis (“grafting”) y co-condensación comúnmente empleados para la preparación de sílices mesoporosas. La construcción de un material PMO consiste en la condensación de precursores organosilícicos de tipo $(R'O)_3-Si-R-Si-(OR')_3$, donde R es el grupo orgánico puente insertado en las paredes de la estructura silícea y R' generalmente es un grupo metilo o etilo, en presencia de un surfactante que actúa como agente director de estructura. Estos materiales presentan elevada superficie específica, estrecha distribución de tamaño de poro en el rango mesoporoso, paredes porosas de amplio grosor y canales hexagonales abiertos completamente accesibles para posteriores procesos de funcionalización. Por ende, estos sólidos híbridos son candidatos ideales para ser aplicados en procesos catalíticos y de adsorción o empleados como soportes cromatográficos, sensores químicos, elementos fotoactivos y agentes de encapsulación y liberación de fármacos, debido a las extraordinarias propiedades mecánicas, ópticas, eléctricas, magnéticas y estructurales que poseen.

Los materiales híbridos basados en grafeno reúnen las excelentes propiedades fisicoquímicas propias del grafeno como material 2D incluyendo su elevada conductividad eléctrica y térmica, flexibilidad, transparencia, resistencia, movilidad electrónica o superficie específica, con los atributos proporcionados por otras especies, creando un material con características mejoradas que surgen de la interacción sinérgica de ambos componentes. La implementación del enfoque híbrido del grafeno llevando a cabo diferentes metodologías sintéticas permite potenciar los rendimientos en multitud de aplicaciones tecnológicas en el campo de sensores, purificación de agua, almacenamiento de energía, biomedicina, fotocatalisis, electrocatalisis y optoelectrónica.

1.2. Marco y contextualización

La presente Memoria de Tesis Doctoral titulada **“Síntesis, caracterización y aplicaciones de materiales de naturaleza híbrida”** dirigida por los Doctores D. Francisco José Romero Salguero y D. César Jiménez Sanchidrián, se encuadra en la línea de investigación “Materiales híbridos orgánico-inorgánicos” desarrollada en la actualidad por el grupo FQM-346 “Catálisis Orgánica y Materiales Nanoestructurados” del Departamento de Química Orgánica de la Universidad de Córdoba.

Fundamentalmente, esta Memoria se ha elaborado gracias a la ayuda predoctoral para la formación de profesorado universitario (FPU) con referencia FPU17/03981 concedida por el Ministerio de Universidades (Gobierno de España) y que ha posibilitado la financiación de esta Tesis Doctoral por un periodo total de 4 años (22/10/2018- 21/10/2022). Los trabajos realizados han contribuido al desarrollo de los proyectos MAT2013-44463-R “Construcción de superficies homoquirales estereoespecíficas sobre materiales híbridos orgánicos-inorgánicos y poliméricos estructurados”, MAT2017-89568-R “Transcripción quiral en catálisis heterogénea” y RTI2018-101611-B-I00 “Transformación fotocatalítica de CO₂ en combustibles solares utilizando nanocomposites basados en hidróxidos dobles laminares y grafenos” subvencionados por el Ministerio de Ciencia, Innovación y Universidades, así como del proyecto RAMÓN ARECES 16 “Catalizadores biomiméticos heterogéneos basados en arquitecturas híbridas orgánico-inorgánicas funcionalizadas para producción de hidrógeno” financiado por la Fundación Ramón Areces. Asimismo, estas investigaciones han recibido subvenciones del Gobierno Regional de la Junta de Andalucía y los Fondos Europeos de Desarrollo Regional (FEDER).

La propuesta de la presente Tesis Doctoral, así como las de los Proyectos de I+D+i donde se engloba, se encuentran estrechamente relacionadas con las líneas estratégicas establecidas en el programa marco de investigación e innovación (I+I) de la Unión Europea (UE) “Horizonte Europa 2021-2027”, concretamente con el “El Pilar 2: Desafíos Globales y Competitividad Industrial Europea” orientado a resolver los grandes desafíos de la sociedad española y mundial (salud, cambio climático, energías renovables, movilidad, seguridad, digital, materiales, etc.).

Asimismo, las temáticas de las investigaciones plasmadas en la presente memoria están estrechamente ligadas con algunos de los 17 Objetivos de Desarrollo Sostenible (Agenda 2030) aprobados en 2015 por parte de la Organización de las Naciones Unidas (ONU) para hacer frente a las metas específicas establecidas en cada uno de ellos, sobre todo aquellas relacionadas con el cambio climático, energía renovable eficiente y sostenible, el desarrollo del sector industrial y la conservación del medio ambiente.

Mediante la defensa de esta Memoria de Tesis Doctoral se pretende optar a la obtención del título de Doctor con Mención Internacional, habida cuenta de que el doctorando reúne los requisitos para tal mención, según el artículo 35 de la Normativa Reguladora de los Estudios de Doctorado de la Universidad de Córdoba:

1.- El doctorando ha realizado una estancia de seis meses de duración en el Departamento de Química del Ångström Laboratory dentro del grupo de investigación Synthetic Molecular Chemistry de la Universidad de Uppsala (Suecia) bajo la supervisión del Dr. Sascha Ott.

2.- Parte de la Memoria de la Tesis Doctoral se ha redactado en una lengua distinta de las lenguas oficiales de España.

3.- Cuenta con los informes favorables de dos doctores expertos con experiencia acreditada, pertenecientes a una institución no española de Educación Superior:

Prof. Carlos Baleizão (Centro de Química Estrutural, Instituto Superior Técnico (IST), University of Lisbon, Lisbon, Portugal)

Prof. Fredy Alexander Rodriguez Rivas (Departamento de Química, Universidad Nacional Autónoma de Honduras, Tegucigalpa, Honduras)

4.- Un miembro del tribunal que ha de evaluar la Tesis es un doctor experto con experiencia acreditada, perteneciente a una institución no española de Educación Superior, y es distinto del responsable de la estancia mencionada en el primer apartado:

Dr. Alvaro Yamil Tesio (Centro de Desarrollo Tecnológico General Manuel Savio, CIDMEJu (CONICET), Universidad Nacional de Jujuy, San Salvador de Jujuy, Argentina)

5.- La presentación de parte de esta Tesis Doctoral se realizará en una lengua distinta de las lenguas oficiales de España.

1.3. Contenido de la Investigación

La presente Tesis Doctoral aborda la síntesis, funcionalización, caracterización y aplicaciones de una extensa variedad de materiales híbridos orgánico-inorgánicos. Los resultados obtenidos en esta investigación han sido clasificados en tres secciones atendiendo a la naturaleza híbrida del material diseñado:

• **Sección 1: Polímeros de coordinación-Metal Organic Frameworks (MOFs):**

- En el artículo *“Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions”* se han sintetizado polímeros de coordinación que contienen zirconio como nodo metálico y ligandos orgánicos procedentes de productos naturales sencillos que contienen centros quirales como son el ácido L-málico, L-tartárico y dibenzoil-L-tartárico. Los materiales fueron preparados en autoclave bajo presión autógena o en reactor tipo batch bajo presión atmosférica. Tras ser caracterizados por diferentes técnicas, se han evaluado como catalizadores heterogéneos quirales en la reacción asimétrica de cianosililación del benzaldehído con cianuro de trimetilsililo dando como resultado la formación de cianohidrininas. La actividad catalítica en términos de conversión y enantioselectividad fue determinada estudiando el efecto de diferentes variables de reacción como la temperatura, el disolvente, la adición de promotores o el sustrato empleado.

- En el artículo *“Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents”* se han sintetizado partículas altamente cristalinas del MOF MIL-88A compuesto por trímeros de octaedros de hierro (III) interconectados a través de dianiones fumarato mediante una metodología rápida asistida por ultrasonidos. La influencia del generador de sonicación y el tiempo de síntesis en la estructura, cristalinidad, morfología y el área superficial fue estudiada detalladamente. Además, los materiales preparados han

sido aplicados en procesos de adsorción de etileno. Estos resultados fueron comparados con los obtenidos por otros MOFs comunes ampliamente reportados en literatura.

- El artículo “*MIL-88A Metal-Organic Framework as a stable sulfur-host cathode for long-cycle Li-S batteries*” estuvo en consonancia con el trabajo anterior. Aprovechando las propiedades texturales y morfológicas de las partículas MIL-88A sintetizadas mediante el método de sonda asistida por ultrasonidos en un corto tiempo de 10 minutos, este material fue empleado como anfitrión para la impregnación de azufre con objeto de ser usado como componente catódico en baterías Litio-Azufre (Li-S), uno de los sistemas más avanzados de almacenamiento de energía. Además, la estabilidad del sistema electroquímico resultante fue evaluada llevando a cabo experimentos de ciclabilidad a tiempos prolongados.

- **Sección 2: Materiales híbridos orgánico-inorgánicos basados en sílice-Periodic Mesoporous Organosilicas (PMOs):**

- El artículo “*Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production*” consistió en una revisión exhaustiva que abordó el campo de la química biomimética de los sistemas catalíticos que imitan el sitio activo de [FeFe]-hidrogenasa aplicados en la producción de hidrógeno dirigida por luz. Los diferentes sistemas fotocatalíticos fueron clasificados por grupos en orden de complejidad creciente y por su desarrollo cronológico:

catalizadores moleculares [2Fe2S], díadas de fotosensibilizador - [FeFe]-hidrogenasa, tríadas de donador de electrones - fotosensibilizador - [FeFe]-hidrogenasa, entidades supramoleculares, conjuntos de semiconductores híbridos, soportes heterogéneos y fotocátodos basados en [2Fe2S] para dispositivos fotoelectroquímicos (PEC).

- El artículo de revisión citado anteriormente sirvió para llevar a cabo el trabajo *“Hydroxyl-decorated diiron complex as a [FeFe]-hydrogenase active site model complex: Light-driven photocatalytic activity and heterogenization on ethylene-bridged periodic mesoporous organosilica”* en que un complejo modelo biomimético del sitio activo de [FeFe]-hidrogenasa (FeFeOH) con un puente de etileno y un grupo hidroxilo colgante fue sintetizado y caracterizado detalladamente. La interacción del grupo hidroxilo presente en el complejo con 3-isocianatopropiltriatoxisilano proporcionó un carbamato triatoxisilano portador de un complejo ditiolato de dihierro (NCOFeFe), convirtiéndose así en un precursor potencialmente prometedor para su anclaje sobre soportes heterogéneos. A continuación, el precursor NCOFeFe fue incorporado mediante un procedimiento de “grafting” en una organosílice periódica mesoporosa con puentes etano (EthanePMO@NCOFeFe). Adicionalmente, tanto los complejos moleculares como los heterogeneizados se evaluaron como catalizadores para la generación de hidrógeno en solución acuosa impulsada por la luz, optimizando todas las condiciones fotocatalíticas: tiempo de reacción, pH, cantidad de catalizador o fotosensibilizador, flujo de fotones y tipo de fuente de luz (LED y lámpara Xe).

- **Sección 3: Materiales híbridos basados en grafeno:**

- En el artículo “*A comparative study of particle size distribution of graphene nanosheets synthesized by an ultrasound-assisted method*” se han preparado nanoláminas de grafeno (GNS) mediante la exfoliación de un micrografito comercial (MG) utilizando una sonda de ultrasonido. La caracterización estructural, superficial y morfológica fue realizada por difracción de rayos X (DRX), espectroscopia Raman, espectroscopia de fotoelectrones de rayos X (XPS) y microscopía electrónica de transmisión (TEM). Un estudio exhaustivo de la distribución del tamaño de partícula se llevó a cabo mediante diferentes técnicas analíticas como la dispersión de luz dinámica (DLS), análisis de seguimiento de nanopartículas (NTA) y fraccionamiento en flujo mediante campo de flujo asimétrico (AF4).
- En el artículo “*Luminescent graphene-based materials via europium complexation on dipyridylpyridazine-functionalized graphene sheets*” se sintetizaron materiales híbridos basados en grafeno mediante reacciones Diels-Alder entre grafito (dienófilo) y la molécula orgánica 3,6-di(2-piridil)-1,2,4,5-tetrazina (dieno). Se obtuvieron grafeno de pocas capas (FLG), grafeno multicapa (MLG) y grafito (MG) funcionalizados con unidades de dipiridilpiridazina dependiendo de la metodología de síntesis aplicada. Los aductos superficiales de dipiridilpiridazina generados en las láminas de grafeno han sido empleados para la formación de complejos de europio, como ejemplos de iones lantánidos emisores en el visible.

- En el artículo “*Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN₄ sites for ORR and OER electrocatalysis*” se propone una nueva síntesis mecanoquímica a baja temperatura y sin disolventes basada en el uso de grafeno multicapa funcionalizado con dipiridilpiridazina como material de partida para la generación de sitios activos de tipo FeN₄. Después de una caracterización exhaustiva, estos materiales fueron aplicados como electrocatalizadores bifuncionales para reacciones electroquímicas de reducción de oxígeno (ORR) y evolución de oxígeno (OER).

Chapter 1

Overall Summary

**SUMMARY OF THE DOCTORAL THESIS
“SYNTHESIS, CHARACTERIZATION AND
APPLICATIONS OF MATERIALS WITH HYBRID
NATURE”**

1.1. Motivation of the Doctoral Thesis

The possibility of carrying out a synergistic combination of the properties of organic compounds and inorganic substrates in a single material with improved characteristics is a constantly growing old scientific challenge that began at the beginning of the 17th century and has extended to the present. In general, organic-inorganic hybrid materials represent the natural interface between two worlds of chemistry, each with very significant contributions to the field of materials science. The integration of both structural units at the nanometric scale gives the resulting material additional characteristic properties to those possessed by the components themselves individually, resulting in various highly relevant advantages for specific applications of great technological and industrial interest. Specifically, the organic-inorganic hybrid materials present the main advantages of inorganic oxides, exhibiting high mechanical, thermal and structural stability, without losing the versatile characteristics of organic polymers, such as flexibility and functional variability. Different synthesis methodologies have been used to prepare hybrid solids, ranging from the simplest mechanochemical procedures based on physical mixtures to more attractive synthesis strategies such as specific sol-gel processes or specific preparations under solvothermal conditions, ultrasound or even microwave radiation. The great versatility offered in the design of hybrid organic-inorganic materials allows their use in a wide range of great important

applications for current processes related to Fine Chemistry. This Doctoral Thesis has been addressed in according to three main thematic blocks of organic-inorganic hybrid materials: *1) coordination polymers, 2) silica-based organic-inorganic hybrid materials and 3) graphene-based hybrid materials.*

Coordination polymers have received a great deal of attention in recent decades. These materials can display a wide variety of relevant properties that can be modulated by a suitable selection of metallic nodes and functional organic connectors. The so-called metal-organic frameworks (MOFs) or metal-organic networks have emerged as an important class of coordination polymers. MOFs are defined as porous crystalline materials formed by the union of metal centers through organic ligands to generate structures extended in various dimensions. Therefore, these materials arouse great interest among the scientific community and can be used in a lot of applications such as gas storage, adsorption of emerging organic pollutants, gas purification and separation, (photo)catalysis or energy.

Among the silica-based organic-inorganic hybrid architectures, periodic mesoporous organosilica materials (PMOs) have represented a fundamental advance in the field of new ordered porous materials with unique characteristics. The integration of functional groups in inorganic silica structures is a particularly attractive strategy from the scientific point of view and broadens the field of application of these materials. Regarding the synthesis methodology, it should be noted that the preparation of a PMO combines the advantages and overcomes the limitations of the post-synthesis anchoring procedures (“grafting”) and co-condensation used for the preparation of mesoporous silicas. The synthesis of a PMO material consists of the condensation of organosilicon precursors of the type $(R'O)_3Si-R-Si-(OR')_3$, where R is the organic bridging group inserted in the walls

of the siliceous structure and R' is generally a methyl or ethyl group, in the presence of a surfactant that acts as a structure-directing agent. These materials have a high surface area, a narrow pore size distribution in the mesoporous range, thick pore walls, and open hexagonal channels that are fully accessible for subsequent functionalization processes. Finally, these hybrid solids are ideal candidates to be applied in catalytic and adsorption processes or used as chromatographic supports, chemical sensors, photoactive elements, and drug encapsulation and release agents, due to their extraordinary mechanical, optical, electrical, magnetic, and structural properties.

Graphene-based hybrid materials combine the excellent physicochemical properties of graphene as a 2D material, including its high electrical and thermal conductivity, flexibility, transparency, resistance, electronic mobility, or specific surface, with the attributes provided by other species, creating a material with enhanced characteristics arising from the synergistic interaction of both components. The implementation of the hybrid approach of graphene, carrying out different synthetic methodologies, allows boosting performance in many technological applications in the field of sensors, water purification, energy storage, biomedicine, photocatalysis, electrocatalysis and optoelectronics.

1.2. Framework and contextualization

This Doctoral Thesis entitled "**Synthesis, characterization and applications of materials with hybrid nature**" supervised by professors Dr. Francisco José Romero Salguero and Dr. César Jiménez Sanchidrián, falls under the research line "Organic-inorganic hybrid materials" currently developed by the group FQM-346 "Organic Catalysis and Nanostructured

Materials" of the Organic Chemistry Department at the University of Córdoba.

This work has been carried out mainly thanks to the predoctoral scholarship for the training of university professors (FPU) with reference FPU17/03981 granted by the Ministry of Universities (Government of Spain) and that has made it possible to finance this Doctoral Thesis for a total period of 4 years (22/10/2018 - 21/10/2022). This research has contributed to the progress of the projects MAT2013-44463-R "Construction of stereospecific homochiral surfaces on hybrid organic-inorganic and structured polymeric materials", MAT2017-89568-R "Chiral transcription in heterogeneous catalysis" and RTI2018-101611-B-I00 "Photocatalytic transformation of CO₂ into solar fuels using nanocomposites based on layered double hydroxides and graphenes" granted by the Ministry of Science, Innovation and Universities, as well as the RAMÓN ARECES 16 project "Heterogeneous biomimetic catalysts based on functionalized organic-inorganic hybrid architectures for hydrogen production" funded by the Ramón Areces Foundation. Likewise, these investigations have received subsidies from the Regional Government of the Junta de Andalucía and the European Regional Development Funds (FEDER).

The proposal of this Doctoral Thesis, as well as those of the I+D+i Projects where it is included, are closely related to the strategic lines established in the framework program for research and innovation (R+I) of the European Union (EU) "Horizon Europe 2021-2027", specifically in "Pilar 2: Global Challenges and European Industrial Competitiveness" aimed at solving the great challenges of Spanish and world society (health, climate change, renewable energies, mobility, security, digital, materials, etc.).

Moreover, the themes of the research reflected in this report are closely linked to some of the 17 Sustainable Development Goals (Agenda 2030) approved in 2015 by the United Nations (UN) to address the specific goals established in each of them, especially those related to climate change, efficient and sustainable renewable energy, the development of the industrial sector and the conservation of the environment.

Through the dissertation of this Doctoral Thesis Report, it is intended to obtain the title of Doctor with International Mention, since the doctoral student meets the necessary requirements, according to article 35 of the Regulations for Doctoral Studies of the University of Córdoba:

1.- The doctoral student has completed a six-month stay at the Chemistry Department of the Ångström Laboratory within the Synthetic Molecular Chemistry research group at Uppsala University (Sweden) under the supervision of professor Dr. Sascha Ott.

2.- Part of the Doctoral Thesis Report has been written in a language other than the official languages of Spain.

3.- It has favourable reports from two expert doctors with accredited experience, belonging to a non-Spanish institution of Higher Education:

Prof. Carlos Baleizão (Centro de Química Estrutural, Instituto Superior Técnico (IST), University of Lisbon, Lisbon, Portugal)

Prof. Fredy Alexander Rodríguez Rivas (Departamento de Química, Universidad Nacional Autónoma de Honduras, Tegucigalpa, Honduras)

4.- A member of the thesis committee who has to evaluate the Thesis is an expert doctor with accredited experience, belonging to a non-Spanish

institution of Higher Education, and is different from the person responsible for the stay mentioned in the first point:

Dr. Alvaro Yamil Tesio (Centro de Desarrollo Tecnológico General Manuel Savio, CIDMEJu (CONICET), Universidad Nacional de Jujuy, San Salvador de Jujuy, Argentina)

5.- The presentation of part of this Doctoral Thesis will be carried out in a language other than the official languages of Spain.

1.3. Research content

This Doctoral Thesis deals with the synthesis, functionalization, characterization, and applications of a wide variety of organic-inorganic hybrid materials. The results obtained in this research have been divided into three sections according to the hybrid nature of the designed material:

- **Section 1: Coordination Polymers-Metal Organic Frameworks (MOFs):**

- In the article “*Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions*”, coordination polymers containing zirconium as a metallic node and organic ligands from simple natural products containing chiral centers such as L-malic, L-tartaric and dibenzoyl-L-tartaric acids, have been synthesized. The materials were prepared in an autoclave under autogenous pressure or in a batch type reactor under atmospheric pressure. After being characterized by different techniques, they have been evaluated as chiral heterogeneous catalysts in the asymmetric cyanosilylation reaction of benzaldehyde with trimethylsilyl

cyanide, resulting in the formation of cyanohydrins. The catalytic activity in terms of conversion and enantioselectivity was determined by studying the effect of different reaction parameters such as temperature, solvent, the addition of promoters or the substrate used.

- In the article “*Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents*”, highly crystalline particles of the MOF MIL-88A composed of trimers of iron (III) octahedrons interconnected through fumarate dianions have been synthesized by a fast ultrasound-assisted methodology. The influence of the sonication generator and the synthesis time on the structure, crystallinity, morphology and surface area was studied in detail. In addition, the prepared materials have been applied in ethylene adsorption processes. These results were compared with those obtained by other common MOFs widely reported in the literature.
- The article “*MIL-88A Metal-Organic Framework as a stable sulfur-host cathode for long-cycle Li-S batteries*” was consistent with the previous work. Taking advantage of the textural and morphological properties of the MIL-88A particles synthesized by the ultrasound-assisted probe method in a short time of 10 minutes, this material was used as a sulfur host to be applied as a cathode component in Lithium-Sulfur (Li-S) batteries, one of the most advanced energy storage systems. In addition, the stability of the resulting electrochemical system was evaluated by carrying out long-term cyclability experiments.

- **Section 2: Silica-based organic-inorganic hybrid materials-Periodic Mesoporous Organosilicas (PMOs):**

- The article “*Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production*” was an exhaustive review that addressed the field of biomimetic chemistry of catalytic systems mimicking the active site of [FeFe]-hydrogenase applied in the light-driven hydrogen production. The different photocatalytic systems were classified by groups in order of increasing complexity and by their chronological development: [2Fe2S] molecular catalysts, photosensitizer-[FeFe]-hydrogenase dyads, electron donor-photosensitizer-[FeFe]-hydrogenase triads, supramolecular entities, hybrid semiconductor arrays, heterogeneous supports and [2Fe2S]-based photocathodes for photoelectrochemical (PEC) devices.
- The review article cited above served to carry out the work “*Hydroxyl-decorated diiron complex as a [FeFe]-hydrogenase active site model complex: Light-driven photocatalytic activity and heterogenization on ethylene-bridged periodic mesoporous organosilica*” in which a biomimetic model complex for the [FeFe]-hydrogenase active site (FeFeOH) with an ethylene bridge and a pendant hydroxyl group was synthesized and characterized in detail. The reaction of the hydroxyl group present in the complex with 3-isocyanatopropyltriethoxysilane provided a triethoxysilane carbamate bearing a complex diiron dithiolate (NCOFeFe), thus becoming a potentially promising precursor for its anchoring on heterogeneous supports. Next, the

precursor NCOFeFe was incorporated by a "grafting" procedure in a periodic mesoporous organosilica with ethane bridges (EthanePMO@NCOFeFe). Additionally, both molecular and heterogenized complexes were evaluated as catalysts for hydrogen evolution reactions in aqueous solution assisted by visible light, optimizing all the photocatalytic conditions: reaction time, pH, amount of catalyst or photosensitizer, photon flux and light source (LED and Xe lamp).

- **Section 3: Graphene-based hybrid materials:**

- In the article "*A comparative study of particle size distribution of graphene nanosheets synthesized by an ultrasound-assisted method*", graphene nanosheets (GNS) have been prepared by exfoliating a commercial micrographite (MG) using an ultrasound probe. Structural, surface, and morphological characterization was performed by X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). An exhaustive study of the particle size distribution was carried out using different analytical techniques such as dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and asymmetrical flow field - flow fractionation (AF4).
- In the article "*Luminescent graphene-based materials via europium complexation on dipyridylpyridazine-functionalized graphene sheets*", graphene-based hybrid materials were synthesized by Diels-Alder reactions between graphite (dienophile) and the organic molecule 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (diene). Few layer graphene (FLG), multilayer graphene

(MLG) and graphite (MG) functionalized with dipyridylpyridazine units were obtained depending on the synthesis methodology applied. Surface adducts of dipyridylpyridazine generated in graphene sheets have been used for the formation of europium complexes, as examples of emitting lanthanide ions in the visible.

- The article “*Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN₄ sites for ORR and OER electrocatalysis*” proposes a new mechanochemical synthesis at low temperature and without solvents based on the use of multilayer graphene functionalized with dipyridylpyridazine as starting material for the generation of FeN₄-type active sites. After extensive characterization, these materials were applied as bifunctional electrocatalysts for electrochemical oxygen reduction (ORR) and oxygen evolution (OER) reactions.

Capítulo 2

Introducción

2.1. Materiales híbridos orgánico-inorgánicos:

Preámbulo

Los materiales híbridos orgánico-inorgánicos representan una de las clases de materiales con mayor atención actualmente por parte de la comunidad científica e industrial, pues son considerados muy prometedores para lograr innovaciones tecnológicas y hacer frente a los principales desafíos a los que se enfrenta la sociedad mundial en el futuro. Por tanto, la ciencia de materiales híbridos ha atraído un enorme interés en muchos campos de investigación con el propósito de llevar a cabo un diseño integrador de materiales multifuncionales a partir de la interfaz creada entre dos mundos tan reconocidos e importantes de la química, cada uno con contribuciones muy significativas y propiedades fisicoquímicas características que resultan en grandes desafíos y oportunidades. El principal reto es conseguir sintetizar combinaciones híbridas que mantengan o potencien las mejores propiedades de cada uno de los componentes eliminando o reduciendo sus limitaciones particulares. Asumir este desafío brinda la oportunidad de desarrollar nuevos materiales con un comportamiento sinérgico que conduzca a un mejor rendimiento o a nuevas propiedades útiles. De hecho, los materiales híbridos suelen implicar una combinación de componentes que se han estudiado a fondo en sus respectivos campos, pero que proporcionan una dimensión adicional a sus propiedades al convertirse en parte del compuesto híbrido.

En comparación con los materiales convencionales, los materiales híbridos orgánico-inorgánicos tienen las características de rigidez, estabilidad dimensional y termoestabilidad derivadas de la fase inorgánica, así como las propiedades de versatilidad y funcionalidad derivadas de la fase orgánica. La fase inorgánica y orgánica puede alcanzar un tamaño nanométrico, lo que mejora drásticamente la interacción interfacial. Además, sus morfologías y propiedades se pueden ajustar en un amplio intervalo, lo que ayuda a extender el rango de aplicación ^[1-5].

Una definición actual de lo que entendemos por material híbrido la estableció la Unión Internacional de Química Pura y Aplicada (IUPAC): *“Un material híbrido está compuesto por una mezcla íntima de componentes inorgánicos, componentes orgánicos o ambos tipos de componentes. Nota: Los componentes suelen interpenetrarse en escalas*

inferiores a 1 μm " [6]. Esta definición incluye, por ejemplo, compuestos de polímero-polímero (también conocidos como mezclas), compuestos de metal-metal, compuestos de metal-cerámica, compuestos de metal-polímero y compuestos de cerámica-polímero. Por tanto, esta clasificación es imprecisa porque comprende una amplia gama de materiales, incluidos muchos tipos de materiales cristalinos inorgánicos y mezclas de polímeros. Una definición más específica sería: *Un material híbrido consta de al menos dos componentes, generalmente un componente inorgánico y un componente orgánico, que están dispersos en forma molecular y regularmente* [7]. Basado en esto, los materiales híbridos son un caso especial de compuestos que muestran una mezcla de los diferentes componentes en la escala de tamaño molecular, es decir, materiales preparados por reacción simultánea y controlada de especies inorgánicas de sílice/metal y precursores orgánicos de diferente naturaleza.

La interfase orgánico-inorgánica referida a la naturaleza de la interacción entre la fase orgánica y la matriz inorgánica tiene un papel fundamental en la modulación de las propiedades fisicoquímicas del material híbrido resultante. Por este motivo, se ha establecido una clasificación de los híbridos en dos grandes categorías según la naturaleza de la interfase orgánico-inorgánica, es decir, según el tipo de interacción química entre los componentes (**Figura 1**) [8,9]:

- En los *materiales híbridos de clase I*, existen interacciones débiles entre los componentes como son las fuerzas de Van der Waals (VdW), enlaces de hidrógeno e interacciones electrostáticas (**Figura 1a**).
- Los *materiales híbridos de clase II* muestran enlaces fuertes, es decir, interacciones covalentes o iónico-covalentes. Las interacciones iónico-covalentes son enlaces covalentes con un carácter iónico considerable que se encuentran a menudo, por ejemplo, en óxidos metálicos binarios o mixtos (**Figura 1b**). En los híbridos de clase II, las interacciones fuertes pueden ir acompañadas de interacciones débiles características de los híbridos clase I.

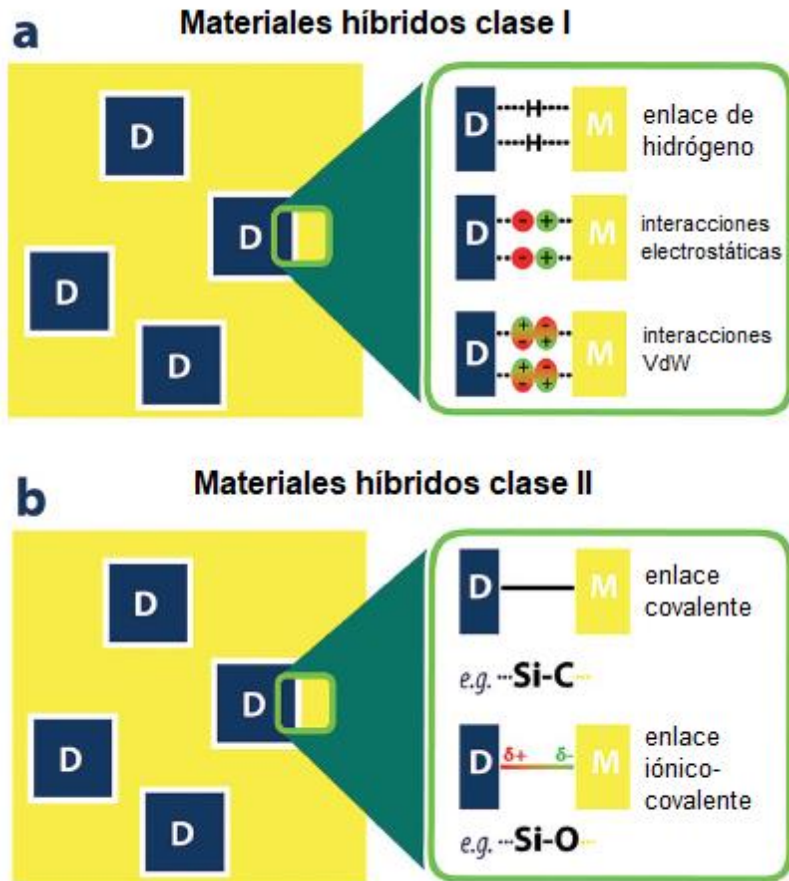


Figura 1. Categorías de materiales híbridos e importancia de la interfaz D-M. D = fase dispersa, M = matriz. (a) Los materiales híbridos de clase I exhiben interacciones débiles entre D y M. De arriba a abajo: enlaces de hidrógeno, interacciones electrostáticas o interacciones de Van der Waals (VdW). (b) Los materiales híbridos de clase II se caracterizan por fuertes interacciones (es decir, enlaces covalentes e iónico-covalentes) [7].

2.1.1. Evolución histórica

Desde el principio de los tiempos, la Naturaleza no esperó las sugerencias del hombre para utilizar el concepto de hibridación organomineral en la creación de materiales híbridos biológicos desarrollando multitud de arquitecturas, materiales y sistemas. De hecho, en un sentido general, la hibridación o el mestizaje son la base de la evolución, desde lo más elemental hasta los organismos más complejos.

Hace millones de años, los procesos de biomineralización produjeron materiales híbridos como, por ejemplo, caparazones de moluscos, conchas, marfil, huesos y dientes de animales con esqueleto óseo, diatomeas, bacterias magnetotácticas, ferritina, dientes de ciertos moluscos (quitones y lapas), etc., donde los biopolímeros (quitina, colágeno, otros azúcares y proteínas) se asocian inteligentemente con una amplia variedad de compuestos inorgánicos como carbonato de calcio, fosfatos de calcio, oxalatos de calcio, sílice, óxidos de hierro o composites ^[10-13]. De hecho, estos materiales híbridos naturales suelen ser sistemas inteligentes altamente integrados que saben cómo llegar a un compromiso entre diferentes funciones: comportamiento mecánico (flexibilidad frente a rigidez), densidad, permeabilidad controlada, color e hidrofobicidad. Dicha integración tiene dos aspectos: la miniaturización, que tiene como objetivo acomodar un número cada vez mayor de funciones elementales en un pequeño volumen, y la hibridación, en particular entre componentes minerales y orgánicos, que enriquece todo el sistema al combinar funciones seleccionadas extraídas de lo mejor de ambos mundos.

Una característica esencial de los materiales biológicos que funcionan de manera eficiente es su organización topológica y estructural en todas las escalas, nanométrica o supramolecular, micrométrica y, a menudo, milimétrica. La resistencia mecánica y la fiabilidad de estos sistemas jerárquicos parecen deberse a su capacidad para responder a fenómenos químicos y/o físicos resultantes de tensiones ejercidas a diferentes escalas. Las altas prestaciones obtenidas por los materiales híbridos del mundo vivo están ligadas a la noción del tiempo, de forma que la propia evolución ha seleccionado el material adecuado para el buen funcionamiento general del ecosistema.

Por su parte, el hombre ya había dado forma desde muy temprano en su historia a la materia y sus primeros logros de materiales híbridos organominerales se asocian, a menudo, con frescos u objetos desarrollados por casualidad, sin duda, pero también gracias a la creatividad de artistas y artesanos. La ciencia de los materiales híbridos comienza mucho más tarde y, en su mayor parte, entre el siglo XVII y la actualidad. Un resumen cronológico de la historia de los materiales híbridos se muestra en la **Figura 2**, donde se pueden distinguir cuatro períodos principales ^[14]. Esta línea temporal muestra una marcada aceleración en la producción de materiales híbridos tanto en cantidad como en calidad desde mediados del siglo XX.

El intervalo establecido al inicio de la escala de tiempo definido como *química prebiótica* se caracteriza históricamente por la aparición de los primeros materiales híbridos orgánicos-inorgánicos a base de arcilla. Presuntamente, los materiales arcillosos-orgánicos se formaron espontáneamente en la naturaleza, asumiendo ampliamente el papel crucial de los minerales arcillosos en el hipotético proceso de abiogénesis del origen de la vida ^[15-17]. De esta manera, está bien establecido que las partículas de arcillas coloidales que integran filosilicatos hinchables conducen a la adsorción entre capas y acomodación de especies orgánicas, dando lugar a complejos organoarcillosos de estabilidad variable. Los procesos de intercalación resultan de interacciones orgánico-inorgánicas que involucran mecanismos tales como fuerzas de Van der Waals, enlaces de hidrógeno y puentes de agua, enlaces electrostáticos, interacciones ion-dipolo, enlaces de coordinación, transferencias de protones y electrones, etc ^[18].

En este contexto, un punto llamativo de interés es que las arcillas exhiben características superficiales capaces de intercalar espontáneamente y catalizar la transformación de diversas especies moleculares de manera repetitiva, mostrando una capacidad de replicación inherente a los cuerpos vivos. De hecho, la capacidad de adsorción, la extensa área superficial, la acidez de la capa intermedia, la densidad de carga o la naturaleza de los cationes de la capa intermedia, son características que permiten procesos cíclicos de adsorción-transformación-desorción y, por lo tanto, pueden considerarse “templates” o materiales plantilla que presentan la capacidad de actuar como "replicadores moleculares". Esta sorprendente propiedad, junto con la capacidad de adsorber y concentrar selectivamente los componentes orgánicos prebióticos producidos durante el origen del planeta, se ha propuesto como una forma alternativa de intentar explicar la formación de sistemas complejos idealmente provistos de propiedades de autorreplicación en la Tierra primitiva. Cabe destacar la alta especificidad y la estereoselectividad quiral en la adsorción molecular selectiva de ciertos minerales arcillosos ^[17]. Por lo tanto, los compuestos intercalados orgánico-arcillosos formados altamente selectivos pueden considerarse compuestos híbridos que desempeñan un papel esencial para el desarrollo de la vida. Apoyando estas teorías, denominadas “hipótesis de la arcilla”, diversos ensayos experimentales confirmaron, por ejemplo, la polimerización de aminoácidos que conducen a polipéptidos y proteínas, las unidades básicas de los sistemas enzimáticos. Además, las arcillas muestran una gran afinidad por los ácidos nucleicos ^[19,20].

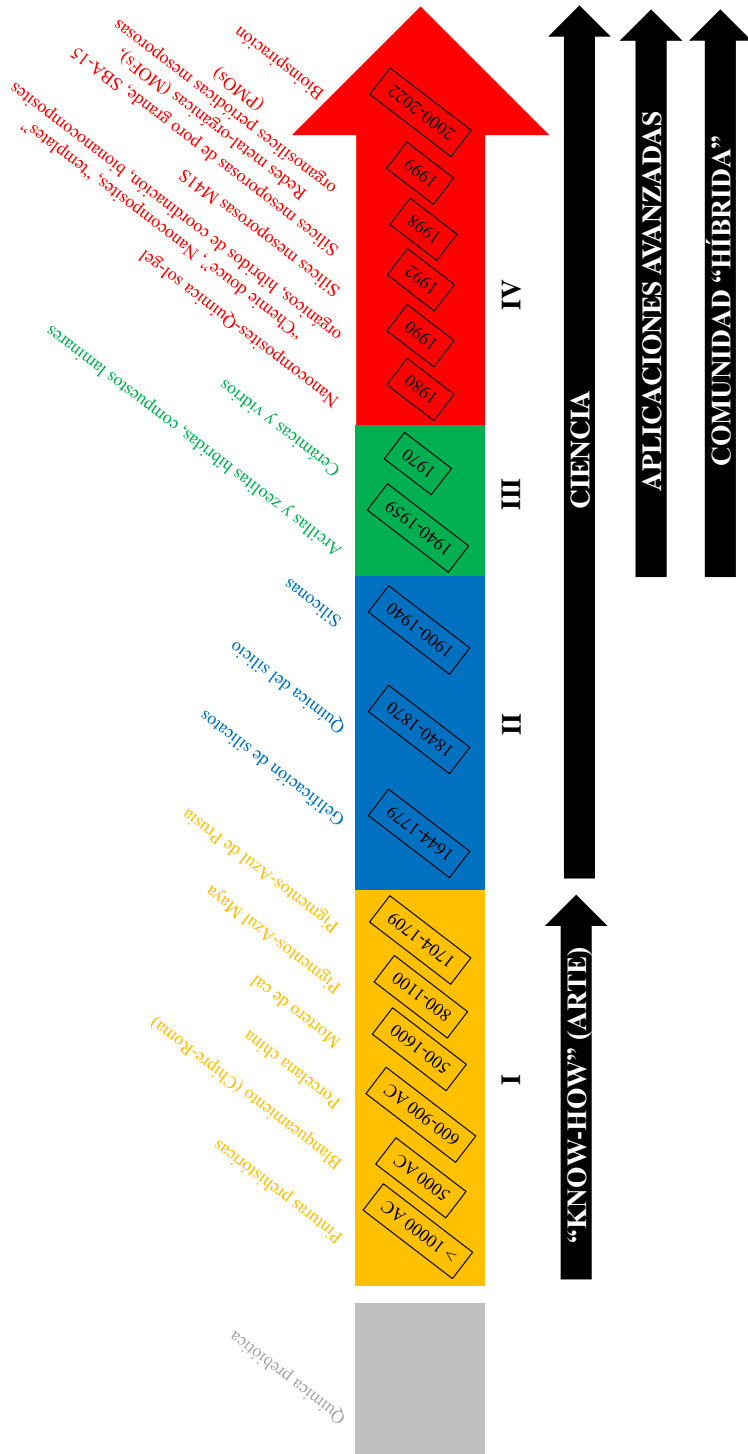


Figura 2. Cronología del desarrollo y evolución multidisciplinar de los materiales híbridos orgánico-inorgánicos.

Curiosamente, arcillas como la montmorillonita y la sepiolita pueden formar híbridos orgánico-inorgánicos muy estables con el ARN y el ADN, lo que proporciona una protección eficaz a los ácidos nucleicos adsorbidos frente a la degradación por irradiación, calor e incluso por acción enzimática (nucleasas), lo que puede considerarse de una importancia que sería crucial en los primeros pasos de la evolución de la vida. Los híbridos a base de arcilla no han sido solo involucrados en la generación de vida prebiótica, sino que también desempeñaron un papel clave como catalizadores en la génesis del petróleo a partir de materia orgánica generada a partir de organismos vivos ^[21].

Los silicatos, principalmente arcillas, así como otros minerales de diversa composición, como óxidos metálicos (óxidos de hierro) y carbonatos (calcita, aragonito, etc.), fueron los “precursores” inorgánicos empleados para producir los primeros materiales híbridos fabricados por el ser humano. Estos cumplían con varios criterios fundamentales: eran abundantes y accesibles, fáciles de moldear y, cuando se mezclan con compuestos orgánicos permiten el desarrollo de objetos/compuestos con nuevas propiedades de interés para un uso específico. Este tipo de compuestos integran el primer período (*período I*) de la línea cronológica que comprende desde la prehistoria (hace 20 000 años) hasta el siglo X d. C. Los primeros ejemplos de aplicación de estos materiales híbridos se remontan a la prehistoria con las pinturas de composites híbridos que se encontraron en los frescos de las cuevas de Altamira, Chauvet y Lascaux, entre otras. Posteriormente, surgieron otros híbridos orgánico-inorgánicos, como los blanqueadores a base de arcilla utilizados en Chipre o la antigua Roma, y las arcillas híbridas utilizadas para la formación de la porcelana china llamadas “cáscara de huevo”, basadas en el mineral de arcilla caolinita intercalado con moléculas de urea. Asimismo, cabe destacar el desarrollo de uno de los morteros más impresionantes en términos de propiedades mecánicas que se fabricó en la antigua China hace 1500 años mezclando sopa de arroz glutinoso con cal y otros ingredientes de mortero estándar ^[22]. Los sólidos inorgánicos, como los minerales de arcilla, se utilizaron también en la antigüedad como matrices huésped para secuestrar especies orgánicas moleculares para preservar sus características durante mucho tiempo. De esta manera, hace varios siglos, durante el período prehispánico tardío, los mayas prepararon un antiguo material orgánico-inorgánico nanoestructurado denominado “Azul Maya” mediante la encapsulación del tinte natural índigo en paligorskita, una arcilla natural fibrosa y microporosa, también conocida como atapulgita ^[23]. El material híbrido

resultante es un sorprendente pigmento extraordinariamente estable ya que resiste la radiación solar y UV, así como los tratamientos térmicos a temperaturas superiores a los 200 °C. También muestra buena estabilidad química frente a ácidos y álcalis concentrados, así como buena capacidad de extracción con solventes orgánicos ^[24]. De hecho, el color azul intenso del pigmento Azul Maya que se usa en la cerámica o en los murales de los templos se conservó durante siglos incluso después de la exposición a la atmósfera cálida y húmeda de América Central. Sorprendentemente, el color original también se ha conservado en situaciones de biodegradación natural producida por los microorganismos ambientales. El Azul Maya se empezó a utilizar inicialmente en Yucatán, el centro de México y Guatemala, desarrollando y mejorando su preparación durante varios siglos (800-1100 d.C.) ^[25]. Como en el caso de las arcillas, la pintura fue el primer dominio aplicativo de los sólidos de coordinación. La comprensión de la química y estructura de estos materiales fue esencial para la evolución de los materiales híbridos basados en polímeros de coordinación (unos pocos siglos después). A principios del siglo XVIII, se descubrió el azul de Prusia, el primer compuesto de coordinación puramente sintético. Más precisamente, se atribuye el descubrimiento a Diesbach y Dippel entre 1704 y 1707 en un laboratorio de Berlín, de ahí el nombre de “Prusia” aunque su primer uso se remonta a unos años más tarde sobre el 1709 ^[26,27].

Durante un segundo período (*período II*) que se extiende de 1600 a 1940, el desarrollo de la química de los silicatos, el silicio y sus alcóxidos, compuestos orgánicos del silicio (organosilanos), dieron origen al desarrollo industrial de las siliconas. Estos últimos son colas y selladores híbridos o agentes de acoplamiento vidrio-polímero que marcaron la denominada era del silicio, un pilar fundamental en el desarrollo de materiales híbridos modernos que tuvieron enorme influencia en la creación de nuevos materiales eficientes durante la Segunda Guerra Mundial. Este espacio temporal se puede dividir en dos ramas principales: la química de los silicatos y la química de los compuestos organosilícicos, que están científicamente relacionadas, pero cronológicamente desplazadas. Debido a la abundancia natural en términos de precursores, la química de los silicatos fue primero. La primera contribución se remonta a 1640 con el químico, fisiólogo y médico flamenco J. B. van Helmont cuando disolvió arena en un medio básico creando una solución de álcali-silicato que podía recuperarse de nuevo en forma de arena (sílice) bajando el pH en un medio ácido ^[28]. A través de este experimento simple y respaldado solo por una balanza, van Helmont reveló que se podía visualizar una química de sílice

en medio líquido, a temperatura ambiente, simplemente jugando con el pH. El mismo experimento fue implementado y mejor controlado más de un siglo después por el químico sueco T. Berman en 1779 ^[29]. Es importante remarcar que describió la formación del primer "gel" de sílice obtenido al controlar el proceso de acidificación de la solución de silicato alcalino. El cambio sustancial en la química moderna del silicio consistió en la implementación de nuevas rutas sintéticas hacia nuevos precursores de silicio molecular y organosilícicos. Esta innovación se puede atribuir primero a uno de los fundadores de la química moderna, el químico sueco J. J. Berzelius en 1823, que al calentar potasio en una vasija de barro, observó que el silicio elemental podía aislarse a través de la reacción entre el fluorosilicato de potasio y el potasio metálico. A partir de silicio aislado, estableció la síntesis de haluros de silicio, especialmente SiCl_4 , un precursor importante para los procesos posteriores de polimerización inorgánica ^[30-32]. El paso hacia la hibridación orgánico-inorgánica de este tipo de materiales fue dirigido hacia la formación de compuestos caracterizados por un enlace carbono-silicio, que fue logrado por dos químicos de renombre, el francés C. Friedel y el estadounidense J. M. Crafts, ampliamente conocidos en Química Orgánica por la reacción de Friedel-Crafts ^[33]. En 1863, implementaron la síntesis del primer compuesto organosilícico, el tetraetilsilano, mediante la reacción entre tetracloruro de silicio y dietil zinc ^[34]. La química de la silicona fue fundada a principios del siglo XX por el químico inglés F. S. Kipping ^[35], quien fue pionero en el uso de los reactivos de Grignard recién descubiertos para sintetizar una amplia gama de nuevos organosilanos y clorosilanos a partir de SiCl_4 . A la hidrólisis de estos silanos le siguió la formación de siliconas, que Kipping describió inicialmente como compuestos pegajosos sin utilidad particular y concluyó que la perspectiva de cualquier avance inmediato e importante en esta sección de la química no parecía muy esperanzadora. Más tarde, en la década de 1940, J. F. Hyde se dio cuenta de que lo que Kipping pensaba que eran compuestos inútiles podrían tener un impacto significativo como agentes de acoplamiento en la industria del vidrio ^[36]. Estas estrategias de hibridación fueron desarrolladas por los fabricantes de vidrio para enfrentar mejor la fuerte competencia proveniente del auge de la química de polímeros. En particular, Hyde demostró que las siliconas poseen propiedades atractivas como alta resistencia térmica y resistividad eléctrica. La producción masiva de siliconas se logró en 1940-1942, gracias a R. Muller (Alemania) y E. G. Rochow (USA) quienes desarrollaron, de forma paralela e independiente, un eficiente proceso industrial para fabricar diversos clorosilanos ^[37]. El

nacimiento de la corporación multinacional estadounidense Dow Corning en 1943 marcó la industrialización de las siliconas que estuvo impulsada principalmente por las necesidades de nuevos materiales para productos militares (juntas, aislantes, guantes, máscaras) durante la Segunda Guerra Mundial.

El tercer período (*período III*), desde la década de 1940 hasta finales de la década de 1970, se caracteriza por el desarrollo de materiales mixtos orgánicos e inorgánicos por parte de diferentes comunidades científicas como las de arcillas, zeolitas o polímeros. Estos materiales eran preparados mezclando eficientemente sus “compuestos básicos” con componentes complementarios de distinta naturaleza (orgánicos con inorgánicos o inorgánicos con orgánicos) para crear nuevas arquitecturas, y/o modular las propiedades fisicoquímicas resultantes. Las primeras síntesis modernas de híbridos orgánico-inorgánicos probablemente se desarrollaron utilizando minerales arcillosos estratificados como la esmectita (montmorillonita y filosilicatos relacionados) intercambiando sus cationes inorgánicos entre capas por cationes orgánicos, como reportaron Gieseking y Hendricks a principios de la década de 1940^[38-40]. Posteriormente, Bradley y MacEwan demostraron la formación de híbridos orgánico-inorgánicos por intercalación de moléculas orgánicas neutras en este mismo tipo de minerales arcillosos^[41,42]. De esta manera, monómeros, oligómeros, polímeros y compuestos orgánicos con diversas funcionalidades, desde aminas hasta compuestos carbonílicos, se han utilizado ampliamente como especies huéspedes capaces de intercalarse en sólidos laminares como arcillas de esmectita y otros filosilicatos como caolinita y haloisita, así como arcillas fibrosas como sepiolita y paligorskita. Este tipo de híbridos se encuentra dentro de los más utilizados en todo el mundo. Cada año se producen decenas de miles de toneladas de arcillas orgánicas para ser empleadas en aplicaciones esenciales a gran escala como, por ejemplo, en adsorción de contaminantes y remediación de derrames de petróleo, y como agentes reológicos para pinturas, grasas, asfaltos, soportes de pesticidas, materiales bioactivos y rellenos para polímeros. Al igual que en el caso de las arcillas, la comunidad de zeolitas comenzó a hibridar e incorporar grupos orgánicos en las décadas de 1950 y 1960 pero desde un punto de vista completamente diferente. Las zeolitas son aluminosilicatos hidratados de las familias de los cationes alcalinos y alcalinotérreos formados a partir de tetraedros entrelazados de alúmina y sílice que, mediante condensación controlada, forman estructuras cristalinas 3D con microporosidad bien definida. Debido a las aberturas y tamaños regulares de sus microcavidades

pueden hospedar selectivamente diferentes moléculas, por lo que las zeolitas también se han denominado "tamices moleculares" y encontraron aplicación en procesos de separación, purificación, catálisis e intercambio iónico ^[43]. El descubrimiento de las zeolitas sintéticas y, por lo tanto, el comienzo de la ciencia y la tecnología de las zeolitas se puede atribuir a las contribuciones de dos científicos, R. M. Barrer (Inglaterra) y R. M. Milton (USA) y dos actores industriales (Union Carbide y Mobil Oil) ^[44]. R. M. Barrer comenzó su investigación pionera en la síntesis de zeolitas con la preparación del análogo sintético del mineral de zeolita mordenita y una nueva zeolita sintética (más tarde identificada como KFI). El trabajo de Barrer a mediados y finales de la década de 1940 inspiró a Robert M. Milton de la empresa denominada División Linde de Union Carbide Corporation. Entre 1949 y 1954, Milton y sus colaboradores descubrieron varias zeolitas importantes (tipos A, X e Y) y brindaron información fundamental sobre las propiedades de sorción de las zeolitas. Posteriormente, debido a las interesantes propiedades ácido-básicas generadas por los ángulos y distancias generados en el interior de sus cavidades, las zeolitas se aplicaron en el campo de la catálisis para reacciones de isomerización (1959, Union Carbide) y en procesos de craqueo de hidrocarburos (1962, Mobil Oil) ^[45]. Sin embargo, en ese momento, las zeolitas puramente inorgánicas presentaban una diversidad estructural limitada y los tamaños de la cavidad eran demasiado pequeños para una serie de aplicaciones catalíticas. Estas limitaciones fueron superadas llevando a cabo la hibridación de estos materiales a través de la utilización de moléculas orgánicas como aditivos durante la condensación de aluminosilicatos en lugar de cationes inorgánicos convencionales (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , etc.) ^[46]. Las décadas comprendidas entre 1950 y 1970 marcaron la aparición de la ciencia "sol-gel", que en un principio fue muy progresiva y, curiosamente, estuvo impulsada por necesidades de carácter práctico. Desde el campo de la cerámica, comenzó en 1952-1956 con los trabajos de Rustum Roy, un físico nacido en la India que llevó a cabo su investigación sobre materiales cerámicos en la Universidad Estatal de Pensilvania ^[47]. Mientras investigaba el equilibrio de fases de los sistemas de óxidos mixtos, propuso varios métodos "sol-gel" para obtener nuevas composiciones de óxidos cerámicos, que involucraban Al, Si, Ti, Zr, etc. (que no podían fabricarse con los métodos tradicionales de polvos cerámicos), mediante coprecipitación de sales o hidrólisis y condensación en presencia de tetraetilortosilicato de etilo (TEOS) ^[48]. En la comunidad del vidrio, se puede atribuir un gran avance hacia la aplicación real a H. Dislich (en

Glasswek Schott, Alemania, 1969), quien desarrolló rutas sol-gel para fabricar recubrimientos ópticos de vidrio, cristalino o sistemas multicomponentes vídrioso-cristalinos sin recurrir a la fusión ^[49].

El cuarto período (*período IV*), desde principios de la década de 1980 hasta la actualidad, engloba el desarrollo avanzado de la química blanda (*chimie douce*), la química sol-gel, la química de la coordinación, la química de compuestos basados en sílice y la química bioinspirada. Estos enfoques permitieron acoplar estrechamente los mundos orgánicos o biológicos con la materia mineral, en un sentido amplio. A partir de finales de la década de 1970, los materiales sol-gel se combinaron fácilmente con componentes/polímeros orgánicos para hacer híbridos orgánicos-inorgánicos de clase I o II debido a la extrema versatilidad y procesabilidad que presentaban llevando a cabo sus síntesis en condiciones suaves ^[50]. Varias estrategias sintéticas diferentes fueron desarrolladas extensamente por químicos inorgánicos, de sol-gel o polímeros ^[51]. En 1985, J. Mark (Universidad de Cincinnati) y G. Wilkes (Virginia Tech) desarrollaron simultáneamente un nuevo tipo de materiales composites, denominado cerámeros, mediante un proceso sol-gel incorporando oxopolímeros metálicos. Estos híbridos de clase II se fabricaron mediante la condensación de polímeros terminados en silanol o alcoxisililo (como el polidimetilsiloxano (PDMS)) con TEOS ^[52-54]. Fundamentado en esto, se propusieron varias estrategias para introducir óxidos metálicos como TiO_2 y ZrO_2 dentro de materiales híbridos basados en polímeros PDMS-TEOS con grupos etoxisililos terminales ^[55,56]. Un enfoque similar se basó en la generación *in situ* de rellenos inorgánicos en una matriz polimérica. Se prepararon varios nanocompuestos monolíticos como PDMS-sílice, PMMA-sílice, PBMA- TiO_2 , hidrolizando el alcóxido metálico en presencia del polímero orgánico y un disolvente apropiado ^[57-59]. Con el objetivo de incrementar la relación de componentes inorgánico/orgánico en el material resultante, Novak y Davies (Berkeley, California, USA) formularon la preparación de redes orgánico-inorgánicas interpenetradas por polimerización orgánica e inorgánica simultánea a principios de la década de 1990 ^[60]. El final de la década de 1980 marcó el desarrollo de las llamadas estrategias "Lego-Like" para fabricar materiales híbridos orgánicos-inorgánicos ^[61]. El enfoque consistió en utilizar objetos preformados bien calibrados llamados nanobloques de construcción (NBBs) en lugar de precursores moleculares inorgánicos. Estos NBBs eran polisilsesquioxanos, organoestaños, polioxometalatos o clústers oxometálicos. Para formar redes híbridas interconectadas, los NBBs se

funcionalizaron a través de componentes polimerizables o se conectaron mediante ligandos orgánicos. En el mismo período, muchos científicos que trabajaban en "sol-gel" comenzaron a relacionar el proceso sol-gel con la biología al encapsular biomoléculas en matrices de sílice para obtener híbridos bioactivos. En 1990 se publicó un trabajo pionero de D. Avnir y M. Ottolenghi (Jerusalén, Israel) en el que se atrapaba una enzima (fosfatasa alcalina, ALP) en un gel de sílice (de tetrametoxisilano) ^[62]. La génesis de los materiales mesoporosos surgió como una convergencia natural entre la química sol-gel y los enfoques basados en "templates" orgánicos ya empleados para los materiales híbridos de arcilla y zeolita ^[63]. La síntesis de materiales mesoporosos de SiO₂ fue descrita por primera vez por Kuroda (Universidad de Waseda, Japón) y colaboradores en 1990 partiendo de kanemita, un polisilicato con estructura en forma de capas ^[64]. El método se basó en la reacción de intercambio iónico de los iones de Na⁺ de la capa intermedia con iones de alquiltrimetilamonio para formar complejos orgánicos/kanemita. Durante la intercalación orgánica, las capas de SiO₂ en el complejo se condensaron para formar redes 3D de SiO₂ y, después de la calcinación, se obtuvieron materiales mesoporosos de sílice con un tamaño de poro ajustable (de 2 a 4 nm), según la longitud de la cadena alquílica ^[65]. El enfoque denominado "liquid-crystal templating" fue propuesto en 1992 por investigadores de la compañía Mobil-Oil. En 1992, Kresge y colaboradores informaron de la formación de una nueva familia de tamices moleculares mesoporosos de silicato/aluminosilicato designados como M41S. Concretamente, reportaron la síntesis de sólidos mesoporosos que poseen redes porosas ordenadas formadas por la condensación de material de silicato entre micelas de tensioactivo iónico autoensambladas. Particularmente, el material más célebre de esta familia de sílices mesoporosos, denominado MCM-41, exhibió una disposición hexagonal de mesoporos uniformes con dimensiones de poro ajustables en el rango de ~15 Å a más de 100 Å ^[66]. En 1998, Stucky y colaboradores (UC Santa Barbara) desarrollaron la síntesis de materiales híbridos de sílice con poros grandes (5-30 nm) mediante el uso de copolímeros tribloque de poli(óxido de alquileo) como agente director de estructura micelar. Este material se denominó material de tipo amorfo de Santa Bárbara, siendo comúnmente conocido con las siglas SBA-15 ^[67]. Posteriormente, utilizando la misma familia de copolímeros en bloque, pudieron sintetizarse óxidos metálicos mesoporosos de poro grande con armazones semicristalinos, incluyendo TiO₂, ZrO₂, Al₂O₃, Nb₂O₅, Ta₂O₅, WO₃, HfO₂, SnO₂ y óxidos mixtos SiAlO_{3.5}, SiTiO₄, ZrTiO₄, Al₂TiO₅ y ZrW₂O₈ ^[68]. Un año más tarde, dos

tipos de materiales híbridos entraron en escena causando una revolución sustancial en el campo de la ciencia de los materiales: las organosílices periódicas mesoporosas (“*Periodic Mesoporous Organosilicas*”, PMOs) y los polímeros de coordinación denominados redes metal-orgánicas (MOFs). Los primeros materiales PMOs fueron diseñados en 1999 por tres grupos de investigación diferentes (Inagaki et al., [69] Stein et al., [70] y Ozin et al. [71]) combinando las características estructurales de la sílice mesoporosa ordenada con la funcionalización química de los polímeros orgánicos. La síntesis de estos materiales se basa en la condensación de precursores organosilícicos de tipo $(R'O)_3Si-RSi(OR')_3$ en presencia de un agente director de estructura o “template orgánico” formando una arquitectura mesoporosa ordenada con puentes orgánicos específicos integrados en la pared de la estructura silícea. Por su parte, los polímeros híbridos de coordinación compuestos por iones metálicos conectados por ligandos orgánicos tienen una larga historia (desde el azul de Prusia), pero atrajeron una enorme atención a finales de la década de 1990 con el descubrimiento de los llamados “metal-organic frameworks” o redes metal-orgánicas, siendo tres investigadores los pioneros en la síntesis de estos materiales a finales de la década de 1990: O. M. Yaghi (Universidad Estatal de Arizona, USA) [72–75], S. Kitagawa (Universidad de Kyoto, Japón) [76] y G. Férey (Institut Lavoisier de Versailles, Francia) [77,78].

En esta época, comienza a nacer una verdadera “escuela de pensamiento” multidisciplinar, donde químicos pertenecientes a comunidades muy diversas (química del estado sólido, de superficies, molecular, de coordinación y de polímeros; fisicoquímica, espectroscopias, etc.), ingenieros, ceramistas, vidrieros y físicos, se empezaron a reunir conjuntamente en simposios nacionales e internacionales [79–81]. De hecho, el encuentro actual más importante que unifica a la amplia comunidad científica de materiales híbridos es la conferencia “*Multifunctional, Hybrid and Nanomaterials*” que se celebra cada dos años desde 2009 (Tours, Estrasburgo, Sorrento, Sitges, Lisboa).

El final del siglo pasado estuvo marcado por una fuerte conciencia mundial acerca de los desafíos ambientales del planeta Tierra. En la ciencia de los materiales, los investigadores focalizaron su atención en llevar a cabo proyectos y labores científicas cuya temática se centrara en tomar como modelo la gran variedad de sistemas, reacciones, mecanismos y procesos desarrollados en la Naturaleza para abordar el diseño de materiales bioinspirados que presenten elevada eficiencia en aplicaciones específicas.

De hecho, un enfoque ecléctico, seguro y económico para el diseño y desarrollo de materiales híbridos avanzados necesariamente necesita tomar ciertas bases del mundo biológico, ya que una de las características fundamentales de este tipo de sistemas es su capacidad para integrar la síntesis molecular en niveles elevados de organización, estructura y funcionalidad ^[82].

Estos enfoques biomiméticos o bioinspirados están dando lugar, sin duda, a una de las áreas de desarrollo científico y tecnológico más prometedoras de este siglo XXI. El procesamiento de materiales y sistemas bioinspirados (materiales inteligentes adaptativos o autorreparables, nanomateriales nuevos o con mejores prestaciones, materiales con estructuras jerárquicas y dimensionalidad controlada, composites 3D, materiales compatibles con las limitaciones ecológicas, biocompatibles o reciclables, etc.) dio lugar a un enorme avance científico que, actualmente, ya está siendo visible en aplicaciones prácticas y a nivel industrial ^[83,84].

2.1.2. Progreso y aplicaciones

Hoy en día, los nanomateriales híbridos han llegado hasta una gran variedad de sectores a nivel de mercado y, científicamente, el interés ha seguido evolucionando positivamente causando un enorme impacto en los últimos 20 años en que la demanda de este tipo de materiales se ha incrementado significativamente ^[85-88]. La **Figura 3** esquematiza de las aplicaciones comerciales de nanomateriales híbridos con mayor influencia en la actualidad.

La microóptica, la microelectrónica y la fotónica (circuitos eléctricos impresos, microlentes, guías de ondas basadas en híbridos revestidos sobre sustratos rígidos o láminas flexibles, circuitos electroópticos impresos, espejos para cavidades de láseres); los revestimientos y protectores inteligentes (decorativos, antipolvo, antirrayaduras, autolimpiantes, antirreflejos, anticorrosión, antivaho, antilluvia); la energía (células fotovoltaicas, pilas de combustible, baterías, membranas híbridas para células de combustible de membrana de intercambio de protones (PEM), capas protectoras en células solares fotovoltaicas, células híbridas de estado sólido sensibilizadas por colorantes, baterías flexibles ultrafinas, etc.); el medio ambiente (catálisis, fotocatalisis, sensores de biocatálisis, biosensores, membranas, adsorbentes, etc.); la biomedicina para el cuidado humano y la cosmética

(implantes, prótesis, portadores terapéuticos, sensores, biosensores, cementos dentales, recubrimientos bioprotectores, reparación de cabello y piel, etc.); industrias del deporte, automóvil, textil y embalaje (neumáticos ecológicos, aligeramiento de peso, refuerzo de polímeros, retardantes de llama, textiles inteligentes, embalajes basados en nanocompuestos, etc.); y la construcción (pinturas de organoarcillas, selladores y madera) [89,90], se han visto fuertemente impactados por la gran versatilidad de la ciencia de materiales híbridos que permite combinar estrategias “bottom-up” y metodologías de procesamiento modernas como la deposición de películas delgadas (inmersión, centrifugado, rasqueta), métodos litográficos (litografía de nanoimpresión, absorción de dos fotones, dip-pen, etc.), electrohilado, impresión por inyección de tinta, sinterización por plasma de chispa, pulverización y electropulverización, grabado con iones reactivos, impresión 3D o 4D, extrusión reactiva, etc.



Figura 3. Aplicaciones industriales con mayor impacto comercial de materiales híbridos orgánico-inorgánicos.

El análisis bibliométrico mostrado en la **Figura 4** pone de manifiesto que el campo de investigación relacionado con los materiales híbridos en sentido general continúa expandiéndose actualmente, adquiriendo gran relevancia en la última década los híbridos orgánico-inorgánicos.

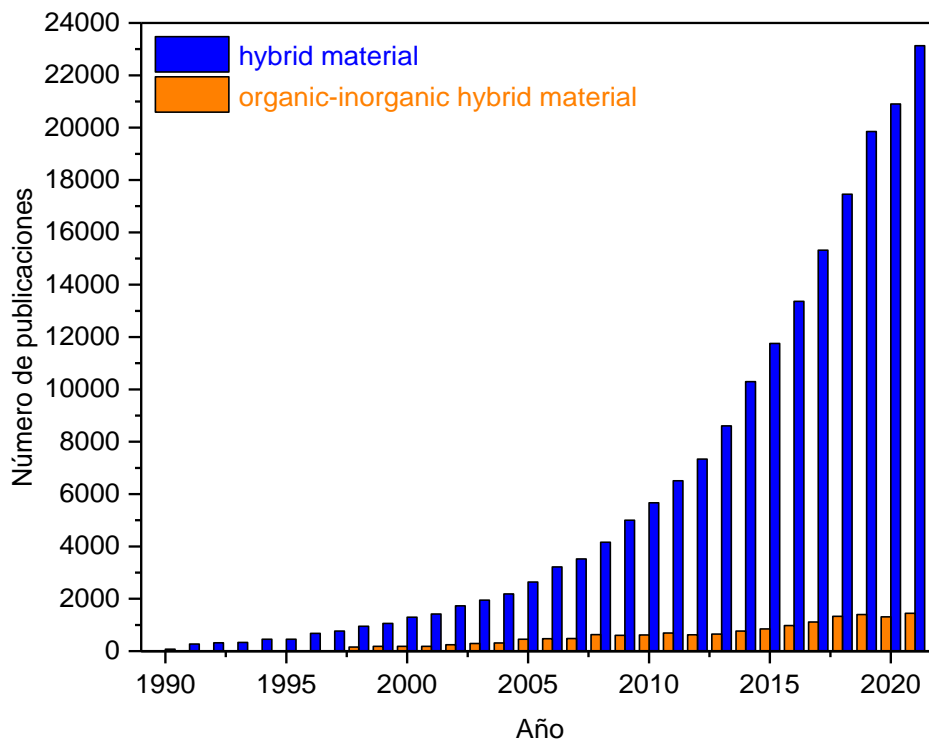


Figura 4. Número de publicaciones por año en el período (1990-2021) según la base de datos *Web of Science* (WOS). Las columnas de color azul y verde corresponden a búsquedas con palabras en el título, resumen o palabras clave conteniendo los términos “hybrid material” y “organic-inorganic hybrid material”, respectivamente.

2.1.3. Metodologías de síntesis

Independientemente de los tipos o aplicaciones, así como de la naturaleza de la interfaz entre los componentes orgánicos e inorgánicos, una característica crucial en el diseño de materiales híbridos se relaciona con las metodologías de síntesis empleadas. Las principales rutas químicas para la preparación de cualquier híbrido se representan esquemáticamente en la **Figura 5**. Seguidamente, se describen de forma general las diferentes estrategias de preparación de materiales híbridos orgánico-inorgánicos:

- La **Ruta A** corresponde a síntesis basadas en “química suave” (soft chemistry) que incluyen la química sol-gel convencional ^[91], el uso de precursores polifuncionales con puentes específicos ^[92] y la síntesis hidrotérmica ^[93].

- **Ruta A1:** A través de rutas sol-gel convencionales, se obtienen redes híbridas amorfas mediante la hidrólisis de alcóxidos metálicos modificados orgánicamente o haluros metálicos condensados con o sin alcóxidos metálicos simples. El solvente puede contener o no una molécula orgánica específica, un biocomponente o polímeros polifuncionales que pueden ser reticulables o que pueden interactuar o quedar atrapados dentro de los componentes inorgánicos a través de un conjunto de interacciones como enlaces de hidrógeno, interacciones π - π , Van der Waals... Estas estrategias son simples, de bajo coste y producen nanocomposites híbridos amorfos muy versátiles que presentan muchas propiedades interesantes en el ámbito comercial. Estos materiales, que exhiben infinitas microestructuras, pueden ser transparentes y moldearse fácilmente en forma de película, polvo o monolito. Generalmente son polidispersos en tamaño y localmente heterogéneos en composición química.
- **Ruta A2:** El uso de precursores como los silsesquioxanos $X_3Si-R'-SiX_3$ (R' es un espaciador orgánico, $X = Cl, Br, O-R$) permite la formación de materiales híbridos orgánicos-inorgánicos moleculares homogéneos que tienen un mejor grado de organización local. En algunos casos, el espaciador orgánico se ha complementado mediante el uso de dos grupos funcionales terminales (tipo urea). La combinación dentro del componente puente orgánico de grupos aromáticos o alquilo y grupos urea permite un mejor autoensamblaje a través de la capacidad de los restos orgánicos para establecer entre ambos enlaces de hidrógeno fuertes y un empaquetamiento eficiente a través de interacciones π - π o hidrofóbicas ^[94].
- **Ruta A3:** La síntesis hidrotermal en disolventes polares (agua, dimetilformamida, etc.) en presencia de moléculas plantilla de naturaleza orgánica ha dado lugar a numerosas zeolitas y, más recientemente, a la nueva generación de sólidos híbridos microporosos cristalinos denominados MOFs.

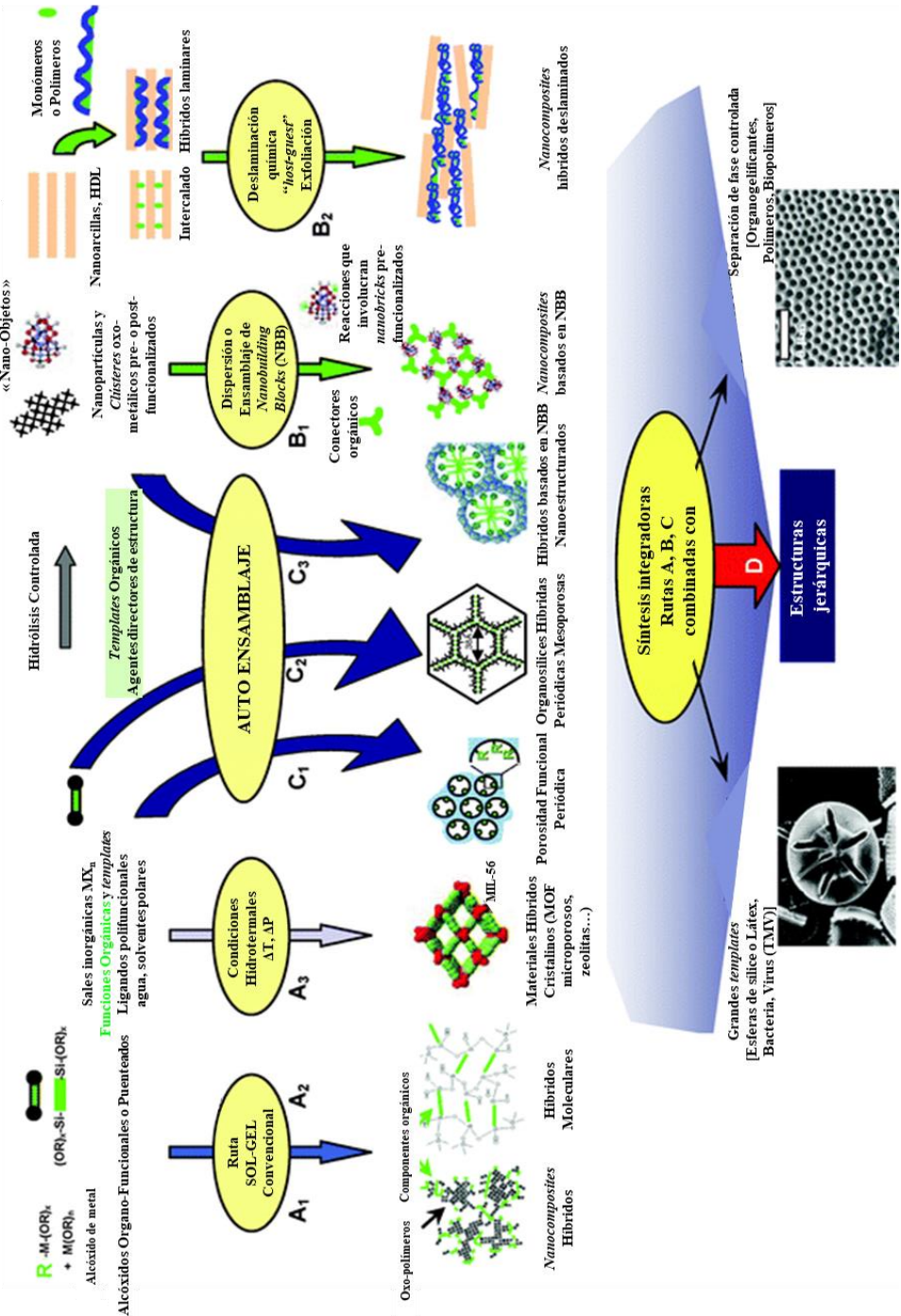


Figura 5. Esquema de las principales rutas químicas para la síntesis de híbridos orgánico-inorgánicos (adaptado de la referencia [9]).

- La **Ruta B** se refiere al ensamblaje (*ruta B1*) o la dispersión (*ruta B2*) de bloques de nanoconstrucción bien definidos (*nanobuilding blocks*, NBBs) basados en objetos preformados perfectamente diseñados que mantienen su integridad en el material final ^[95]. Este es un método de síntesis adecuado para alcanzar una mejor definición del componente inorgánico. Los NBBs pueden ser clústeres, nanopartículas pre- o post-funcionalizadas con unidades orgánicas (óxidos metálicos, metales, calcogenuros, etc.), “*nano-core-shells*” o compuestos laminares (arcillas, hidróxidos dobles laminares, fosfatos laminares, óxidos o calcogenuros) capaces de incorporar compuestos orgánicos intercalados. Estos NBBs pueden funcionalizarse con ligandos orgánicos polimerizables o conectarse a través de espaciadores orgánicos, como moléculas o polímeros telequéricos, o dendrímeros funcionales. El uso de especies altamente precondensadas presenta varias ventajas como la menor reactividad hacia la hidrólisis o el ataque de fracciones nucleófilas que los alcóxidos metálicos. Además, los componentes de nanoconstrucción son nanométricos, monodispersos, y con estructuras mejor definidas, lo que facilita la caracterización de los materiales resultantes. La variedad brindada por los bloques de nanoconstrucción en cuanto a naturaleza, estructura y funcionalidad, permite disponer de una extensa gama de diferentes arquitecturas e interfaces orgánico-inorgánicas, asociadas con diferentes estrategias de ensamblaje. Además, la preparación paso a paso de estos materiales suele permitir un alto control sobre su estructura. Un conjunto importante de materiales híbridos basados en NNBs son los que resultan de la intercalación, expansión y exfoliación de nanoarcillas o hidróxidos dobles laminares (HDLs) intercalados con polímeros orgánicos (*host-guest chemistry*) dando lugar a nanocomposites híbridos deslaminados.
- **Ruta C-Procedimientos de autoensamblaje:**
 - En los últimos diez años se ha explorado un nuevo campo, que corresponde a la ingeniería de redes inorgánicas o híbridas, constituyendo una estrategia denominada “crecimiento dirigido por surfactantes orgánicos” o “*templated growth by organic surfactants*” (**Ruta C1**) ^[96–100]. El éxito de esta metodología está claramente relacionado con la capacidad que tienen los científicos de materiales para

controlar y ajustar las interfaces híbridas. En este campo, las fases híbridas orgánico-inorgánicas son muy interesantes debido a la versatilidad que demuestran en la construcción de toda una gama continua de nanocomposites, desde dispersiones ordenadas de bloques inorgánicos en una matriz híbrida hasta nanosegregaciones altamente controladas de polímeros orgánicos dentro de matrices inorgánicas. En este último caso, uno de los ejemplos más llamativos es la síntesis de redes híbridas mesoestructuradas.

- Una estrategia reciente desarrollada por varios grupos consiste en el crecimiento moldeado de híbridos mesoporosos utilizando silsesquioxanos con puentes orgánicos como precursores y surfactantes como moléculas plantilla o “*templates*” orgánicos (**Ruta C2**). Este enfoque produce una nueva clase de sílices híbridas mesoporosas organizadas periódicamente con funcionalidades orgánicas integradas dentro de las paredes (PMOs). Estos materiales presentan un alto grado de ordenamiento y su mesoporosidad les permite llevar a cabo posteriores reacciones de funcionalización orgánica a través del injerto superficial (“*surface grafting*”) ^[101].
- La **Ruta C3** corresponde a la combinación de las estrategias de autoensamblaje y NBBs. Por tanto, esta metodología incorpora el enfoque de los bloques de nanoconstrucción y el uso de plantillas orgánicas que se autoensamblan permitiendo controlar el proceso de ensamblaje. Como resultado, estos materiales presentan una gran variedad de interfaces entre los componentes orgánicos e inorgánicos (enlace covalente, complejación, interacciones electrostáticas, etc.). Estos NBBs con funcionalidades ajustables pueden, a través de procesos de reconocimiento molecular, permitir el desarrollo de una nueva química vectorial ^[102,103].
- **Ruta D-Síntesis integradoras:** Las estrategias mencionadas anteriormente ofrecen principalmente el diseño y ensamblaje controlados de materiales híbridos en el rango de 1 Å a 500 Å. Recientemente, se han desarrollado métodos de micromoldeo, en los que el uso de fenómenos de separación de fases controlados, gotas

de emulsión, perlas de látex, hilos bacterianos, plantillas coloidales u organogelificantes conducen al control de las formas de objetos complejos en la escala micrométrica. La combinación entre estas estrategias y las descritas con anterioridad a lo largo de las rutas A, B y C, permiten la construcción de materiales jerárquicamente organizados en términos de estructura y función. Estos procedimientos de síntesis están inspirados en los observados en los sistemas naturales desde hace algunos cientos de millones de años. Aprender y conocer el "*savoir faire*" de los sistemas y organismos vivos híbridos a partir de la comprensión de sus reglas, modos de transcripción, mecanismos de reacción biomoleculares y metabolismos funcionales, podría permitirnos diseñar y construir nuevos materiales híbridos cada vez más avanzados y sofisticados [104,105].

2.1.4. Expectativas de futuro

Las nanociencias serán uno de los campos que contribuirán a un alto nivel de desarrollo científico y tecnológico en el siglo XXI. En este ámbito, los materiales híbridos orgánicos-(bio)-inorgánicos desempeñarán un papel fundamental en el desarrollo de materiales funcionales avanzados. La investigación en este tipo de materiales estará respaldada principalmente por el creciente interés de químicos, físicos, biólogos y científicos de materiales para aprovechar al máximo esta oportunidad de crear materiales inteligentes que se beneficien de lo mejor de los tres reinos: inorgánico, orgánico y biológico. Incluso las estrategias bioinspiradas utilizadas para imitar los procesos de crecimiento que ocurren en la biomineralización serán tomadas para diseñar híbridos estructurados innovadores multiescala (de escala nanométrica a escala milimétrica), organizados jerárquicamente en términos de estructura y funcionalidad.

Además de la gran versatilidad en las propiedades químico-físicas y en la conformación, los nanocompuestos híbridos presentan la ventaja primordial tanto para facilitar la integración como para la miniaturización, abriendo así un campo de aplicaciones prometedoras en muchos campos: óptica, electrónica, iónica, mecánica, membranas, funcional y recubrimientos protectores, catálisis, sensores, biología, medicina, biotecnología, etc. De hecho, muchos materiales híbridos han ido apareciendo como prototipos o productos comerciales durante la última década.

Hoy en día, los enfoques moleculares de la química del estado sólido y la nanoquímica han alcanzado un nivel muy alto de sofisticación. Los químicos pueden prácticamente personalizar cualquier especie molecular (moléculas, grupos, partículas de tamaño nanométrico, compuestos nanolaminares, nanotubos, etc.) y diseñar nuevos materiales híbridos funcionales con propiedades mejoradas. A este nivel de conocimiento y comprensión en nanociencia, y teniendo en cuenta las nuevas y más estrictas exigencias que impone la sociedad actual, la fabricación de materiales y dispositivos inteligentes con estructuras complejas, alto nivel de integración y miniaturización, reciclables y respetuosos con el medio ambiente, es justo una cuestión de imaginación de los científicos y de concienciar a las industrias de sus oportunidades y beneficios.

Basado en esto, la evolución futura de la comunidad científica se vinculará directamente al concepto de *hibridación del pensamiento* (“*hybridization of thought*”). Echando un vistazo al retrato típico de los científicos que marcaron la historia de los materiales híbridos, uno de los rasgos comunes es sin duda su apertura mental (*open-mindedness*). El típico "científico híbrido" es capaz de dejarse influir por otras formas de pensar, compartir conocimientos y crear puentes entre diferentes dominios (mineralogía, biología, química orgánica, inorgánica y física, ciencia de polímeros, ingeniería, etc.) impulsado por la curiosidad académica o por necesidades prácticas/industriales. En este sentido, el campo de los materiales híbridos ahora está impulsado por esa misma mentalidad abierta y probablemente esté en constante evolución, cruzando nuevos dominios en otras áreas científicas (informática, estadística, sociología, arqueología, derecho, ciencias de la tierra, etc.) y, al mismo tiempo, también en el ámbito educativo considerándose de suma importancia promover un nuevo camino académico multidisciplinario "híbrido".

En este contexto de investigación en el que se garantiza que los materiales híbridos avanzados jugarán un papel crucial en el futuro de la sociedad mundial, se enmarca la presente Tesis Doctoral dedicada al estudio de tres grandes bloques de la ciencia de los materiales híbridos orgánico-inorgánicos: **1) polímeros de coordinación y redes metal-orgánicas, 2) materiales híbridos orgánico-inorgánicos basados en sílices y 3) materiales híbridos basados en grafeno**; abordando desde su síntesis y caracterización detallada hasta su aplicación en diferentes disciplinas de investigación con elevado interés científico en la actualidad como la catálisis, adsorción, fotofísica y energía.

2.2. Polímeros de coordinación-Metal Organic Frameworks (MOFs)

La Química de Coordinación ha experimentado un enorme crecimiento en los últimos años, proporcionando arquitecturas híbridas orgánico-inorgánicas de una, dos y tres dimensiones (1D, 2D y 3D) diseñadas a partir de una variedad de bloques de construcción moleculares con diferentes interacciones entre ellos. Los compuestos de coordinación con estructuras infinitas ha sido un área intensamente investigada, en particular, los materiales contruidos a partir de iones metálicos o complejos polinucleares a los que se coordinan ligandos orgánicos polidentados mediante enlaces de coordinación, resultando en materiales híbridos multifuncionales denominados “**polímeros de coordinación**” [106–108]. Mediante la selección de unidades orgánicas de longitud, geometría y funcionalidad específicas coordinadas a especies metálicas adecuadas es posible diseñar materiales con propiedades únicas en términos de porosidad, cristalinidad, estabilidad y flexibilidad permitiendo crear entornos particulares en el interior de su red porosa para llevar a cabo modificaciones estructurales determinadas o reacciones químicas concretas. El término polímero de coordinación fue utilizado por primera vez en un trabajo de revisión publicado en 1964 por el científico J. C. Bailar, cuando comparó polímeros orgánicos con compuestos inorgánicos que eran considerados especies poliméricas estableciendo así una nueva clase de compuestos poliméricos con propiedades definidas sintetizados mediante metodologías específicas a partir de iones metálicos y moléculas de naturaleza orgánica [109]. Desde ese momento, los polímeros de coordinación han ido tomando una posición importante en el área de materiales porosos y han añadido una nueva categoría a la clasificación convencional (**Figura 6**). Cabe destacar que los compuestos porosos han atraído gran atención entre las comunidades de químicos, físicos y científicos de materiales debido al creciente interés en la creación de espacios de tamaño nanométrico y la reactividad que tiene lugar en el interior de ellos, siendo ambos factores de extraordinaria utilidad en determinadas aplicaciones con elevada demanda en el sector industrial. Hasta mediados de la década de 1990, había básicamente dos tipos de materiales porosos: *materiales inorgánicos* y *materiales basados en carbono*.

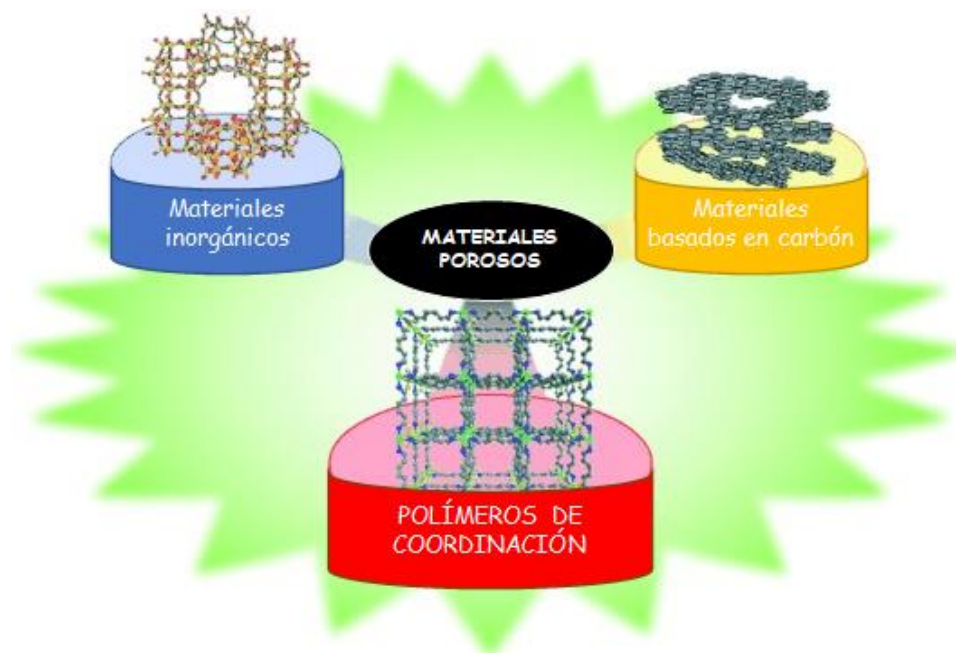


Figura 6. Categorías de materiales porosos (adaptado de la referencia ^[107]).

En el caso de sólidos inorgánicos microporosos, las dos subclases más representativas son los aluminosilicatos (zeolitas) y aluminofosfatos (AIPOs). Las zeolitas son aluminosilicatos cristalinos alcalinos o alcalinotérreos hidratados con dimensionalidad 3D que tienen como fórmula general $M^{n+}_{x/n}[(AlO_2)_x(SiO_2)_y]^{x-n} \cdot w H_2O$ (M =metal) ^[43,110]. Su red está construida a partir de tetraedros TO_4 compartiendo los vértices de dichos tetraedros ($T = Al, Si$). De esta forma, se crean túneles o redes interconectados en los que se insertan moléculas de agua e iones M^{n+} , donde la carga negativa de la red es neutralizada por la carga positiva de los cationes ubicados dentro de los poros del material. La porosidad se proporciona entonces a través de la eliminación de las moléculas de agua, aunque la estructura generalmente no se ve afectada por esto, y el tamaño de poro depende de la tipología de zeolita sintetizada estando concentrado en un intervalo entre 1–10 Å. Las cavidades, cuya estructura generalmente está determinada por la cantidad de poliedros que forman las cavidades porosas, se exploraron minuciosamente para cumplir los requisitos requeridos en procesos catalíticos y de separación de gases ^[111,112]. La primera síntesis de zeolitas fue reportada por francés Henry Etienne Sainte-Claire Deville en 1862, quien afirmó haber preparado el mineral zeolítico levynite (levyne) ^[113]. Por su parte, los denominados AIPOs se basan en

tetraedros de iones Al^{3+} y P^{5+} unidos por sus vértices, constituidos por átomos de oxígeno, y que construyen una estructura neutra 3D con canales y/o poros de dimensiones moleculares con tamaños de poro modulables comprendidos en el rango de las zeolitas ^[114]. Desde entonces no han dejado de describirse nuevos materiales zeolíticos y sus aplicaciones. Muchos aluminofosfatos sintéticos tienen estructuras cristalinas que no se observan en las zeolitas naturales. La primera publicación sobre aluminofosfatos cristalinos microporosos -otra gran familia de materiales estructurados- fue reportada por un grupo de investigación de la *Union Carbide Corporation* (Nueva York), liderado por Stephen T. Wilson y Edith M. Flanigen, en la que analizaban las propiedades de este nuevo material para su empleo como tamiz molecular ^[115]. Desde entonces, no solo se han descubierto varios óxidos cristalinos relacionados, como silicoaluminofosfatos, metalosilicatos, metaloaluminofosfatos y metalofosfatos, sino también calcogenuros, haluros y nitruros porosos ^[116,117].

Por otro lado, los materiales porosos basados en carbón son referidos principalmente a los llamados carbones activados que tienen una alta porosidad abierta y un área superficial elevada, pero tienen una estructura cristalina desordenada. Son referidos a un conjunto de materiales con una composición amorfa no gráfica que presentan una estructura interna bien desarrollada de micro (<2 nm), meso (2–50 nm) y macroporos (>50 nm), así como una amplia variedad de grupos funcionales superficiales, lo que los convierte en compuestos muy versátiles que pueden utilizarse en multitud de aplicaciones ^[118,119]. La característica estructural esencial de estos sólidos es una red distorsionada de capas de carbono hexagonales defectuosas, entrecruzadas por grupos puente alifáticos y organizadas de manera aleatoria. Los grupos funcionales simples y los heteroátomos se incorporan a la red carbonosa a través de su unión a la periferia de las capas de carbono.

Recientemente, se han desarrollado los polímeros de coordinación porosos (PCPs), que se engloban en un grupo aparte de las dos clases anteriormente mencionadas de materiales porosos ^[107,108,120–122]. Son completamente regulares, tienen alta porosidad, y redes altamente diseñables emergiendo como una nueva familia de materiales funcionales con una rica ingeniería estructural con una enorme variabilidad de tipologías y aplicaciones en diversas áreas de investigación. Sus síntesis se realizan generalmente en condiciones suaves y la elección de una cierta combinación de unidades moleculares orgánico-inorgánicas conduce a la

red extendida deseada para ser utilizada en una aplicación concreta. Este tipo de arquitecturas de coordinación tienen lugar mediante el ensamblaje de un conjunto de átomos presentes en el ligando orgánico en torno a un centro metálico en forma de “clúster” o átomo aislado a través de los denominados enlaces de coordinación. Este tipo de enlaces se basan en la donación de un par de electrones libres por parte del componente que actúa como base de Lewis, en este caso los átomos del ligando orgánico, al catión metálico que acepta dichos electrones comportándose como un ácido de Lewis ^[123]. Asimismo, pueden entrar en juego fenómenos de atracción electrostática entre el catión con carga positiva y los átomos del ligando orgánico cargados negativamente, u otras interacciones no covalentes como enlaces de hidrógeno, interacciones π - π y fuerzas de Van der Waals que pueden determinar la naturaleza del PCP resultante. La expansión definitiva de este tipo de materiales vino marcada a mediados de la década de los 90 con la aparición de los denominados MOFs (*Metal Organic Frameworks*) o redes metal-orgánicas, reportado por primera vez por los investigadores Omar M. Yagui de la Universidad del Estado de Arizona (USA) y S. Kitagawa de la Universidad Metropolitana de Tokio (Japón). Omar M. Yagui consiguió sintetizar un compuesto de estructura tridimensional de cobre formado por redes interpenetradas de fórmula $\text{Cu}(4,4'\text{-bpy})_{1,5}\text{NO}_3(\text{H}_2\text{O})_{1,25}$ ^[72]. Por su parte, el grupo de S. Kitagawa consiguió sintetizar polímeros de coordinación con estructuras 3D $\{[\text{M}_2(4,4'\text{-bpy})_3(\text{NO}_3)_4](\text{H}_2\text{O})_x\}_n$ ($\text{M} = \text{Co.}$, $x = 4$; $\text{M} = \text{Ni}$, $x = 4$; $\text{M} = \text{Zn}$, $x = 2$), que se forman a partir de nitratos metálicos $\text{M}(\text{NO}_3)_2$ y ligandos orgánicos 4,4'-bipiridina ^[76].

Los MOFs son considerados una subclase de polímeros de coordinación cuya terminología está íntimamente asociada a propiedades como la cristalinidad, porosidad, tridimensionalidad, naturaleza de ligandos y fortaleza de enlaces. Debido a la gran atención que han tenido durante las dos últimas décadas por parte de la comunidad científica, el significado de las nomenclaturas relacionadas con estos sistemas (polímeros de coordinación, redes de coordinación y MOFs) ha sido controvertida y ha dado lugar a confusiones en muchos casos ^[124]. Por ello, la IUPAC en el año 2012 unificó los criterios de definición de estos materiales proponiendo una clasificación jerárquica (**Figura 7**): el término genérico es polímero de coordinación (“*coordination polymer*”), siendo las redes de coordinación (“*coordination networks*”) una subclase de polímeros de coordinación y, a su vez, las redes metal-orgánicas (“*metal organic frameworks*”) una subclase de redes de coordinación ^[125]:

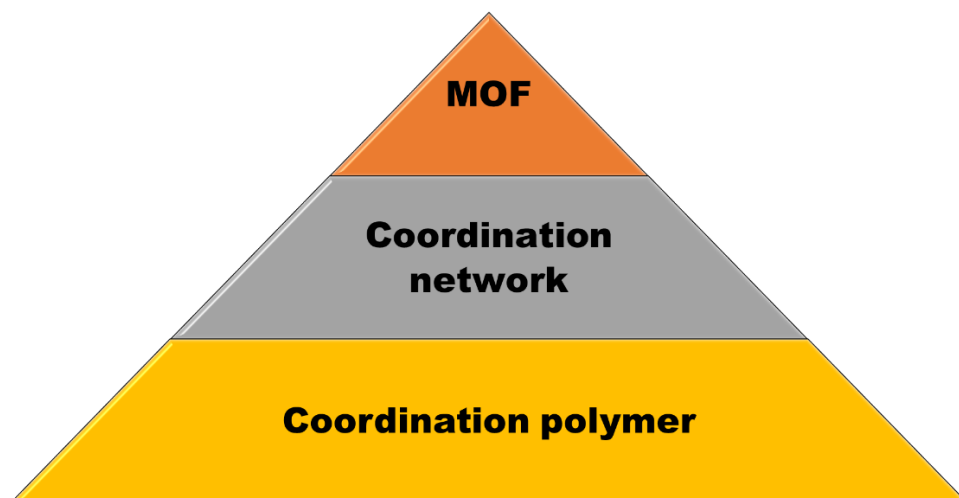


Figura 7. Clasificación jerárquica propuesta por la IUPAC para definir los términos polímero de coordinación, red de coordinación y MOF.

- **Polímero de coordinación** es todo compuesto de coordinación con entidades de coordinación que se repiten extendiéndose en 1, 2, o 3 dimensiones. Los polímeros de coordinación no tienen que poseer necesariamente características cristalinas y, generalmente, están compuestos de grupos carboxilatos pudiendo ser considerados a veces como sales. El prefijo 1D-, 2D- o 3D- es aceptable para indicar el grado de extensión del polímero de coordinación. Además, al usar este término se debe tener en cuenta que la definición de la IUPAC de “polímero” es más inclusiva que el uso coloquial empleado entre químicos e ingenieros. Las recomendaciones actuales son las siguientes ^[126]: *polímero* es una sustancia compuesta de macromoléculas mientras que *molécula polimérica* (macromolécula) es una molécula de masa molecular relativa alta, cuya estructura consiste esencialmente en la repetición múltiple de unidades derivadas, real o conceptualmente, de moléculas de masa molecular relativamente baja (monómeros). Un ejemplo clásico de polímero de coordinación de cadena extendida en una dimensión es el compuesto de cobalto (II) con puentes orgánicos 4,4'-bipiridina ^[127] representado en la **Figura 8**.

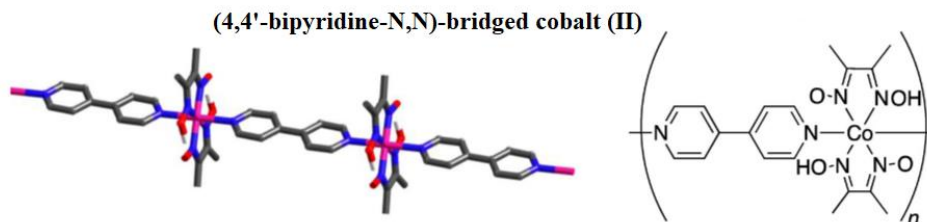


Figura 8. Ejemplo representativo de polímero de coordinación 1D (adaptado de la referencia ^[125]).

- **Red de coordinación:** Se define como un compuesto de coordinación que se extiende, a través de entidades de coordinación repetitivas, en 1 dimensión, pero con enlaces cruzados entre dos o más cadenas individuales, bucles o enlaces en forma de espiral. Asimismo, engloba a compuestos de coordinación que se extienden a través de entidades de coordinación repetitivas en 2 o 3 dimensiones. En la **Figura 9** se pueden apreciar ejemplos representativos de redes de coordinación formadas mediante enlaces cruzados entre cadenas individuales ^[128] (**Figura 9a**) o bucles ^[129] (**Figura 9b**).

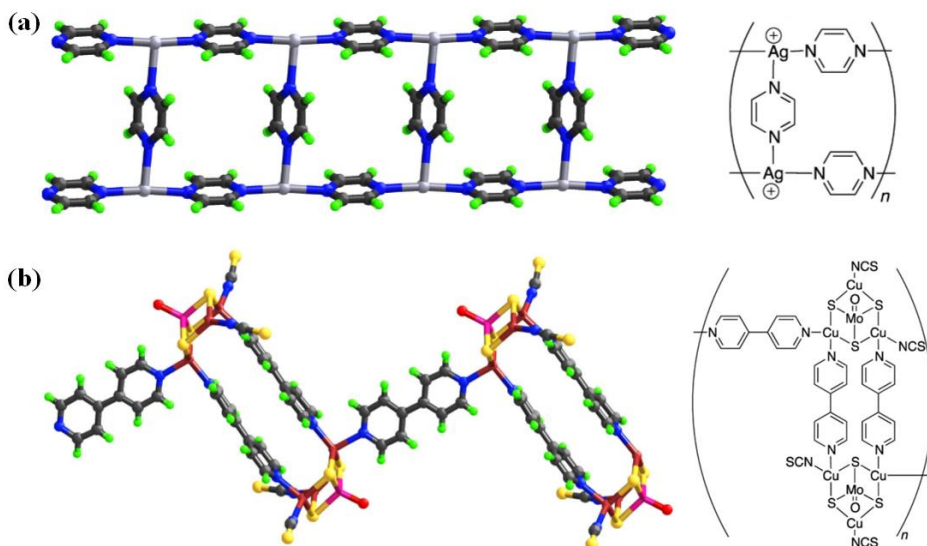


Figura 9. Ejemplos representativos que hacen referencia al concepto de redes de coordinación formadas a través de (a) enlaces cruzados entre cadenas individuales o (b) en bucles individuales (adaptado de la referencia ^[125]).

- **Red metal-orgánica:** Se define como una red de coordinación construida mediante ligandos orgánicos que presenta huecos potenciales en su estructura generando así una determinada porosidad que puede variar dependiendo de la temperatura, la presión u otros estímulos externos, así como por la evacuación de especies (solventes o moléculas huésped) que puedan estar contenidas en las cavidades estructurales. Como ejemplo general, en la **Figura 10** se muestra el MOF-5 diseñado por el grupo de Omar M. Yagui ^[74]

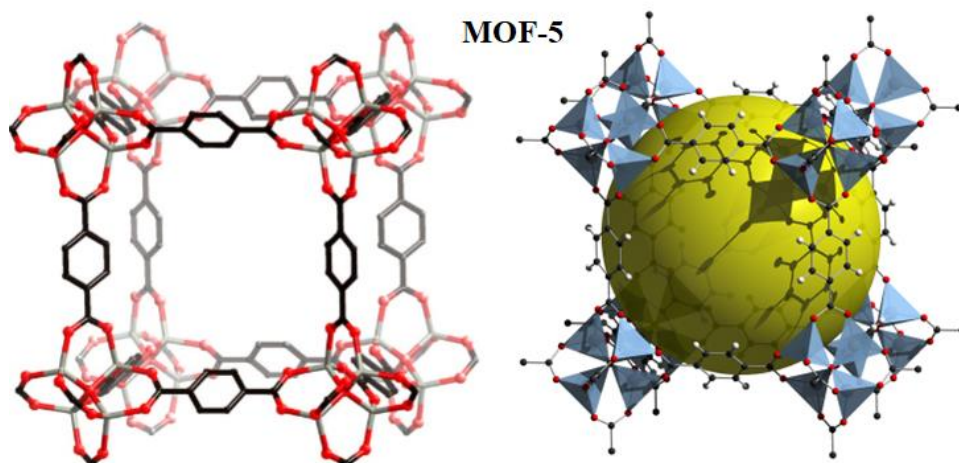


Figura 10. Representación del MOF-5 basado en zinc y ligandos orgánicos benzeno-1,4-dicarboxilatos diseñado por el grupo de Omar M. Yaghi donde cada unidad $[Zn_4O]$ está unida octaédricamente por seis ligandos benzeno-1,4-dicarboxilatos (adaptado de la referencia ^[125]).

Teniendo en cuenta las terminologías definidas anteriormente, se puede enunciar que los materiales de tipo MOF son una clase de polímeros de coordinación cuya característica principal es que poseen elevada porosidad y cristalinidad, con estructura completamente ordenada y construidos principalmente por una red de iones metálicos (átomos o clústers) interconectados a través de ligandos orgánicos multidentados (linkers) en redes de una, dos o tres dimensiones (**Figura 11**). Normalmente, ácidos carboxílicos aromáticos bivalentes o trivalentes se utilizan para crear la red que rodea al átomo central que puede ser cobre, aluminio, zirconio o vanadio, entre otros.

El desarrollo de los MOFs depende de sus modificaciones de síntesis y post-síntesis, pero se clasifican principalmente como MOF normales (*primera generación*), MOF funcionales (*segunda generación*) y MOF inteligentes (*tercera generación*). Los MOF de primera generación se refieren a los preparados de manera convencional a partir de unidades orgánicas e inorgánicas moleculares. Los MOF de segunda generación se derivan de los MOF de primera generación, pero se llevan a cabo algunas modificaciones químicas. De manera similar, los MOF de tercera generación se construyen mediante la conjugación de biomoléculas como algunos fármacos orgánicos, cationes, toxinas, gases y ciertas moléculas bioactivas ^[130,131].

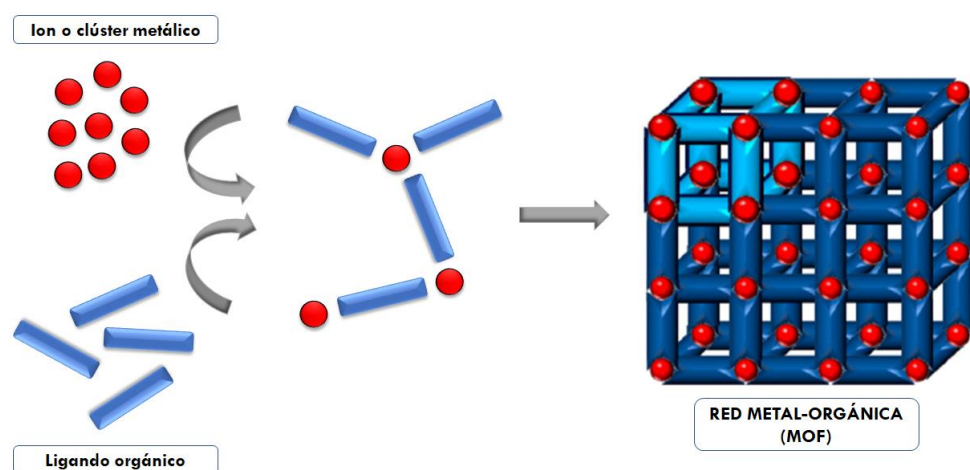


Figura 11. Esquema de preparación de una red metal-orgánica tipo MOF.

En general, los MOFs tienen ciertas características muy importantes que los aventajan de los polímeros orgánicos y sólidos microporosos inorgánicos comunes, destacando la posibilidad de llevar a cabo un diseño sistemático de sus estructuras a partir de la selección óptima de las unidades de construcción. La morfología, porosidad, tamaño de partícula y distribución de grupos funcionales dependen directamente del ligando orgánico y clúster metálico escogidos, así como la metodología de síntesis adoptada.

Estas propiedades pueden ser moduladas específicamente para aplicaciones determinadas, por lo que varios factores deben tenerse en cuenta: 1) geometría, ángulo, forma y naturaleza química de los grupos dentados del ligando orgánico, 2) geometría del entorno coordinativo, número de coordinación y naturaleza química del clúster metálico, 3)

grupos funcionales presentes en la estructura del ligando que no coordinan y 4) la presencia de agentes moduladores, moléculas plantilla y disolventes.

La rápida expansión de este tipo de materiales entre la comunidad científica tuvo lugar como consecuencia de sus extraordinarias propiedades fisicoquímicas y diversidad de aplicaciones constituyendo a partir de su descubrimiento un punto de inflexión en el desarrollo del campo de materiales funcionales porosos cristalinos.

Prueba de ello, el crecimiento exponencial en el número de trabajos publicados con el término “*metal organic frameworks*” desde el año 1994 hasta el 2021 superando incluso desde el 2012 el número de publicaciones conteniendo el término “*coordination polymers*” (Figura 12).

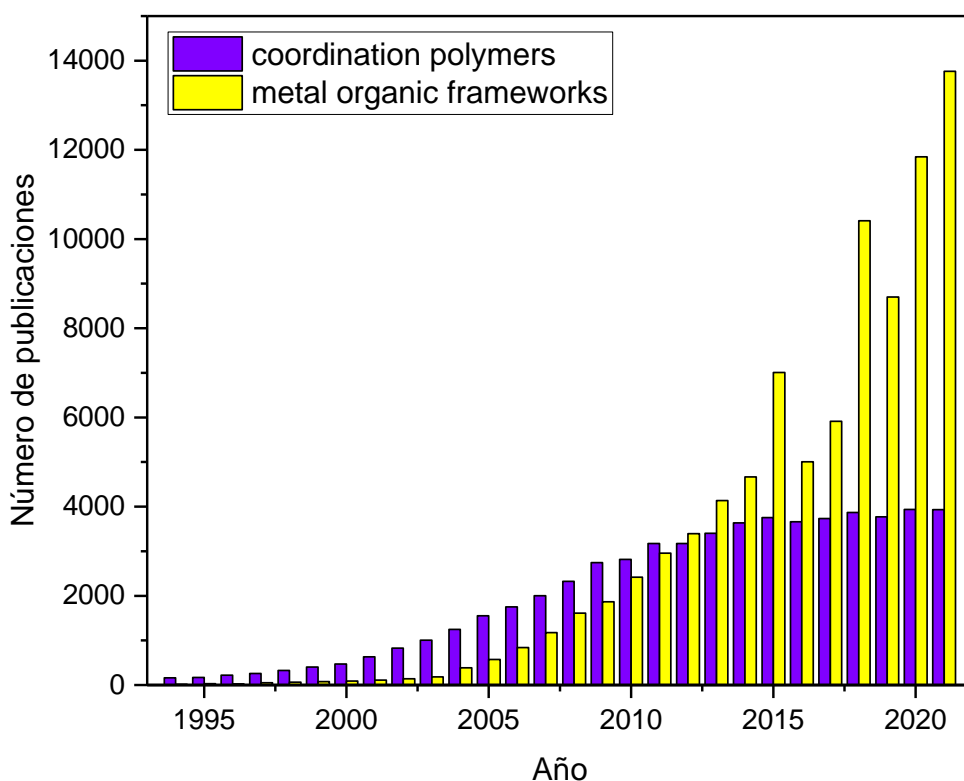


Figura 12. Número de publicaciones por año en el período (1994-2021) según la base de datos *Web of Science* (WOS). Las columnas de color violeta y amarillo corresponden a búsquedas con palabras en el título, resumen o palabras clave conteniendo los términos “*coordination polymers*” y “*metal organic frameworks*”, respectivamente.

2.2.1. Propiedades de los MOFs

A modo ilustrativo, la **Figura 13** representa las propiedades fisicoquímicas fundamentales, las rutas de síntesis principales y las aplicaciones más comunes de los MOFs. Entre las características más importantes de los MOFs, cabe destacar: i) elevada área superficial y porosidad, ii) tamaño de poro y de partícula modulables, iii) cristalinidad, flexibilidad, rigidez y ordenamiento estructural, iv) tridimensionalidad, v) morfologías definidas, vi) propiedades conductoras, ópticas, electrónicas, luminiscentes, magnéticas y quirales dependiendo del metal y ligando orgánico incorporado en la red, vii) resistencia mecánica, viii) intercambio iónico, ix) capacidad de funcionalizar la superficie de los poros mediante reacciones post-síntesis, y x) versatilidad de arquitecturas ^[132–139].

Aunque muchas son las ventajas de este tipo de materiales, la estabilidad química e hidrotérmica en relación a la porosidad y cristalinidad a largo plazo hacia ácidos, bases, aire, agua y peróxidos continúa siendo el principal desafío para la comunidad científica ^[140].

La metodología de síntesis adoptada para el diseño de los MOFs juega un papel esencial en la generación de las propiedades mencionadas anteriormente. Para ello, es indispensable introducir el concepto de *síntesis reticular* como una subclase de Ingeniería Cristalina, un término enunciado por Omar M. Yaghi ^[141] para hacer referencia al diseño de materiales funcionales tipo MOFs entendiendo las interacciones moleculares existentes entre ellos, el empaquetamiento del cristal y la topología de la red con objeto de predecir la arquitectura supramolecular resultante con las características fisicoquímicas y porosidad deseadas. En esencia, la síntesis reticular se puede describir como el proceso de ensamblar bloques de construcción moleculares rígidos cuidadosamente diseñados en estructuras ordenadas predeterminadas (redes), que se mantienen unidas por fuertes enlaces de coordinación e interacciones no covalentes.

En este ámbito, el mismo investigador introduce el concepto de SBUs (*Secondary Building Units*) para comprender y predecir las topologías de estructuras MOFs ^[142]. Los SBUs son unidades basadas en complejos moleculares y entidades de agrupamiento en las que se pueden utilizar modos de coordinación de ligandos y entornos de coordinación de metales para la transformación de estos fragmentos en redes porosas extendidas utilizando determinados ligandos.

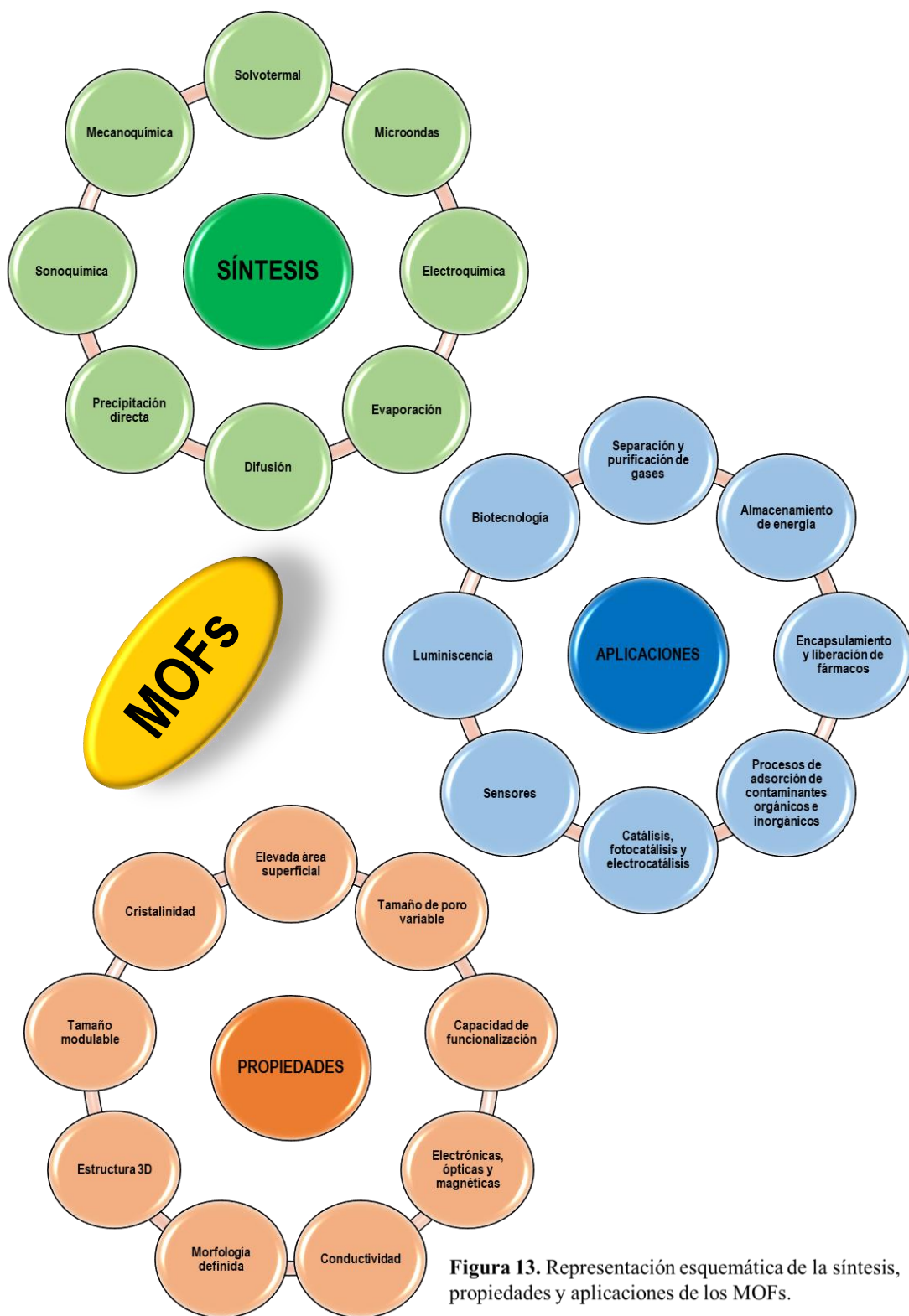


Figura 13. Representación esquemática de la síntesis, propiedades y aplicaciones de los MOFs.

Por tanto, pueden ser entendidos como módulos sintéticos para la construcción dirigida de estructuras poliméricas robustas con porosidad permanente y tamaño de poro controlado en función de la naturaleza química, geometría y dimensiones de los ligandos y los propios SBUs.

Como se ha comentado anteriormente, las unidades de construcción principales en una red metal-orgánica son los conectores o nodos metálicos y los ligandos orgánicos (enfoque propuesto por Robson ^[143]) que actúan como reactivos de partida con los que se construye el armazón principal del MOF. Además, hay otros componentes auxiliares, como ligandos de bloqueo, contraaniones, huéspedes no enlazantes o moléculas plantilla. Las características importantes de los conectores y ligandos son el número y la orientación de sus sitios de unión (números y geometrías de coordinación).

Centrando la atención en el clúster metálico, los iones de metales de transición se utilizan a menudo como conectores versátiles en la construcción de polímeros de coordinación y MOFs. La geometría y entorno de coordinación de estos centros o clústeres metálicos permiten controlar la direccionalidad, el grado de expansión y la geometría de la red.

Según el metal y su estado de oxidación, los números de coordinación pueden variar de 2 a 7, dando lugar a diversas geometrías, que pueden ser lineales, en forma de T o de Y, tetraédricas, plano-cuadradas, piramidal-cuadradas, bipiramidal-trigonal, octaédrica, piramidal-trigonal, pentagonal-bipiramidal, y las formas distorsionadas correspondientes (**Figura 14**). Los grandes números de coordinación de 7 a 10 y la geometría de coordinación poliédrica de los iones de lantánidos son útiles para la generación de topologías de red nuevas e inusuales. Además, los centros iónicos de lantánidos coordinadamente insaturados pueden generarse mediante la eliminación de moléculas de disolvente coordinadas.

En lugar de un ion de metal aislado, los conectores basados en complejos metálicos tienen la ventaja de ofrecer control de los ángulos de enlace y restringir el número de sitios de coordinación. Los sitios que no son necesarios pueden bloquearse mediante ligandos quelantes o macrocíclicos que se unen directamente al conector metálico y, por lo tanto, dejan sitios específicos libres para ligandos orgánicos ^[107].

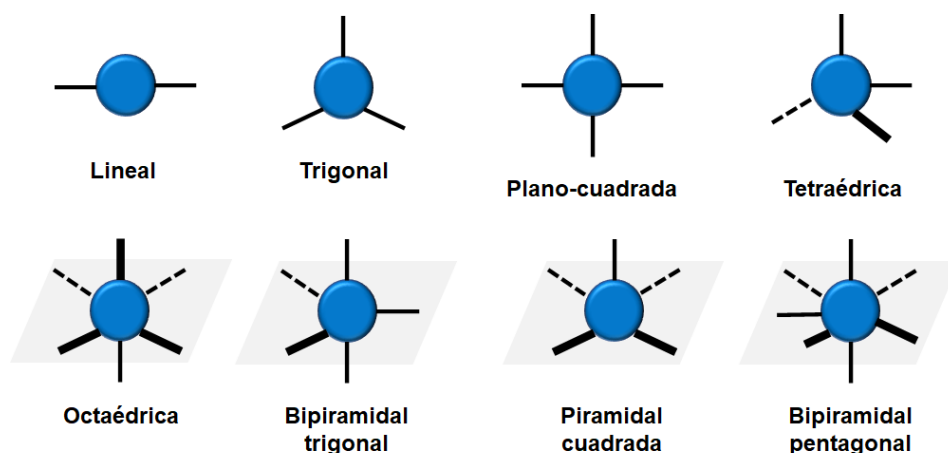


Figura 14. Geometrías generales para los entornos de coordinación de los metales de transición que actúan como conectores.

Respecto a los ligandos, cabe mencionar que ofrecen una amplia variedad de sitios de enlace con fortaleza y direccionalidad ajustadas, actuando como puentes entre los centros metálicos mediante enlaces covalentes que estabilizan la estructura polimérica. Teniendo en cuenta que los MOFs son estructuras extendidas tridimensionalmente, se hace imprescindible el empleo de ligandos orgánicos multidentados con diferente número de centros coordinativos, lo que determinará la geometría angular del material resultante. Si el ligando posee uno, dos, tres o cuatro sitios de coordinación se nombrará mono-, bi-, tri- y tetra-tópico, respectivamente (**Figura 15**).

Las características del ligando, como la longitud, el volumen, átomos dadores y los ángulos de enlace, determinan el grado de expansión, la topología y la estructura porosa de la red metal-orgánica^[144]. A menudo son preferibles los ligandos con esqueletos rígidos porque facilitan la predicción de la geometría de la red antes de la síntesis y, además, también ayudan a mantener la estructura de poros abiertos. Los ligandos orgánicos se clasifican principalmente en tres grandes grupos en función de su carga eléctrica: ligandos orgánicos neutros, aniónicos y catiónicos (**Figura 16**).

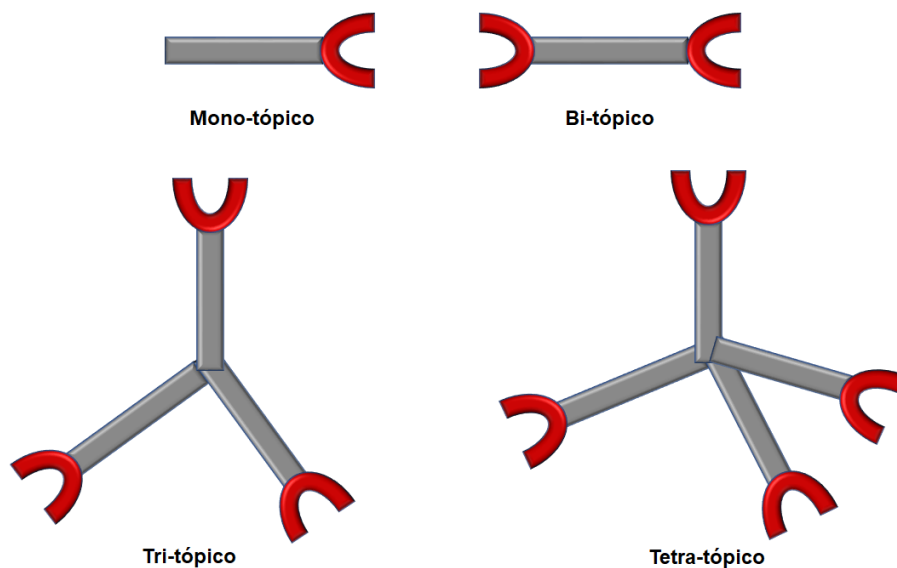


Figura 15. Tipos de centros de coordinación existentes en enlazadores orgánicos

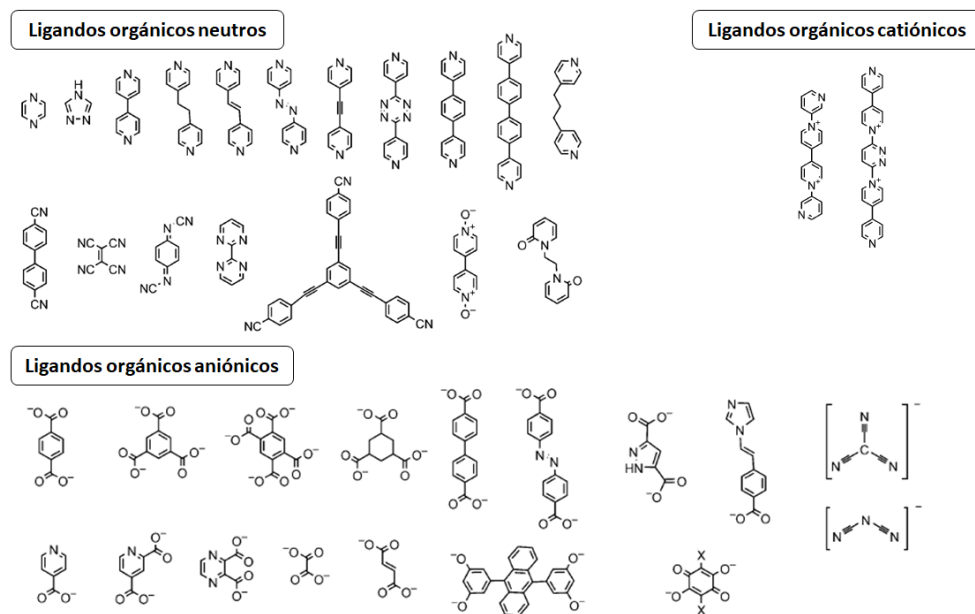


Figura 16. Ejemplos de ligandos orgánicos neutros, aniónicos y catiónicos empleados para la preparación de redes metal-orgánicas (adaptado de la referencia ^[107])

Los ligandos orgánicos neutros más utilizados son la pirazina (pyz) y la 4,4'-bipiridina (bpy) que coordinados a cationes metálicos dan lugar a MOFs con carga positiva requiriendo una especie molecular cargada negativamente (molécula huésped o molécula plantilla) para asegurar la neutralidad de la estructura. Los ligandos orgánicos aniónicos más utilizados son los carboxilatos (ácido fumárico, ácido propanodioico, ácido etanodioico y ácidos benceno-1,3-tricarboxílicos, entre otros) porque tienen la capacidad de coordinarse a iones o clústers metálicos con carga positiva a través de más de un enlace de coordinación por molécula de ligando (monodentados, bidentados o quelatos o bis-monodentados) formando una gran diversidad de armazones tridimensionales poliméricos neutros o cargados negativamente (presencia de molécula huésped catiónica) con elevada estabilidad estructural. Hay pocos ejemplos de redes metal-orgánicas construidas con ligandos orgánicos catiónicos debido a la muy baja afinidad existente por los iones metálicos catiónicos [145-148].

2.2.2. Metodologías de síntesis de los MOFs

Actualmente, existen una gran variedad de rutas metodológicas para la síntesis de MOFs aplicando estrategias basadas en la mezcla de disoluciones de una sal metálica y un ligando orgánico para obtener la arquitectura polimérica deseada a través del denominado autoensamblaje coordinativo o “*coordination-driven self-assembly*” en que se producen los enlaces de coordinación que integran la estructura de la red. Además, las variables experimentales de síntesis como la temperatura, tiempo de reacción, estequiometría metal-ligando, disolventes, concentración, presión, pH, presencia de agentes modulantes, etc., tienen una influencia fundamental en la obtención de una determinada red metal-orgánica.

En base a esto, se han desarrollado diferentes métodos de síntesis para la preparación de materiales MOFs, los cuales son descritos brevemente a continuación [149-155]:

- **Síntesis hidrotérmal y solvotérmal:** Este método de preparación de MOFs ha sido el convencionalmente utilizado empleando sales solubles como fuente de metales (por ejemplo, sulfatos, nitratos o acetatos metálicos) y ligandos orgánicos solubles en el solvente o mezcla de solventes de reacción (**Figura 17**). La síntesis hidrotérmal se refiere al uso de agua como disolvente, mientras que la síntesis solvotérmal implica el uso de disolventes orgánicos como alcoholes,

piridinas y dialquilformamidas ^[156]. La elección del disolvente depende de su capacidad para disolver el ligando orgánico y la sal metálica. En ambos casos, la reacción tiene lugar en un reactor autoclave de acero inoxidable revestido de teflón en el que se acumula una presión autógena ($> 1\text{ atm}$) y temperaturas superiores a la temperatura de ebullición del disolvente empleado en reacción. Los parámetros más cruciales durante el autoensamblaje coordinativo son la temperatura, la concentración de sales metálicas, la estequiometría metal-ligando, la solubilidad de los reactivos en el solvente y el pH de la solución. El intervalo de temperatura típico oscila entre 80 y 260 °C durante un periodo temporal que puede ir desde algunas horas hasta varios días. Aunque este procedimiento puede producir adecuada cristalinidad del material, los largos tiempos de reacción y la difícil escalabilidad son las principales desventajas de este método.

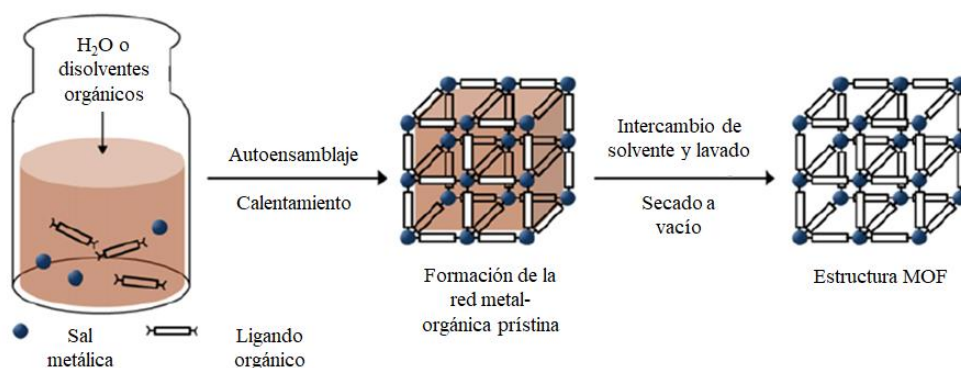


Figura 17. Esquema del proceso de síntesis solvotermal para la obtención de materiales MOFs (adaptado de la referencia ^[150]).

- **Síntesis por precipitación directa:** Este procedimiento consiste en adicionar una disolución que contiene la sal metálica sobre otra que contiene el ligando orgánico produciéndose un reconocimiento molecular en el momento de la mezcla que da lugar a la formación de los cristales ^[157]. La temperatura seleccionada puede ser variable, utilizando en algunas ocasiones la propia temperatura ambiental y en otras condiciones de reflujo, manteniendo siempre presión atmosférica. Es considerado una ruta sintética simple, reproducible, económica y fácilmente escalable.

- ***Síntesis por difusión:*** El estándar del método de difusión es la interacción gradual de varias especies disueltas en la interfase [158,159]. Se basa en la capacidad de difusión en sentido contrario de dos disoluciones conteniendo la sal metálica y el ligando orgánico, independientemente, estando ambos divididos por una capa de solvente puro en el interior de un vial o tubo de ensayo. En algunos casos se aplican geles como medios de cristalización y difusión intermedios, específicamente para reducir el ritmo de difusión y evitar la precipitación del material de partida, aumentando así la cristalinidad de la red y pudiendo generar monocristales usualmente empleados para ser estudiados mediante difracción de monocristal. La desventaja principal de este método es el elevado tiempo requerido hasta lograr la cristalización de la red [154].
- ***Síntesis por evaporación:*** El método de evaporación lenta es el método convencional más antiguo para hacer crecer cristales de algunos compuestos químicos y se ha utilizado como un procedimiento muy simple para sintetizar algunos MOFs. Consiste en llevar a cabo una disolución con la sal metálica y el ligando orgánico de partida, concentrando ambos posteriormente por evaporación espontánea del solvente o mezcla de solventes a una temperatura específica [160]. Como ventajas tiene la ausencia de fuente energética externa que promueva la reacción y las bajas temperaturas de síntesis. La principal desventaja radica en los elevados tiempos de síntesis requeridos para conseguir la cristalinidad deseada, aunque pueden reducirse si el rendimiento de la reacción tiene prioridad sobre una alta calidad del cristal aumentando la concentración de precursores y usando agitación.
- ***Síntesis asistida por microondas:*** Las técnicas de síntesis por microondas se han aplicado ampliamente para la síntesis rápida de materiales nanoporosos en condiciones hidrotermales y, en los últimos años, también para la preparación de MOFs [150,153,161–163]. Además de la cristalización rápida, las ventajas potenciales de esta técnica incluyen la eficiencia energética, fácil control del tamaño y forma de partículas, altas conversiones y selectividades y cortos tiempos de reacción. El equipo de microondas comercial proporciona salidas de potencia ajustables (ondas a una frecuencia de 300 MHz a 300 GHz) y tiene un controlador de temperatura y un controlador de presión de fibra óptica. En la síntesis por microondas,

una mezcla de sustrato en un disolvente adecuado se transfiere a un recipiente de teflón, se sella y se coloca en la unidad de microondas calentándose durante el tiempo apropiado a la temperatura establecida. Durante el proceso de síntesis, un campo eléctrico oscilante aplicado se combina con el momento dipolar permanente de las moléculas en el medio de síntesis induciendo rotaciones moleculares, dando como resultado un calentamiento rápido de la fase líquida (**Figura 18**).

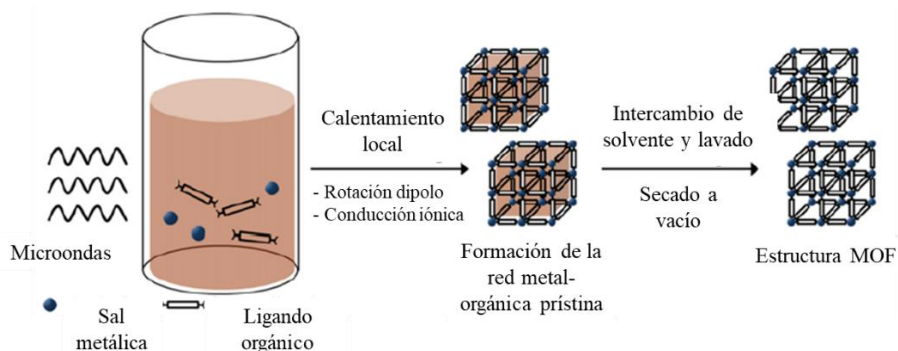


Figura 18. Esquema del proceso de síntesis asistido por microondas para la obtención de materiales MOFs (adaptado de la referencia ^[150]).

- **Síntesis mecanoquímica:** Las reacciones químicas y varios fenómenos físicos (mecanofísica) pueden ser generados por la fuerza mecánica. En la síntesis mecanoquímica, tiene lugar la ruptura mecánica de los enlaces intramoleculares seguida de una transformación química (**Figura 19**). El método utiliza fuerzas mecánicas, para formar enlaces de coordinación mediante la molienda manual de los reactivos a temperatura ambiente o, más a menudo, en molinos de bolas automáticos ^[149,150,153,160,163].

En un proceso típico de molienda por bolas, la energía requerida para iniciar las reacciones químicas es proporcionada por la fricción y el impacto entre las bolas y los reactivos alcanzando elevadas temperaturas y presiones en áreas muy restringidas. Se necesita un alto impacto de la bola para inducir una reacción química; de lo contrario, solo pueden ocurrir deformaciones elásticas. Un proceso de molienda de alta energía provoca tensión estructural, rotura de enlaces y formación de radicales reactivos. Como resultado, quedan expuestas capas reactivas de átomos, lo que facilita las reacciones químicas en la interfaz de los reactivos sólidos obteniendo el material resultante, en este caso un MOF ^[164].

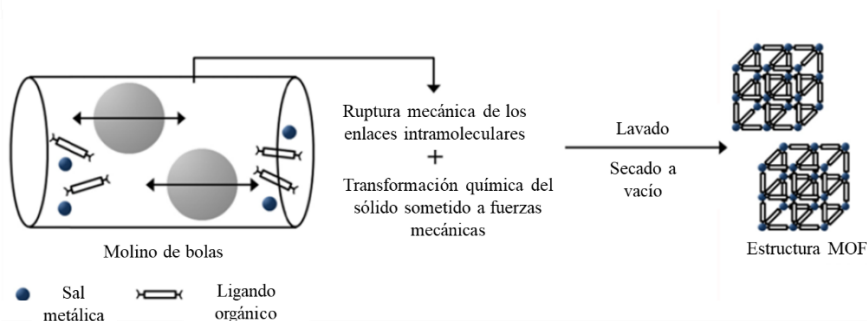


Figura 19. Esquema del proceso de síntesis mecanoquímica para la obtención de materiales MOFs (adaptado de la referencia ^[150]).

La adición de pequeñas cantidades de disolventes, denominándose esta variedad de síntesis mecanoquímica como molienda asistida por líquido e ion (*ion- and liquid-assisted grinding, ILAG*), puede acelerar las reacciones debido a un aumento de la movilidad de los reactivos a nivel molecular. El líquido también puede funcionar como agente director de estructura. Más recientemente, se informó que la extensión del método a la molienda asistida por iones y líquidos es altamente eficiente para la construcción selectiva de MOFs en laminares pilareados (*pillar-layered MOFs*) ^[164-167].

El interés en la síntesis de MOFs activada mecánicamente se debe a múltiples razones: i) son medioambientalmente sostenibles, puesto que las reacciones se pueden llevar a cabo a temperatura ambiente sin necesidad de utilizar disolventes, lo que es especialmente ventajoso cuando se pueden evitar los disolventes orgánicos, ii) la aceleración del tiempo de reacción, normalmente comprendido en el rango de 10 y 60 min, iii) la reducción del tamaño de partícula, y iv) la mejora en fenómenos de transferencia de masas ^[149,153,163].

La aplicación de la mecanoquímica a la síntesis de MOFs es además atractiva porque es una alternativa a la síntesis solvo(hidro)termal a alta temperatura y presión debido a los problemas que esta última acarrea en cuanto a la escalabilidad de reactores autoclaves que deben diseñarse con mucho cuidado en planta piloto, lo que consume un coste enorme por cuestiones de seguridad. Por ello, el método mecanoquímico constituye una ruta de síntesis basada en la química verde y respetuoso con el medio ambiente, que produce materiales de alta pureza y rendimientos eficientes a tiempos cortos de reacción.

- **Síntesis electroquímica:** Debido a las condiciones suaves de fabricación, el crecimiento más rápido de los cristales y la facilidad de escalabilidad, el método electroquímico se perfila como una técnica prometedora y respetuosa con el medio ambiente para la fabricación de MOFs. Como existe la posibilidad de controlar las condiciones de reacción durante el proceso de síntesis, la síntesis electroquímica tiene muchas oportunidades en sectores industriales donde las sales metálicas se pueden producir de manera continua durante el proceso.

El concepto general se basa en tres pasos previos: el ligando orgánico y un electrolito se mezclan en un solvente selectivo, los iones metálicos se obtienen mediante la disolución anódica y el valor de pH aumenta al incrementar la concentración de iones hidroxilos en la solución. Como resultado de la disolución anódica, la nucleación de los cristales de MOF comienza cerca de la superficie del electrodo con la consiguiente formación de una fina capa de MOF [150,153,160,163,168]. De forma más detallada, el método electroquímico utiliza un electrodo para generar los iones metálicos sumergiendo el electrodo en una solución del ligando orgánico que incluye un material electrolítico. Después de aplicar un voltaje establecido, los iones metálicos se producen alrededor de la superficie del electrodo y luego reaccionan directamente con los ligandos desprotonados en la solución para formar los cristales MOF cerca de la superficie del electrodo (**Figura 20**).

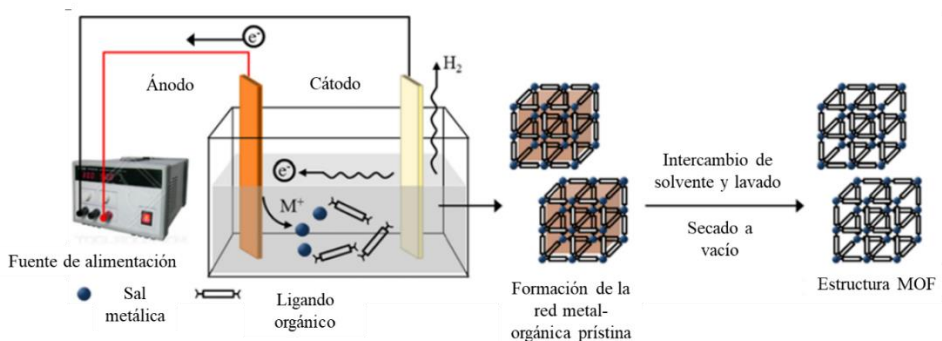


Figura 20. Esquema del proceso de síntesis electroquímica para la obtención de materiales MOFs (adaptado de la referencia [150]).

La calidad del material depende de varios parámetros, incluido el voltaje aplicado, la corriente específica, el espacio entre los electrodos, la duración de la síntesis, el tipo de solvente, la naturaleza química del ligando orgánico, la concentración de electrolito o el contenido de agua.

- Síntesis sonoquímica:** El método sonoquímico generalmente usa la energía de la radiación de ultrasonidos (rango: 20 kHz-10 MHz) para acelerar la reacción entre los centros metálicos y los ligandos orgánicos en el solvente ^[149,150,153,160,163,169,170]. Este procedimiento basado en la nucleación homogénea y acelerada también puede lograr una reducción en el tiempo de cristalización y un tamaño de partículas significativamente más pequeño que los métodos de síntesis solvotermal convencional. Como se muestra en la **Figura 21**, una disolución de la sal metálica y ligando orgánico se introduce en un reactor de vidrio (Ej: tubo Pyrex), el cual es sometido a radiación ultrasónica a través de un baño de ultrasonidos o sonda ultrasónica inmersa en la propia disolución con una potencia de salida ajustable sin refrigeración externa.

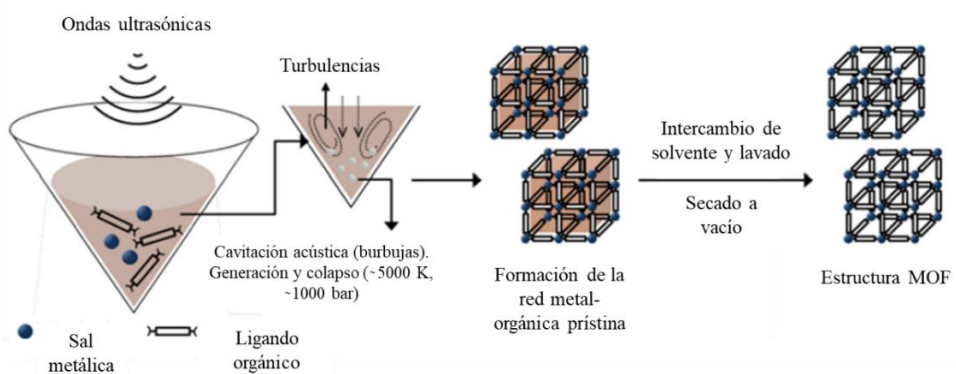


Figura 21. Esquema del proceso de síntesis asistido por ultrasonidos para la obtención de materiales MOFs (adaptado de la referencia ^[150]).

Cuando se aplican ultrasonidos sobre la disolución, se originan puntos de elevada temperatura que producen la evaporación instantánea del disolvente (cavitación), lo que origina numerosas burbujas que oscilan en el seno del líquido. A medida que las burbujas crecen hasta un cierto tamaño, luego se colapsan en muy poco tiempo y se logra un nivel de energía enorme, lo que provoca un aumento local de la temperatura (hasta 5000 K) y la presión

(hasta 1000 bar), así como una rápida liberación de energía con velocidades de calentamiento y enfriamiento de $>1010 \text{ K s}^{-1}$. Esta energía se distribuye al entorno a través del colapso. Por lo tanto, el ultrasonido es capaz de realizar cambios químicos o físicos a través de la disolución de los propios precursores. El proceso de cavitación acústica implica la formación, crecimiento y rápido colapso de microburbujas en la disolución de precursores como resultado de las fluctuaciones de presión que ocurren en el campo de ultrasonidos aplicado. Además, las condiciones extremas pueden elevar la temperatura y potenciar la formación de radicales libres; en consecuencia, las reacciones químicas son promovidas por la formación inmediata de los núcleos de cristalización.

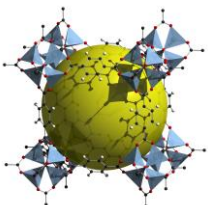
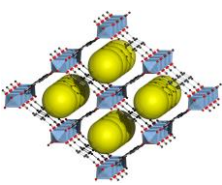
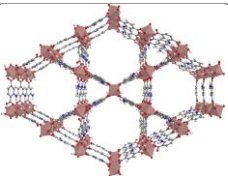
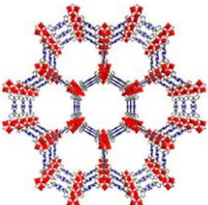
En general, las características del producto obtenido se ven afectadas por la duración de la ultrasonicación, la temperatura y la potencia de ultrasonido aplicada. Además, la morfología, el tamaño de los cristales y el rendimiento dependen esencialmente del tiempo de reacción y de la concentración inicial de los precursores. Un aumento en el tiempo de reacción conduce a un aumento en las dimensiones y el rendimiento de los cristales de MOF. El tamaño del cristal depende directamente de las concentraciones iniciales de los precursores. A baja concentración, aunque el rendimiento del MOF aumenta con un mayor aumento en el tiempo de reacción, se pueden crear cristales de mayor tamaño con formas irregulares ^[171]. Los métodos sonoquímicos pueden generar centros de nucleación homogéneos, con una reducción considerable del tiempo de cristalización en comparación con los métodos hidrotermales convencionales.

Por tanto, el principal objetivo de la síntesis sonoquímica es diseñar un método que sea rápido, respetuoso con el medio ambiente, energéticamente eficiente, fácil de usar, escalable y que pueda aplicarse a temperatura ambiente. Esta metodología de preparación de redes metal-orgánicas cobra especial relevancia en la presente Tesis Doctoral, pues ha sido la ruta de síntesis seleccionada en las investigaciones desarrolladas para la obtención de los materiales MOFs.

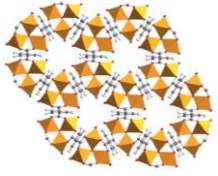
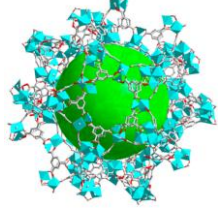

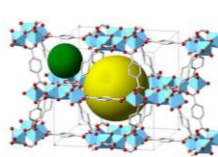
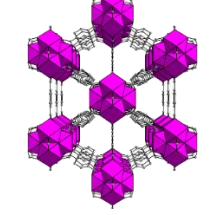
2.2.3. Estructuras más comunes de los MOFs y nomenclatura

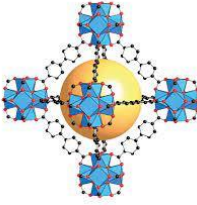
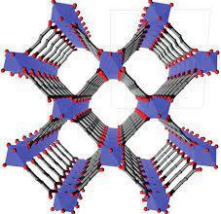
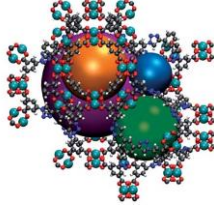
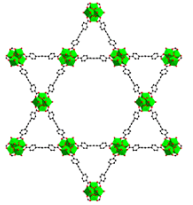
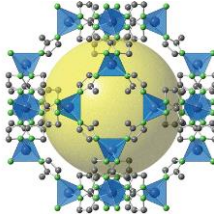
Seguidamente, en la **Tabla 1** se exponen los ejemplos más representativos de estructuras MOFs que han sido preparadas mediante algunas de las metodologías de síntesis anteriormente expuestas y utilizadas en términos generales para un mayor número de aplicaciones científicas. Específicamente, se detallan la nomenclatura, la representación estructura y fórmula, la sal metálica y ligando orgánico de partida y las características texturales de mayor relevancia como son el tamaño de poro y el área superficial. Cabe destacar que, además de los MOFs mostrados, el número de posibles combinaciones de metal-ligando es incontable y existen miles de estructuras adicionales. De hecho, el Centro de datos cristalográficos de Cambridge (*Cambridge Crystallographic Data Center, CCDC*, <https://www.ccdc.cam.ac.uk/>) contiene más de 75.000 estructuras MOF registradas diferentes. Respecto a la nomenclatura, existe una amplia variedad de abreviaturas para referirse a diferentes clases de MOFs ^[172]. Muchos MOFs se integran en grupos con denominaciones de letras similares, no de acuerdo con la semejanza de sus estructuras, sino según la ubicación de su invención. **MIL**: Materiales del Instituto de Lavoisier (*Materials of Institute of Lavoisier*), **HKUST**: Universidad de Ciencia y Tecnología de Hong Kong (*Hong Kong University of Science and Technology*), **UiO**: Universidad de Oslo (*University of Oslo*), **NU**: Universidad de Northwestern (*Northwestern University*), **ZJU**: Universidad de Zhejiang (*Zhejiang University*), **NOTT**: Universidad de Nottingham (*University of Nottingham*) o **DUT**: Universidad Tecnológica de Dresden (*Dresden University of Technology*). Otras nomenclaturas se relacionan con la topología, la estructura tridimensional de la red metal-orgánica y la naturaleza del ligando orgánico utilizado, como **ZIFs**: Estructuras de Imidazolato Zeolítico (*Zeolytic Imidazolate Frameworks*), **IRMOF**: Estructura isoreticular metal-orgánico (*Isorecticular Metal-Organic Framework*), **MOP**: Poliedros organometálicos (*Metal-Organic Polyhedra*) o **PCN**: Red de Coordinación Porosa (*Porous Coordination Network*). Debido a la falta de uniformidad en la nomenclatura de estos materiales, varios MOF tienen más de un nombre, es decir, HKUST-1 = MOF-199 = Basolite™ C300 o MIL-5 = IRMOF-1. Asimismo, el acrónimo MOF se emplea regularmente como término global para este grupo de compuestos; sin embargo, significa una estructura organometálica distinta si un número ordinal va siguiendo al término **MOF**, por ejemplo, MOF-808.

Tabla 1. Estructuras MOFs más conocidas entre la comunidad científica con sus correspondientes clústeres metálicos y ligandos orgánicos, así como con sus características texturales más importantes.

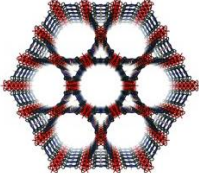
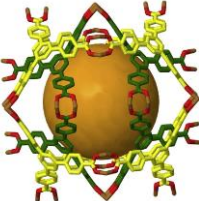
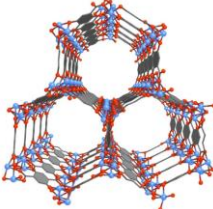
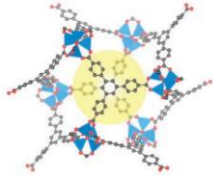
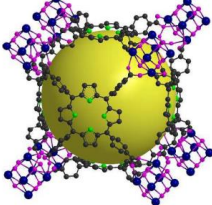
Nomenclatura	Representación estructural/Fórmula	Sal metálica/ligando orgánico/geometría	Tamaño de poro (Å)/Superficie específica (m ² g ⁻¹)	Ref.
MIL-5 o IRMOF-1	 Zn ₄ O(BDC) ₃	Zn(NO ₃) ₂ / BDC Clústeres inorgánicos [Zn ₄ O] ⁺⁶ unidos octaédricamente a seis ligandos BDC ⁻²	12 y 15/2900 (Langmuir)	[74,173,174]
MIL-53 (Cr)	 [Cr(OH)(BDC)]	Cr(NO ₃) ₃ / BDC Cadenas inorgánicas [Cr-OH] conectadas a cuatro cadenas inorgánicas vecinas mediante ligandos BDC. Cada centro metálico está coordinado octaédricamente a seis átomos de oxígeno	11.4 (alto) y 9.4 (ancho)/1500 (Langmuir)	[175]
In-MIL-68-NH ₂	 In(BDC-NH ₂)(OH)·(DMF) _x (H ₂ O) _y (x=1.5)	In(NO ₃) ₃ · x H ₂ O /NH ₂ -BDC Cadenas infinitas de octaedros de InO ₄ (OH) ₂ que comparten vértices unidos a unidades de μ-OH y BDC-NH ₂	6 y 16/1288 (Langmuir)	[176]
MIL-88A	 [Fe ₃ O(C ₄ H ₂ O ₄) ₃][(H ₂ O) ₂ (X)]	FeCl ₃ ·6H ₂ O/Ácido fumárico Trímeros oxocéntricos de octaedros de hierro (III) conectados por dianiones fumarato	6/24(BET)	[177,178]

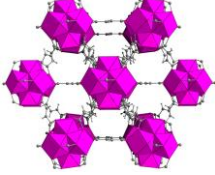

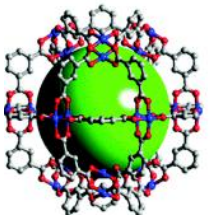
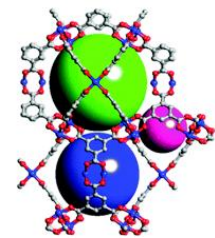
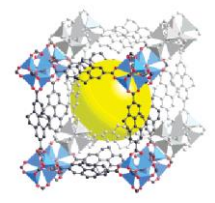
Polímeros de coordinación-Metal Organic Frameworks (MOFs)


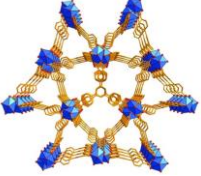
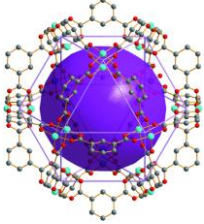
<p>MIL-88B (Fe)</p>	 <p>$C_{24}H_{12}Fe_3O_{13}$</p>	<p>$FeCl_3 \cdot 6H_2O/BDC$</p> <p>Trímeros oxocéntricos de octaedros de hierro (III) conectados por dianiones BDC</p>	<p>17.8/994 (BET)</p>	<p>[179]</p>
<p>MIL-100 (Fe)</p>	 <p>$[Fe_3O(NO_3)(H_2O)_2\{C_6H_3(CO_2)_3\}_2]_n$</p>	<p>$Fe(NO_3)_3 \cdot 9H_2O/BTC$</p> <p>Trímeros oxocéntricos de octaedros de hierro (III) conectados por dianiones BTC</p>	<p>25 y 29 (celdas), 4.7-5.5 y 8.6 (poros)/2800 (Langmuir)</p>	<p>[180]</p>
<p>MIL-101 (Cr)</p>	 <p>$Cr_3F(H_2O)_2O[(O_2C)-C_6H_4-(CO_2)]_3 \cdot nH_2O (n \sim 25)$</p>	<p>$Cr(NO_3)_3 \cdot 9H_2O/BDC$</p> <p>Trímeros de octaedros de cromo (III) interconectados por dianiones BDC</p>	<p>29 y 34 (celdas), 12 y 14.7-16 (poros)/5900 (Langmuir)</p>	<p>[181,182]</p>
<p>MIL-125</p>	 <p>$Ti_8O_8(OH)_4 \cdot (O_2CC_6H_5-CO_2)_6$</p>	<p>Isopropóxido de titanio (IV)/BDC</p> <p>Octámeros cíclicos contruidos a partir de octaedros $TiO_5(OH)$ unidos a otros 12 octámeros cíclicos a través de ligandos BDC</p>	<p>6 y 12.5/1550 (BET)</p>	<p>[183,184]</p>
<p>UiO-66</p>	 <p>$Zr_6O_4(OH)_4(BDC)_6$</p>	<p>$ZrCl_4/BDC$</p> <p>Nodos de óxido de zirconio $Zr_6O_4(OH)_4$ coordinados octaédricamente por 12 átomos de oxígeno procedentes de los ligandos BDC</p>	<p>6/1187 (Langmuir)</p>	<p>[185,186]</p>

<p>UiO-67</p>	 <p>$Zr_6O_4(OH)_4(BPDC)_6$</p>	<p>$ZrCl_4/BPDC$</p> <p>Nodos de óxido de zirconio $Zr_6O_4(OH)_4$ coordinados octaédricamente por 12 átomos de oxígeno procedentes de los ligandos BPDC</p>	<p>8/3000 (Langmuir)</p>	<p>[185]</p>
<p>Basolite A520</p>	 <p>$Al(OH)(C_4H_2O_4) \cdot 3.5 H_2O$</p>	<p>$Al_2(SO_4)_3 \cdot 18H_2O$/ Ácido fumárico</p> <p>Cadenas de octaedros de AlO_4 que comparten esquinas unidos por grupos carboxilatos del ácido fumárico para formar poros 1D en forma de rombo</p>	<p>5.8/1010 (Langmuir)</p>	<p>[187–189]</p>
<p>NU-125</p>	 <p>$C_{36}H_{21}Cu_3N_9O_{15}$</p>	<p>$Cu(NO_3)_2 \cdot 2.5H_2O$/ LH_6</p> <p>Nodos Cu (II) coordinadas por los carboxilatos de L^6 en forma de rueda de paletas</p>	<p>11, 15, 16 y 24/3120 (BET)</p>	<p>[190]</p>
<p>NU-1000 (Zr)</p>	 <p>$Zr_6(\mu_3-OH)_4(\mu_3-O)_4(OH)_4(H_2O)_4(TBAPy^+)_2$</p>	<p>$ZrOCl_2 \cdot 8H_2O$</p> <p>Nodos de $Zr_6(\mu_3-OH)_4(\mu_3-O)_4(OH)_4(OH_2)_4$ 8 veces conectados por ligandos tetratónicos basados en pireno ($TBAPy^+$)</p>	<p>12 y 31/2220 (BET)</p>	<p>[191]</p>
<p>ZIF-8</p>	 <p>$C_8H_{12}N_4Zn$</p>	<p>$Zn(NO_3)_2 \cdot 4H_2O$/2- metilimidazol</p> <p>Tetraedros de ZnN_4 donde los iones de zinc están coordinados por cuatro anillos de imidazolato</p>	<p>3.4 y 11.6/1810 (Langmuir)</p>	<p>[192]</p>

Polímeros de coordinación-Metal Organic Frameworks (MOFs)

<p>PCN-222 (Fe)</p>	 <p>$C_{48}H_{32}ClFeN_4O_{16}Zr_3$</p>	<p>$ZrCl_4/FeTCPPCl$</p> <p>Clústeres octaédricos $Zr_6(OH)_8$ conectados a ocho ligandos TCPP con geometría plano-cuadrada</p>	<p>13 y 32/2220 (BET)</p>	<p>[193]</p>
<p>MOF-14</p>	 <p>$\{[Cu_3(BTB)_2(H_2O)_3] \cdot (DMF)_9(H_2O)_2\}$</p>	<p>$Cu(NO_3)_2 \cdot 3H_2O/H_3BTB$</p> <p>Ligandos BTB unidos a iones de Cu(II) formando clústeres (ruedas de paletas). Cada BTB está coordinados a tres clústeres y cada clúster a cuatro unidades BTB (rojo Pt_3O_4)</p>	<p>8 y 14/1502 (Langmuir)</p>	<p>[194,195]</p>
<p>MOF-74 (Zn)</p>	 <p>$Zn_2(DHBDC)(DMF)_2 \cdot (H_2O)_2$</p>	<p>$Zn(NO_3)_2 \cdot 6H_2O/(H_2DHBDC)$</p> <p>Clústeres octaédricos ZnO_6 coordinados 6 veces por 3 grupos carboxilatos, 2 grupos hidroxilos y una molécula de DMF. Estructura de varillas helicoidales.</p>	<p>11/816 (BET)</p>	<p>[173,196]</p>
<p>MOF-177</p>	 <p>$Zn_4O(BTB)_2 \cdot (DEF)_{15} (H_2O)_3$</p>	<p>$Zn(NO_3)_2 \cdot 6H_2O/H_3BTB$</p> <p>Clústeres de $Zn_4O(BTB)_2$ coordinados octaédricamente a seis ligandos orgánicos BTB</p>	<p>11 y 17/4500 (Langmuir)</p>	<p>[173,197]</p>
<p>MOF-525</p>	 <p>$Zr_6O_4(OH)_4(TCPP-H_2)_3$</p>	<p>$ZrOCl_2 \cdot 8H_2O/H_4TCPP$</p> <p>Clústeres $Zr_6O_4(OH)_4$ cuboctaédricos unidos por ligandos porfirina TCPP</p>	<p>20/2620 (BET)</p>	<p>[198]</p>

<p>MOF-801</p>	 <p>$Zr_6O_4(OH)_4(C_4H_2O_4)_6$</p>	<p>ZrCl₄/Ácido fumárico</p> <p>Grupos inorgánicos [Zr₆O₄(OH)₄]¹²⁺ de doce conexiones a través de dianiones fumarato</p>	<p>4.8, 5.6 y 7.4/856 (BET)</p>	<p>[199,200]</p>
<p>MOF-808</p>	 <p>$Zr_6O_4(OH)_4(BTC)_2(HCOO)_6$</p>	<p>ZrCl₄/BTC</p> <p>Oxoclústerers hexaméricos octaédricos [Zr₆O₄(OH)₄] conectados por 6 ligandos BTC</p>	<p>4.8 y 18.4/2030 (BET)</p>	<p>[201]</p>
<p>MOP-1</p>	 <p>$Cu_{24}(m-BDC)_{24}(DMF)_{14}(H_2O)_{10} \cdot (H_2O)_{50}(DMF)_6(C_2H_5OH)_6$</p>	<p>Cu(NO₃)₂·2.5H₂O/ <i>m</i>-BDC</p> <p>12 unidades cuboctaédricas Cu₂(CO₂)₄ en forma de rueda de paletas unidas por <i>m</i>-BDC para dar un gran poliedro de carboxilato metálico</p>	<p>25/341 (BET)</p>	<p>[202,203]</p>
<p>HKUST-1 o Basolite™ C300</p>	 <p>$[Cu_3(BTC)_2(H_2O)_3]_n$</p>	<p>Cu(NO₃)₂·3H₂O/ BTC</p> <p>Unidades diméricas de tetracarboxilato cúprico. 12 átomos de oxígeno de los grupos carboxilatos BTC coordinan tres iones Cu²⁺ (esfera de coordinación pseudooctaédrica)</p>	<p>10 y 14/917.6 (BET)</p>	<p>[204]</p>
<p>IRMOF-11</p>	 <p>$Zn_4O_4(HPDC)_3$</p>	<p>Zn(NO₃)₂·6H₂O/ HPDC</p> <p>Clústeres inorgánicos Zn₄O(O₂C-)₆ conectados octaédricamente a ligandos HPDC</p>	<p>7 y 12/2096 (Langmuir)</p>	<p>[173,205]</p>

<p>DUT-49</p>	 <p>Cu₂(BBCDC)</p>	<p>Cu(NO₃)₂·3H₂O/ H₄BBCDC</p> <p>Nodos cuboctaédricos de Cu²⁺ con doce sitios de coordinación a través de ligandos carbazol</p>	<p>12, 18 y 26/5476 (BET)</p>	<p>[206]</p>
<p>ZJU-28</p>	 <p>(Me₂NH₂)₃[In₃(BTB)] ·12 DMF·22 H₂O</p>	<p>InCl₃/H₃BTB</p> <p>Ocho centros de indio coordinados actúan como nodos conectados cada uno por cuatro ligandos H₃BTB</p>	<p>8.2 y 9.4/643 (BET)</p>	<p>[207,208]</p>
<p>NOTT-11</p>	 <p>[Cu₃(L)(H₂O)₃]₄·8DM SO·15DMF·3H₂O</p>	<p>Cu(NO₃)₂·3H₂O/ TDBB</p> <p>Estructura de jaula cuboctaédrica de 24 isoftalatos TDBB⁶⁻ y 12 nodos metálicos de rueda de paleta {Cu₂(RCO₂)₄}</p>	<p>7.2, 8.6, 10.9, 12.6 y 21/3800 (BET)</p>	<p>[209]</p>

BDC: ácido 1,4-bencenodicarboxílico, BPDC: ácido bifenil-4,4-dicarboxílico, BTC: ácido 1,3,5-bencenotricarboxílico, LH₆: C₃₆H₂₁N₉O₁₂, TBAPy: 1,3,6,8-tetrakis(p-benzoato)pireno, TCPP=tetrakis(4-carboxifenil)porfirina, H₂DHBDC: ácido 2,5 dihidroxitereftálico, H₃BTB: ácido 4,4',4''-benceno-1,3,5-triil-tribenzoico, DMF: dimetilformamida, DEF: dietilformamida, HPDC: ácido 4,5,9,10-tetrahidropireno-2,7-dicarboxílico, H₄TCPP: tetrakis(4-carboxifenil)porfirina,, H₄BBCDC: ácido 9,9'-(1,1'-[bifenil]-4,4'-diil)bis(9H-carbazol-3,6-dicarboxílico), TDBB: 1,3,5-tris(3',5'-dicarboxi[1,1'-bifenil]-4-il)benceno.

2.2.4. Aplicaciones de los MOFs

La versatilidad de características estructurales y la diversidad de propiedades fisicoquímicas de los MOFs los convierten en materiales potencialmente prometedores para un amplio rango de aplicaciones de enorme interés: *i) catálisis, ii) adsorción, separación y almacenamiento de gases, iii) aplicaciones de detección (sensing), iv) luminiscencia y óptica, v) aplicaciones piezoeléctricas/ferroeléctricas, termoeléctricas y dieléctricas, vi) magnetismo, vii) conductividad de protones, viii) biomedicina (almacenamiento y liberación de fármacos), ix) aplicaciones analíticas, x) aplicaciones medioambientales (adsorción de contaminantes orgánicos y metales pesados) y xi) conversión y almacenamiento de energía.*

El creciente interés de la comunidad científica por las aplicaciones de los MOFs ha dado lugar a la publicación de varias revisiones científicas que recopilan las últimas investigaciones reportadas para cada una de las áreas aplicativas mencionadas anteriormente [131,135,138,156,163,210–212]. Seguidamente, se describen en términos generales cada una de estas aplicaciones comentando conceptualmente sus características más significativas:

i) Catálisis: Desde la perspectiva de la catálisis, los materiales MOF presentan fascinantes ventajas destacando: (1) capacidad de ajuste estructural, (2) diversidad de componentes en la estructura MOF, es decir, ligandos, nodos y poros, (3) existencia de varios sitios catalíticos en un solo MOF, (4) entornos porosos uniformes y altamente sintonizables, (5) reconocimiento y transporte de productos y sustratos, (6) estructura bien definida y ajustable que permite comprender el mecanismo catalítico, (7) relación estructura-función a nivel molecular, y (8) catálisis controlada en una amplia gama de reacciones catalíticas. Teniendo en cuenta los puntos mencionados anteriormente, los materiales MOFs han sido aplicados a diferentes áreas dentro del campo de la catálisis como *catálisis heterogénea, electrocatálisis, fotocatálisis o biocatálisis*. Los MOF se han utilizado ampliamente como *catalizadores heterogéneos* para la obtención de productos de interés en Química Fina, que son extremadamente importantes en la industria química [213–216]. Las propiedades que hacen que los MOF sean adecuados como catalizadores heterogéneos están relacionadas con la aceptable rigidez y robustez requeridas para procesos catalíticos en condiciones extremas, su porosidad y gran área superficial que facilitan la actividad catalítica, la presencia de poros y canales necesarios para la selectividad catalítica y los ligandos orgánicos que pueden ajustar la reactividad y selectividad. Los sitios activos catalíticos de los MOF pueden ser los nodos metálicos, los ligandos funcionalizados y los poros de la estructura. La síntesis de productos químicos de alto valor añadido se realiza más comúnmente a través de reacciones de oxidación (por ejemplo, epoxidación, sulfoxidación, oxidación aeróbica), reacciones de cicloadición 1,3, reacciones de transesterificación, reacciones de formación de enlaces C-C (p. ej., reacción de Heck, acoplamiento de Sonogashira y acoplamiento de Suzuki) y reacciones de hidrogenación de

moléculas orgánicas insaturadas. Los MOFs como catalizadores heterogéneos pueden actuar como ácidos de Lewis por la reactividad de los iones o nodos metálicos, así como de los ligandos orgánicos, o como soporte de unidades que transportan el oxígeno o los metales nobles necesarios para llevar a cabo la reacción catalítica.

Un campo catalítico especial es el uso de MOF quirales en catálisis quiral o en catálisis asimétrica [217-222]. Hay dos formas principales de diseñar estos catalizadores: el primero consiste en construir un MOF completo a partir de ligandos quirales, mientras que el segundo es modificar posteriormente el MOF con una funcionalidad quiral. Este tipo de catalizadores heterogéneos ha mostrado rendimientos de reacción muy elevados en términos de conversión y enantioselectividad en reacciones químicas de interés, por lo que esta estrategia se postula muy prometedora en el futuro para el campo de la catálisis asimétrica, pues permitirá obtener moléculas orgánicas ópticamente puras.

Durante las últimas décadas, los dispositivos electroquímicos, incluidas las celdas de combustible, las baterías, los supercondensadores y las celdas electrolíticas, han llamado mucho la atención. Una variedad de semirreacciones tiene lugar en estos dispositivos electroquímicos: (1) reacción de evolución de hidrógeno (HER), (2) reacción de oxidación de hidrógeno (HOR), (3) reacción de evolución de oxígeno (OER), (4) reacción de reducción de oxígeno (ORR), (5) reducción de CO₂ (CO₂RR), (6) oxidación de azufre, (7) oxidación de metales y (8) reducción de iones metálicos. En el campo de la electrocatálisis, cabe mencionar que en algunas de estas semirreacciones se requiere un exceso de energía y un gran sobrepotencial (HER, HOR, OER, ORR, CO₂RR) y, normalmente, poseen una cinética de reacción lenta proporcionando energías y potenciales de reacción más bajos que los calculados teóricamente. Los requisitos para que los MOFs muestren actividad en *electrocatalisis* es poseer tres factores electroquímicos fundamentales: onset-potential, densidad de corriente y sitios activos redox en los centros metálicos [131,138,230,163,223-229]. Las reacciones electrocatalíticas tienen lugar en disoluciones de electrolitos donde se requiere una elevada acidez o basicidad, por lo que es muy importante el desarrollo de MOFs con excelentes estabildades químicas que muestren conductividad iónica en H₂O y medios ácidos/básicos. Por tanto, el objetivo

consiste en diseñar MOF altamente estables aumentando la fuerza de unión de la coordinación metal-ligando para incrementar la estabilidad química, y esto se puede lograr combinando ligandos de carboxilato con iones metálicos de alto estado de oxidación o combinando ligandos de azolato muy básicos con iones de metales blandos.

Los MOFs también han surgido como materiales prometedores en procesos de *fotocatálisis* ^[131,138,163,231–235] debido a la elevada superficie específica, los sitios activos definidos, el control de las propiedades semiconductoras y los componentes estructurales ajustables teniendo la capacidad de incorporar co-catalizadores tales como metales y óxidos metálicos. Su actividad fotocatalítica puede ser llevada a cabo a través de diferentes mecanismos que involucran partes de los MOF que absorben luz, como el mecanismo de transferencia de carga de ligando a metal (*ligand-to-metal charge-transfer mechanism*, LMCT), el mecanismo de transferencia de carga de ligando a ligando (*ligand-to-ligand charge transfer*, LLCT), la transferencia de carga de metal a ligando (*metal-to-ligand charge transfer*, MLCT), o mecanismo de transferencia de carga de metal a metal (*metal-to-metal charge transfer*, MMCT), y vías de excitación duales. Los tres parámetros más importantes de un fotocatalizador son el rango de respuesta del espectro, la separación efectiva de electrones y huecos y la eficiencia de la reacción redox de los portadores de carga. Los MOF pueden presentar un comportamiento similar al de los semiconductores en el sentido de que los ligandos orgánicos proporcionan el orbital molecular ocupado más alto (HOMO) y los nodos metálicos proporcionan el orbital molecular desocupado más bajo (LUMO). La irradiación de los MOF por una fuente de luz adecuada generalmente da como resultado un proceso de transferencia de carga de ligando a metal (LMCT) en el que los electrones de los ligandos se transfieren a los nodos metálicos, lo que resulta en la separación de huecos y electrones. Los poros intrínsecos y la elevada área superficial de los MOFs facilitan la adsorción de moléculas reactivas, lo que brinda más oportunidades para acceder a los sitios activos beneficiando el estudio detallado del mecanismo de reacción fotocatalítica y evitando los fenómenos indeseables de recombinación electrón-hueco. La capacidad de modular los centros activos y ligandos orgánicos permite extender la región de absorción de luz, investigar

los efectos de transporte de carga, la fotogeneración de portadores de carga, ampliar el tiempo de vida de los estados de transición fotoexcitados y generar una adecuada separación de carga para evitar fenómenos de recombinación. Esto puede ser logrado llevando a cabo rutas de preparación de MOFs que impliquen estrategias como la funcionalización y modificación de los ligandos orgánicos, dopaje de metales, modificación con nanopartículas de metales nobles o materiales basados en carbón, sensibilización con diferentes moléculas sensibilizadoras (por ejemplo, colorantes y complejos metálicos), decoración con un co-catalizador y acoplamiento con un semiconductor; lo que da lugar al desarrollo de fotocatalizadores altamente eficientes con actividades fotocatalíticas mejoradas.

Respecto al campo de la *biocatálisis* [236–239], los MOFs tienen ventajas incomparables respecto a otros materiales convencionales que se atribuyen a sus características únicas. Existen diversas clases de agentes biocatalíticos incorporados en MOFs: enzimas naturales, modelos artificiales de enzimas, nanoenzimas, biocatalizadores basados en organismos y biocatalizadores de MOF que responden a estímulos. La elevada porosidad y estabilidad química/física sirven para promover la estabilidad y reciclabilidad de enzimas naturales o células enteras, mientras que el tamaño ajustable, el entorno poroso y los sitios de interacción permiten que la mayoría de las enzimas se inmovilicen e incluso pueden facilitar activamente la transferencia de masa de sustratos y productos. Por otro lado, los MOF mismos pueden funcionar como enzimas biomiméticas debido a sus grupos funcionales inherentemente catalíticos o como materiales de soporte pasivos para biocatalizadores.

ii) Adsorción, separación y almacenamiento de gases: El hidrógeno (H_2) y el (CH_4) representan recursos energéticos alternativos para los vehículos del futuro, y su uso efectivo sigue siendo un desafío para la industria automotriz con el objetivo de reducir la dependencia global de combustibles fósiles. La captura de gases industriales tóxicos, como NH_3 y H_2S , e hidrocarburos volátiles, como el benceno, así como la eliminación de SO_2 y NO_x de los gases de combustión, son de gran importancia para la protección del medio ambiente. Un paso muy crítico en la industria química es la separación de mezclas de gases, como la captura de CO_2 en mezclas CO_2/CH_4 , separación de CO_2/N_2 , purificación de O_2 , etc. En este

sentido, los MOFs poseen características excelentes para aplicaciones consistentes en la adsorción, separación y almacenamiento de gases debido a sus geometrías de poro ajustables, marcos flexibles, estructuras porosas ordenadas y elevadas áreas superficiales ^[138,140,163,210,223]. Concretamente, han recibido una creciente atención en: i) almacenamiento de H₂ ^[240–242] y CH₄ ^[205,243,244] de forma segura en estructuras MOFs microporosas para ser empleados como portadores de energía renovables en motores de combustión o celdas de combustible, en el caso del H₂, o en la combustión de gas natural, donde el CH₄ es el componente principal, ii) adsorción de CO₂ ^[245–251] para reducir el impacto medioambiental, así como otros gases tóxicos subproductos de procesos de combustión como el SO₂ y los NO_x ^[252–256], y iii) separación selectiva en mezclas gaseosas (H₂/N₂, H₂/CO₂, H₂/CH₄, CO₂/CH₄, CO₂/N₂, hidrocarburos, etc.) actuando como tamices moleculares con porosidad modulable mediante interacciones adsorbato-superficie ^[245,257–263].

iii) Luminiscencia y óptica: La luminiscencia es el proceso en el que se produce la emisión de luz tras la absorción de energía de una radiación incidente generada por una fuente de excitación externa. Los materiales MOF luminiscentes se basan generalmente en elementos activos como, por ejemplo, elementos de tierras raras emisoras de luz como europio y terbio o en procesos estimulados por un cromóforo orgánico que es responsable tanto del proceso de excitación como del de emisión ^[210,264–268]. Por tanto, la luminiscencia de los MOFs se puede ajustar a través de sustituciones de ligandos orgánicos y metálicos, o mediante la incorporación de moléculas huésped y puede ser el resultado de varios mecanismos. Uno de ellos es la denominada “*luminiscencia centrada en el ligando*” en la que la absorción y emisión de los fotones se produce a través del propio ligando. Este es el mecanismo más común en los MOFs, especialmente cuando ligandos orgánicos tienen un sistema π conjugado o aromático. Junto a este mecanismo, también pueden ocurrir otros en los que la absorción y emisión de fotones tiene lugar en diferentes partes del MOF, por ejemplo, LLCT (cuando hay un apilamiento intermolecular entre ligandos adyacentes), LMCT, MLCT y MMCT. Asimismo, pueden existir otros fenómenos de emisión de luminiscencia como los efectos antena o la funcionalización de superficies con unidades emisoras de luz.

Respecto a las ventajas que tiene el uso de MOFs luminiscentes en comparación con otros materiales en estado sólido, se puede mencionar que exhiben tiempos de vida de fluorescencia eficiencias cuánticas mejoradas debido a que su estructura reticular rígida dificulta el libre movimiento de los ligandos, al mismo tiempo que aumenta la transferencia de energía. De esta forma, el control de las propiedades ópticas, fotofísicas y electrónicas en las características luminiscentes de los materiales MOFs para lograr la emisión de luz a frecuencias o longitudes de onda deseables, permitirá su integración en dispositivos tecnológicos ópticos, fotónicos y optoelectrónicos.

iv) Aplicaciones de detección (sensing): Los MOF luminiscentes son considerados potencialmente prometedores para desarrollar diferentes tipos de sensores debido a la capacidad de poder diseñar propiedades luminiscentes ajustables y a la captura selectiva por tamaño o forma de moléculas de analito [138,140,163,210,223]. Son especialmente atractivos como nuevos materiales de detección porque muestran un área superficial elevada que mejora la sensibilidad de detección, características estructurales específicas (sitios metálicos accesibles, tamaños de poros ajustables, etc.) que promueven selectividad mejorada mediante interacciones anfitrión-huésped (*guest-host*), y porosidad flexible que permite la liberación y absorción reversibles de moléculas pequeñas, cationes y aniones o biomoléculas [269-275]. En general, un cambio en la intensidad de las propiedades de luminiscencia de un determinado MOF se puede utilizar como sonda en el reconocimiento del analito que interactúa. Este cambio de intensidad, dependiendo de la naturaleza electrónica del analito, se suele emplear como método de detección en MOF basado en luminiscencia. Una vía más fiable y eficiente es la aparición y/o desaparición de un pico de emisión. Diversas funcionalidades químicas han sido incorporadas en el nano-espacio de coordinación de los materiales MOF y se han mostrado efectivos para aplicaciones de detección para biomoléculas, iones metálicos, explosivos, toxinas ambientales y otros. Concretamente, los MOF conteniendo metales lantánidos (Ln-MOF) se han estudiado ampliamente en varias aplicaciones de sensores debido a su porosidad inherente y las propiedades luminiscentes particulares de los iones Ln^{3+} [276-278]. La mayoría de los sensores Ln-MOF muestran cambios en la intensidad de la luminiscencia, incluida la

mejora de la luminiscencia (respuesta de encendido, *turn-on response*) y extinción (respuesta de apagado, *turn-off response*) al reconocer los analitos. Los iones Eu^{3+} y Tb^{3+} se utilizan comúnmente como centros luminiscentes en sensores Ln-MOF debido a su fuerte emisión roja característica a alrededor de 614 nm y emisión verde alrededor de 541 nm, respectivamente. Los Ln-MOF logran detectar especies iónicas, moléculas pequeñas, químicos explosivos y pH, así como también temperaturas específicas. Además, las características estructurales y químicas inherentes de los Ln-MOF los hacen considerablemente útiles en aplicaciones de biodetección y bioimagen.

- v) **Aplicaciones piezoeléctricas/ferroeléctricas, termoeléctricas y dieléctricas:** Los materiales piezoeléctricos convierten la energía mecánica en energía eléctrica a través del efecto piezoeléctrico directo y pueden considerarse recolectores de energía para generarla cuando no se dispone de electricidad directa o baterías. Una subclase son los materiales ferroeléctricos, que exhiben polarización eléctrica espontánea cuya dirección puede invertirse aplicando campos eléctricos externos. Los materiales piezoeléctricos/ferroeléctricos, como materiales cristalinos y cerámicos, polímeros y cristales líquidos, encuentran aplicaciones potenciales en los cristales de cuarzo piezoeléctricos como transductores ultrasónicos, sensores, filtros, motores ultrasónicos, recolectores de energía, dispositivos ópticos, etc. Entre ellos, los MOFs han mostrado interesantes propiedades piezoeléctricas y ferroeléctricas con polarización espontánea [279–281]. Los materiales termoeléctricos, que pueden generar potencial eléctrico a partir de una diferencia de temperatura, constituyen un enfoque ecológico para generación de energía a partir del calor residual. Además de los compuestos inorgánicos, como óxidos y aleaciones, se han desarrollado MOFs conductores como nuevos materiales termoeléctricos potenciales para la fabricación de dispositivos termoeléctricos [282,283]. Este enfoque incluye MOF de metales de transición de la primera fila combinados con ligandos tiolato, inclusión de moléculas huésped o nanoclústeres metálicos para mejorar la conductividad del material [163]. Los dispositivos semiconductores se basan en materiales dieléctricos, que muestran constantes dieléctricas muy bajas ($k < 3,9$ como en SiO_2). Los MOFs presentan constantes dieléctricas bajas establecidas dentro del rango anteriormente mencionado considerándose materiales prometedores

para la futura industria de la microelectrónica [284,285]. Además, presentan otras características importantes para ser empleados en este campo aplicativo como buena estabilidad térmica a altas temperaturas, comportamiento mecánico predecible, aislamiento eléctrico y adhesión a otras capas intermedias [163].

vi) Aplicaciones fundadas en el magnetismo: Un objetivo importante de la investigación de materiales magnéticos es la mejora de las propiedades de los imanes, así como la exploración de nuevas funciones, en particular en combinación con otros fenómenos útiles. Las propiedades magnéticas como el ferromagnetismo, el antiferromagnetismo y el ferrimagnetismo de los sistemas polimetálicos se derivan de las interacciones de intercambio cooperativo entre los iones metálicos paramagnéticos o los radicales orgánicos a través de entidades puente diamagnéticas. Por lo tanto, sus comportamientos magnéticos dependen de la naturaleza intrínseca tanto del metal como del ligando orgánico, así como del nivel particular de organización creado por la interacción de coordinación metal-ligando. Como resultado, al buscar el magnetismo de los MOFs, el diseño del ligando es crucial tanto para organizar los iones metálicos paramagnéticos en una topología deseada como para transmitir de manera eficiente las interacciones de intercambio entre los iones metálicos de manera controlada. Además, la porosidad de los MOF proporciona fenómenos interesantes adicionales con respecto a las propiedades magnéticas y el uso de técnicas de coordinación química o ingeniería de cristales permite el diseño sistemático de MOF con propiedades magnéticas ajustables. Los estudios magnéticos de MOFs están integrados en el área de imanes moleculares y el diseño de materiales magnéticos de baja dimensión, sensores magnéticos y materiales multifuncionales [286-288].

vii) Conductividad de protones: Recientemente, los MOFs han atraído un interés considerable como materiales conductores de protones debido a que pueden acomodar varios transportadores de protones en sus poros/canales y pueden proporcionar información útil sobre la vía y el mecanismo de conducción de protones [289,290]. Aunque ha sido un campo bastante incipiente, ya se ha logrado un progreso significativo aprovechando estas ventajas junto a su elevada cristalinidad y área superficial para aplicaciones vinculadas a celdas

de combustibles donde pueden actuar como electrolitos. Si bien la carga negativa de la red no es un requisito previo para la conducción de protones, muchos de ellos son MOF aniónicos cuya carga se compensa con pequeñas aminas protonadas o protones unidos a las moléculas del solvente mediante enlaces de hidrógeno, o protones débilmente unidos a los grupos funcionales de los ligandos orgánicos (con menos frecuencia en carboxilatos y, más a menudo, en ligandos sulfónicos y fosfonatos). Un problema común de muchos MOF conductores de protones es su buena conductividad a una humedad relativa (HR) alta, pero una conductividad significativamente baja a una HR reducida. Sin embargo, la conductividad de protones asistida por agua de los MOFs en condiciones húmedas puede ser comparable a la de Nafion, un polímero orgánico que se usa actualmente para aplicaciones prácticas en celdas de combustible [138,291].

viii) *Biomedicina (almacenamiento y liberación de fármacos):* Los MOFs y sus materiales derivados se han estudiado cada vez más como portadores y dosificadores de fármacos, agentes de bioimagen y agentes terapéuticos contra el cáncer debido a sus excelentes propiedades fisicoquímicas [223,292–294]. La mayoría de los transportadores de fármacos conocidos, como los liposomas, las nanopartículas y las micelas, muestran una carga de fármaco deficiente (menos del 5 %) y una liberación rápida del fármaco. Por lo tanto, los MOF porosos con altas cargas de fármacos se consideran candidatos para aplicaciones de administración y liberación controlada [295]. Los requisitos para los vehículos de fármacos eficientes son la alta carga de fármacos, el control de la liberación del fármaco, el control de la degradación de la matriz y la baja toxicidad [296,297]. La carga de los fármacos en los MOF se puede lograr por encapsulación no covalente en el MOF a través de procesos de fisisorción, por modificación post-sintética de los ligandos orgánicos después de la síntesis del MOF, por el uso de los fármacos como ligandos orgánicos en la construcción de los MOF y mediante la unión de los fármacos a las subunidades del MOF mediante enlaces covalentes [163,298]. Uno de los temas más importantes para la aplicación de MOF como posibles sistemas de administración de fármacos en organismos vivos es la biotoxicidad, es decir, los MOF pueden causar efectos negativos cuando son administrados en seres humanos. Por este motivo, se han

desarrollado MOF biológicos basados en principios activos farmacéuticos, como aminoácidos, proteínas, péptidos e iones metálicos de baja toxicidad, como el zinc y el hierro (BioMOF) para paliar estos problemas de toxicidad [299,300].

ix) Aplicaciones analíticas: Los MOFs se han estudiado recientemente como materiales absorbentes avanzados en la preparación de muestras de moléculas orgánicas pequeñas, como hidrocarburos policíclicos aromáticos (PAH), productos farmacéuticos, bifenilos policlorados (PCB), compuestos orgánicos volátiles (VOC), herbicidas y pesticidas [163,301-303]. La extracción en fase sólida (SPE) de biomacromoléculas (péptidos, fosfopéptidos, glicopéptidos, ácidos nucleicos y proteínas) de fluidos biológicos (plasma humano, orina, suero, saliva, clara de huevo y leche) mediante el uso de MOFs como adsorbentes es uno de los métodos más eficientes [304-306]. Además, los MOF se utilizan como absorbentes para la preparación de muestras de matrices alimentarias, como leche, bebidas, productos cárnicos, pollo y pescado, antes del análisis con métodos cromatográficos y espectrométricos [307]. Su alta estabilidad térmica y el sencillo diseño de nanocristales hacen que los MOFs hayan sido empleados para enfrentar los desafíos analíticos en la recolección de muestras, la preconcentración, la extracción y la separación cromatográfica para mejorar la sensibilidad, la selectividad y el límite de detección. Específicamente, pueden mencionarse cinco aplicaciones analíticas importantes que integran el uso de materiales MOFs: (1) MOFs de microtamaño a gran escala como adsorbentes para muestreo en campo y extracción en fase sólida (SPE); (2) MOFs de tamaño nanométrico y películas delgadas diseñadas de MOF como recubrimientos para microextracción en fase sólida (SPME), microbalanza de cristal de cuarzo (QCM) y espectrometría de masas de tiempo de vuelo de ionización por desorción láser asistida por matriz (MALDI-TOF-MS); (3) MOF como fases estacionarias para cromatografía líquida de alta resolución (HPLC); (4) plataforma de tamices moleculares en tándem basada en MOFs para extracción selectiva y HPLC; (5) MOF resistentes a solventes de tamaño micrométrico como fases estacionarias para HPLC [308,309].

x) Aplicaciones medioambientales: Generalmente, los efluentes de aguas residuales contienen una gran variedad de contaminantes

orgánicos persistentes (*persistent organic pollutants, POPs*) peligrosos como bisfenol A (BPA), colorantes sintéticos, antibióticos (clorhidrato de tetraciclina (TC) y *p*-nitro-fenol (PNP) o metales pesados como cadmio, zinc, cromo, níquel, mercurio y plomo, que son asimilados en el suelo y pueden afectar el crecimiento de plantas y microorganismos. La degradación fotocatalítica de los POPs por los MOFs atrajo la atención de los investigadores recientemente debido a su interfaz donante-aceptor bien ordenada y su porosidad excepcional ^[310,311]. La primera propiedad facilita la separación eficiente electrón-hueco tras la fotoexcitación, mientras que la segunda permite la difusión de los contaminantes objetivo en las cavidades internas para lograr un mayor contacto. Las interacciones π - π entre los POPs y los ligandos orgánicos de los MOFs también favorecen una adsorción eficiente y la elevada capacidad de modular estructuralmente los MOFs aumenta aún más su atractivo como fotocatalizador novedoso. Adicionalmente, MOFs prístinos y MOFs funcionalizados superficialmente estables en medio acuoso también han sido utilizados en la eliminación selectiva de ciertos metales pesados de soluciones acuosas mediante procesos de adsorción, mostrando elevada capacidad de adsorción y eficiente selectividad, o mediante reacciones de reducción fotocatalítica ^[312–314].

xi) Dispositivos de conversión y almacenamiento de energía: Los materiales MOFs pueden exhibir rendimientos prometedores en aplicaciones de conversión y almacenamiento de energía debido a sus destacadas características estructurales, elevada área superficial, porosidad controlada, conductividad iónica, propiedades fisicoquímicas (estabilidad, flexibilidad, tamaño de partícula, morfología, etc.) y producción a gran escala ^[315]. Respecto a dispositivos de conversión de energía, cabe destacar su participación en celdas solares y de combustible, en diodos emisores de luz blanca, así como en los principales dispositivos de almacenamiento energético, donde son uno de los principales componentes: baterías (baterías de iones de litio (Li-ion, Li-S y Li-O₂), baterías de iones de sodio (Na-ion), baterías de zinc-aire (Zn-O₂) y baterías de aluminio-aire (Al-O₂)) y supercondensadores ^[316–320].

2.3. Materiales híbridos orgánico-inorgánicos mesoporosos ordenados basados en sílice

El desarrollo de materiales híbridos orgánico-inorgánicos mesoporosos con grandes áreas superficiales específicas y tamaños de poro ajustables en el intervalo de 2-15 nm obtenidos a través del acoplamiento de componentes inorgánicos y orgánicos asistido por moléculas plantilla o “templates”, es actualmente un área de extensa de investigación con aplicaciones potenciales en adsorción, cromatografía, catálisis, tecnología de sensores y almacenamiento de gases. Según la definición de la IUPAC [321], los materiales porosos se pueden clasificar en tres grupos: i) los materiales *microporosos* que tienen diámetros de poro inferiores a 20 Å (2 nm), ii) los materiales *mesoporosos* que tienen diámetros de poro que oscilan entre 20 y 500 Å (2-50 nm), y iii) los materiales *macroporosos* que tienen diámetros de poro superiores a 500 Å (50 nm). El creciente interés de la comunidad científica por los denominados materiales mesoporosos comenzó en 1992 con el desarrollo de una clase de sílices mesoporosos periódicas con poros uniformes en el rango de los mesoporosos de 15 a 100 Å y elevadas áreas superficiales ($\sim 1000 \text{ m}^2/\text{g}$) conocidas como M41S por parte de la Mobil Research and Development Corporation [66,96,322]. Estos materiales son silicatos o aluminosilicatos preparados mediante el uso de surfactantes catiónicos de tipo alquiltrimetilamonio como agentes directores de estructura y reemplazaron a los tamices moleculares basados en zeolita, que estaban restringidos a tamaños de poro pequeño de alrededor de 15 Å [323–325]. La familia M41S presenta tres materiales mesoporosos con diferente ordenamiento estructural: (1) MCM-41 (*Mobil Composition of Matter number 41*): estructura hexagonal bidimensional (2D) con simetría de grupo espacial $P6mm$, (2) MCM-48 (*Mobil Composition of Matter number 48*): sistema cúbico tridimensional (3D) con simetría de grupo espacial $Ia3d$, y (3) MCM-50 (*Mobil Composition of Matter number 50*): estructura laminar con simetría de grupo espacial $p2$ (**Figura 22**) [326–329]. Respecto a su estructura, cabe destacar que las paredes silíceas de estos materiales no presentan ordenamiento y tiene gran cantidad de defectos estructurales como consecuencia de los procesos de hidrólisis y posterior condensación, la cual no es completa, pues existen grupos hidroxilos colgantes enlazados a los átomos de silicio que integran la pared del material (comúnmente denominados grupos silanoles).

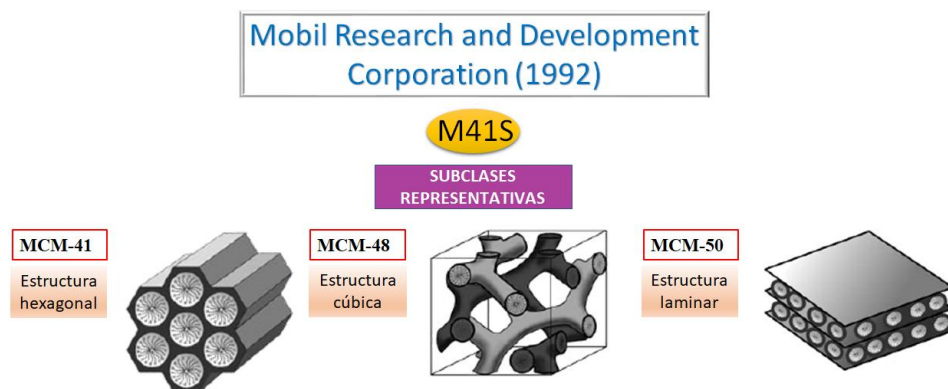


Figura 22. Estructuras de materiales mesoporosos de la familia M41S (adaptado de la referencia ^[329]).

Si se comparan las familias de materiales inorgánicos con elevada superficie específica como son las sílices mesoporosas y las zeolitas, se puede argumentar que mientras que las zeolitas son sólidos totalmente cristalinos, a diferencia de los geles de sílice obtenidos por el método sol-gel que presentan una estructura porosa completamente desordenada, los denominados materiales mesoporosos ordenados tienen un ordenamiento mesoscópico, es decir, son cristalinos a escala mesoscópica pero amorfos a escala de celda unidad. La síntesis de esta nueva familia de silicatos mesoporosos M41S implica un proceso sol-gel ^[330,331] bajo condiciones hidrotermales basada en la hidrólisis y policondensación de precursores de tipo alcóxido metálico como fuentes de silicio, $M(OR)_n$, siendo M un metal y R un grupo alquilo (metilo o etilo), en presencia de un surfactante o agente director de estructura, una especie mineralizante y un disolvente. Dentro del grupo de estos materiales, la sílice MCM-41 ha sido la más extensamente investigada, siendo sintetizada mediante el autoensamblaje y condensación simultánea de geles de aluminosilicatos en presencia del surfactante catiónico bromuro de hexadeciltrimetilamonio (CTAB) a través de un mecanismo de plantilla de cristal líquido (*liquid-crystal templating mechanism, LCT*) ^[66,96]. En este ámbito, dos mecanismos fueron propuestos para la formación de estos materiales M41s con mesoestructura hexagonal mediante fases cristal líquido ^[329] (**Figura 23**):

- **“True liquid-crystal templating mechanism”**: El primer mecanismo consiste en que las moléculas de surfactante bajo determinadas condiciones de temperatura y concentración forman micelas en forma de cilindros para, posteriormente, formar

estructuras hexagonales ordenadas de cristal líquido. Esta fase cristal-líquido formada previamente a la adición de las especies inorgánicas dirige el crecimiento de las mesoestructuras inorgánicas, al tener lugar la migración y polimerización de las especies de silicio alrededor de la estructura cilíndrica. Por tanto, es necesario que la concentración de surfactante inicial sea lo suficientemente elevada como para que la fase cristal líquido se forme sin requerir la presencia del precursor inorgánico (ejemplos: tetraetilortosilicato (TEOS, $\text{Si}(\text{OEt})_4$) o tetrametilortosilicato (TMOS, $\text{Si}(\text{OMe})_4$)).

- **“Cooperative self-assembly mechanism”**: En el segundo mecanismo, la incorporación de especies inorgánicas en la mezcla inicial de síntesis promueve la generación de la fase cristal líquido y facilita la propia formación de las mesoestructuras inorgánicas requiriendo menor concentración de surfactante.

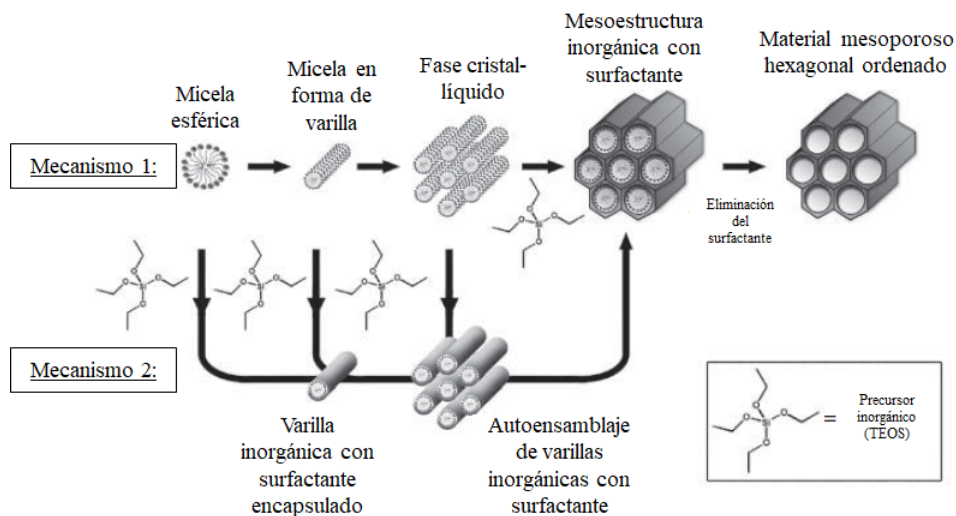


Figura 23. Mecanismos implicados en la formación de mesoestructuras dirigidas por agentes directores de estructura: 1) *True liquid-crystal templating*, y 2) *Cooperative self-assembly* (adaptado de la referencia [329]).

El desarrollo de los materiales M41s supuso un gran avance científico en el área de materiales mesoporosos de naturaleza silíceo. Sin embargo, a efectos prácticos presentaron dos inconvenientes principalmente: i) el uso de surfactantes moleculares como agentes directores de estructura genera mesoestructuras con un grosor de pared

reducido en el rango de 0.8-1.3 nm afectando negativamente a la estabilidad del material (especialmente en condiciones de humedad en que los enlaces siloxano son atacados por el agua dando lugar a grupos silanoles libres), y ii) el tamaño de poro reducido ^[140]. Para solventar esta problemática, el siguiente avance para la síntesis de materiales mesoporosos ordenados basados en sílice con tamaño de poro grande y paredes gruesas consistió en el uso de otras plantillas supramoleculares constituyendo una alternativa atractiva debido a sus propiedades: ordenamiento mesoestructurado, carácter anfifílico no iónico, disponibilidad comercial, bajo coste económico y su biodegradabilidad. Estos surfactantes son los denominados “Pluronic”, una marca de la entidad empresarial BASF, y se definen como una serie de copolímeros en bloque de polietilenglicol, polipropilenglicol y polietilenglicol (PEG-PPG-PEG).

En 1998, Dongyuan Zhao (Universidad de Fudan), que estaba haciendo un postdoctorado con Galen Stucky en Santa Bárbara, y colaboradores desarrollaron una serie de materiales llamados SBA (acrónimo de Santa Bárbara) ^[67]. Estos autores, usando copolímeros de tres bloques no iónicos comerciales como surfactantes del tipo PEG_nPPG_mPEG_n lograron desarrollar materiales silícicos ordenados con mesoporos grandes, en el rango de 4.5-30 nm, paredes más gruesas entre 3.0 y 7.0 nm y áreas superficiales alrededor de 800 m² g⁻¹ ^[332,333]. Generalmente, para la síntesis de este tipo de materiales se utiliza una fuente de sílice (generalmente TEOS), que se hidroliza en una solución bifásica que contiene un surfactante, usualmente el surfactante catiónico CTAB, copolímeros de dos o tres bloques o surfactantes no iónicos de la familia Brij. Dentro de la familias de las SBAs, el material más ampliamente investigado ha sido la SBA-15 con estructura porosa hexagonal 2D (*p6mm*), sintetizado por primera vez en medio fuertemente ácido con TEOS como fuentes de silicio y Pluronic 123 como agente director de estructura ^[332]. El surfactante Pluronic P123 es un copolímero en bloque con masa molar de 3600 g·mol⁻¹ y fórmula (PEG)₂₀-(PPG)₇₀-(PEG)₂₀, donde la letra "P" de su nomenclatura significa "pasta" haciendo referencia a la forma de agregación del tensioactivo (otras letras comúnmente utilizadas son la "F" para "escamas" y "L" para "líquidos"). Por otro lado, cabe destacar que las variaciones en las concentraciones o el tipo de agente director de estructura dan lugar a diferentes geometrías de poros obteniendo diferentes materiales del tipo SBA con estructuras variables como la SBA-11, con estructura cúbica perteneciente al grupo espacial *Pm3m*, SBA-12 con estructura

hexagonal 3D perteneciente al grupo espacial $P63mmc$, y SBA-16, con estructura cúbica perteneciente al grupo espacial $Im3m$, siendo preparados utilizando como surfactantes Pluronic F-127 ((PEG)₁₀₀-(PPG)₆₅-(PEG)₁₀₀), Brij-56 (C₁₆PEG₁₀) y Brij-76 (C₁₈PEG₁₀), respectivamente [328]. A pesar de que los materiales SBA-15 y MCM-41 son materiales similares con mesoestructura hexagonal 2D, el material SBA-15 tiene poros más grandes y mayor grosor de pared, el doble en ambos casos, que hace que aumente su estabilidad en medio acuoso y bajo exposición del aire [334]. Esto permite hospedar moléculas de mayor tamaño, lo que hace al material SBA-15 especialmente atractivo para aplicaciones de adsorción y catálisis. Otra diferencia remarcable entre la SBA-15 y la MCM-41 es que las paredes porosas del material SBA-15 están formadas por una enorme cantidad de microporos internos e incluso pequeños mesoporos, mientras que esto no ocurre para la MCM-41.

A pesar del enorme avance científico que supuso el descubrimiento de estas familias de materiales basados en sílices mesoporosas ordenadas, todavía existían algunos inconvenientes importantes relacionados con la elevada polaridad superficial limitando su aplicación en medios apolares. En este aspecto, los investigadores focalizaron su atención en la integración de componentes orgánicos dentro de la estructura de sílice inorgánica para lograr la simbiosis de las propiedades de ambos componentes. La posibilidad de combinar la enorme variedad de grupos funcionales, propios de la química orgánica, con las ventajas de un sustrato inorgánico térmicamente estable y robusto para dar lugar a estructuras mesoporosas orgánico-inorgánicas basadas en sílice bien definidas con propiedades únicas y polaridad ajustable, resulta científicamente una estrategia muy atractiva que amplía la utilidad de estos sólidos haciéndolos potencialmente interesantes en una extensa variedad de aplicaciones.

2.3.1. Metodologías de síntesis de materiales híbridos orgánico-inorgánicos basados en sílice

La síntesis de estos materiales híbridos orgánico-inorgánicos mesoporosos ordenados con naturaleza silíceo puede llevarse a cabo mediante tres procedimientos diferentes [329,335,336] mostrados en la **Figura 24**: 1) modificación superficial de un material inorgánico de sílice (“*grafting*”), 2) condensación simultánea de la fuente de sílice y el

precursor organosilícico (“*co-condensación*”), y **3**) incorporación de grupos orgánicos como moléculas puente, de forma directa y específica dentro de las paredes de los poros del material mediante el uso de precursores disilánicos (*Organosílices Periódicas Mesoporosas o PMOs, del inglés “periodic mesoporous organosilicas”*).

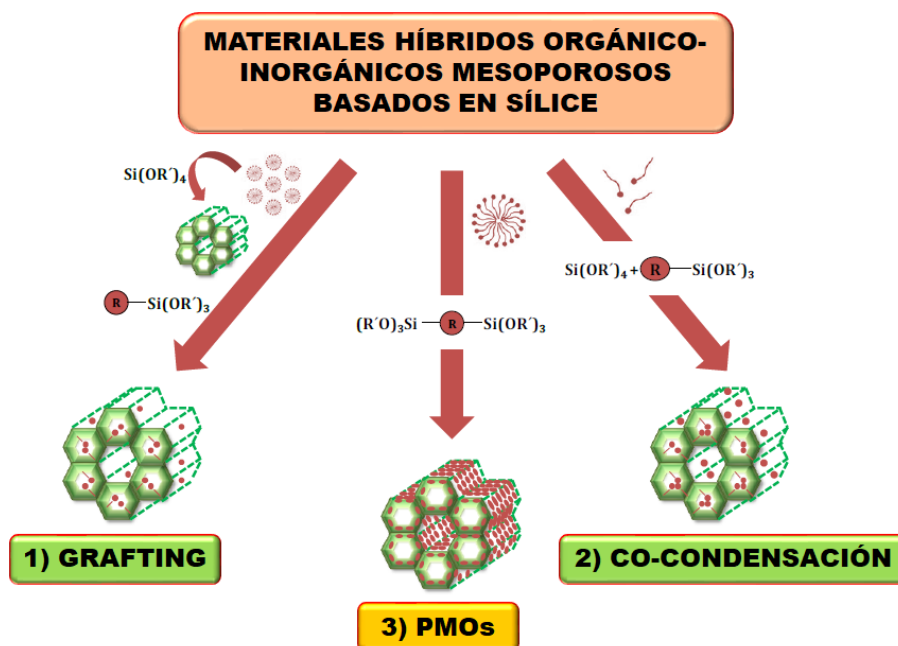


Figura 24. Representación esquemática de las diferentes rutas de síntesis para diseñar materiales híbridos orgánico-inorgánicos mesoporosos ordenados basados en sílice.

- 1) **Modificación superficial de un material inorgánico mesoporoso basado en sílice (“grafting”):** El procedimiento de “grafting” consiste en la funcionalización post-síntesis de los grupos silanoles superficiales libres localizados en la pared de la mesoestructura de sílice con moléculas precursoras de grupos funcionales orgánicos, generalmente compuestos organosilícicos del tipo $(\text{R}'\text{O})_3\text{SiR}$ (R = grupo orgánico) o, menos frecuentemente, clorosilanos (ClSiR_3) o silazanos ($\text{HN}(\text{SiR}_3)_2$) (**Figura 25**). Los materiales resultantes integran un grupo funcional orgánico superficial en la estructura mesoporosa de sílice, el cual puede ser modificado simplemente variando la naturaleza de R en el precursor organosilícico, aunque la cantidad incorporada queda limitada por el número de grupos silanoles libres superficiales.

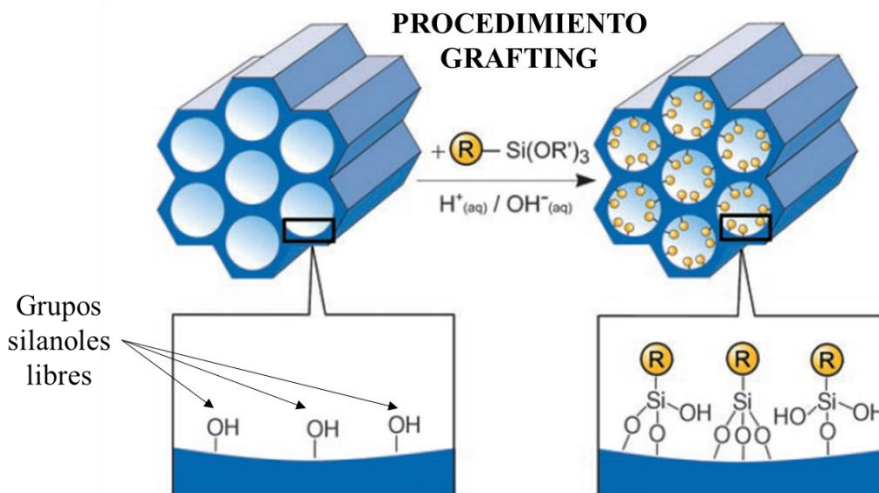


Figura 25. Representación esquemática del procedimiento de “grafting” (funcionalización postsintética) para la modificación orgánica de fases mesoporosas de sílice con organosilanos terminales del tipo $(\text{R}'\text{O})_3\text{SiR}$, donde R es un grupo funcional orgánico (adaptado de la referencia ^[329]).

Existen diferentes estrategias de anclaje del organosilano; entre ellas cabe destacar las siguientes ^[337]: **a)** anclaje con grupos superficiales pasivos con el objetivo de neutralizar los grupos silanoles superficiales con grupos poco reactivos como compuestos de naturaleza silícica conteniendo cadenas alquílicas (hexametildisilazano y dipropiltetrametildisilazano, entre otros) o grupos fenilo (difeniltetrametildisilazano), lo que permite controlar la hidrofobicidad de estos materiales resultando interesante para ciertas aplicaciones, **b)** anclaje con grupos superficiales reactivos como olefinas, nitrilos, alquiltioles, alquilaminas, alquilhaluros, epóxidos, etc, y **c)** anclaje selectivo, llevado a cabo cuando se pretende funcionalizar la superficie externa e interna con diferentes grupos orgánicos.

La síntesis basada en el procedimiento “grafting” presenta varias ventajas: i) la conservación de la mesoestructura inicial del material tras el proceso de funcionalización, ii) el gran número de sílices híbridas orgánico-inorgánicas que pueden ser preparadas con propiedades fisicoquímicas específicas debido al enorme número de organosilanos disponibles, iii) la obtención de materiales con baja constante dieléctrica, mediante el uso de precursores organosilícicos de gran volumen que pueden ser selectivamente enlazados en las

cavidades porosas, lo que conduce al cierre de las mismas alojando aire en su interior, y iv) elevado grado de funcionalización cuando existe una elevada concentración de grupos silanoles en superficie tras la eliminación del surfactante.

Dos aspectos deben tenerse en cuenta, ya que pueden ser inconvenientes de este tipo de metodología de síntesis: i) la homogeneidad controlada del proceso de inmovilización de los organosilanos determinada por la accesibilidad y difusión en el sistema poroso, las propiedades, es decir, el tamaño, forma, simetría y orientación de los poros del material, así como por la reactividad o afinidad química de las especies organosilícicas y los grupos silanoles superficiales, y ii) el control de la velocidad de policondensación del precursor organosilícico, ya que es fundamental evitar que reaccione consigo mismo e interactúe únicamente con los grupos silanoles superficiales. El tipo de disolvente, la naturaleza química del organosilano, la temperatura de reacción y la cantidad de agua superficial serán factores que influirán en que se lleve a cabo la autocondensación del precursor organosilícico y/o el proceso de “grafting”. Por tanto, se considera fundamental la optimización de estos parámetros para lograr una síntesis efectiva mediante esta ruta de síntesis.

- 2) **Co-condensación - Síntesis directa:** Un método alternativo para sintetizar estructuras mesoporosas de sílice orgánicamente funcionalizadas es el método de co-condensación que se lleva a cabo de forma directa en un solo paso (*one-pot*) y consiste en la condensación simultánea de especies silíceas tipo tetraalcoxisilano $(RO)_4Si$, como por ejemplo TMOS o TEOS, con organoalcoxisilanos terminales del tipo $RSi(OEt)_3$ en presencia de un agente director de estructura dando lugar a materiales con funcionalidades orgánicas ancladas covalentemente en las paredes de los poros (**Figura 26**) ^[338]. Este proceso puede producirse en condiciones ácidas, básicas o neutras y difiere del método “grafting” en que el precursor organosilícico participa directamente en el proceso de condensación y autoensamblaje (del inglés, “*cooperative self-assembly*”). La naturaleza química del grupo funcional orgánico del organosilano juega un papel clave en la formación de la estructura mesoporosa durante la síntesis, puesto que este puede interferir en la formación de agregados micelares dando lugar a un material con estructura amorfa y desordenada.

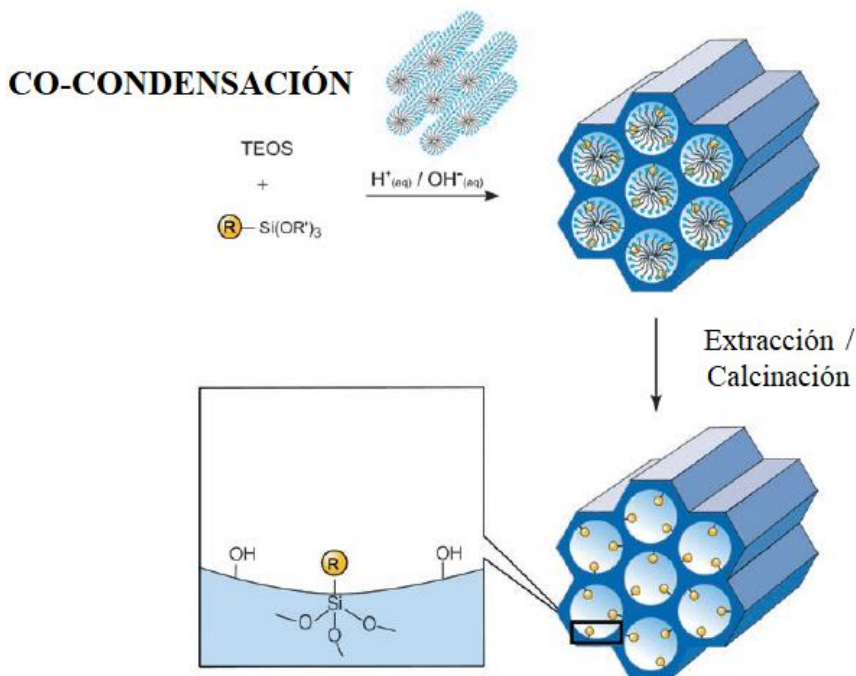


Figura 26. Representación esquemática del procedimiento de co-condensación (síntesis directa en un solo paso) para la modificación orgánica de fases mesoporosas de sílice con organosilanos terminales del tipo $(R'O)_3SiR$, donde R es un grupo funcional orgánico (adaptado de la referencia ^[329]).

Respecto a las ventajas de esta ruta sintética en comparación con el método “grafting” explicado anteriormente, cabe mencionar las siguientes ^[336,339]: i) la distribución más homogénea de los grupos orgánicos incorporados en la estructura mesoporosa, puesto que estos son incorporados en las propias paredes de los poros de la matriz silícea, ii) los rendimientos de la funcionalización orgánica con el precursor organosilícico son superiores, y iii) la condensación simultánea del tetraalcoxisilano y el organosilano permite la formación directa del material híbrido mesoporoso evitando procesos post-sintéticos. Sin embargo, una serie de desventajas derivadas de la aplicación de esta metodología de síntesis deben destacarse ^[329,336,337,340]: i) la disminución grado de ordenamiento mesoscópico de los materiales con el aumento de la concentración de organoalcoxisilano en la mezcla de síntesis, ii) las posibles reacciones de homocondensación de los precursores debido a las

diferentes velocidades de hidrólisis/condensación y a la excesiva concentración de organosilano en el medio de reacción, afectando negativamente a los procesos de co-condensación, lo que puede resultar en una pérdida de homogeneidad en la distribución de los grupos funcionales orgánicos y una reducción de la superficie específica, así como el volumen y el diámetro de poro, iii) la determinación de la ubicación de los grupos orgánicos incorporados que pueden estar localizados en la superficie interna o externa de los poros, en las propias paredes de la matriz de sílice o repartidos arbitrariamente por toda la estructura porosa, y iv) la destrucción de la funcionalidad orgánica cuando se aplican métodos de calcinación para eliminar el surfactante, por lo que deben seleccionarse métodos de extracción para preservar los grupos orgánicos en el material organosilícico mesoporoso.

- 3) **Organosílices Periódicas Mesoporosas (PMOs):** En 1999, tres grupos de investigación diferentes liderados por S. Inagaki ^[69], A. Stein ^[70] y G.A. Ozin ^[71] desarrollaron por primera vez una nueva familia de materiales híbridos orgánico-inorgánicos mesoporosos de naturaleza silícea, denominados PMOs sintetizados mediante reacciones de hidrólisis y condensación comúnmente conocidas en procesos sol-gel de precursores organosilícicos (bis-silanos) del tipo $(R'O)_3Si-RSi(OR')_3$ (siendo R' generalmente un grupo etoxilo -OCH₂CH₃ o metoxilo -OCH₃), en presencia de un agente director de estructura en medio ácido o básico (**Figura 27**). A diferencia de las sílices funcionalizadas con grupos orgánicos mediante procesos post-síntesis (“grafting”) o síntesis directa (co-condensación), donde los grupos orgánicos se ubican en la superficie de la mesoestructura, en el caso de los PMOs las unidades orgánicas están incrustadas en las paredes de los poros de la estructura tridimensional de la matriz silícea a través de dos enlaces covalentes, quedando homogéneamente distribuidas en las paredes de los poros. La organosílice mesoporosa se va formando alrededor de las micelas durante la síntesis y, después de un período de envejecimiento, el surfactante es eliminado mediante un proceso de extracción o tratamiento térmico suave resultando un material PMO altamente poroso.

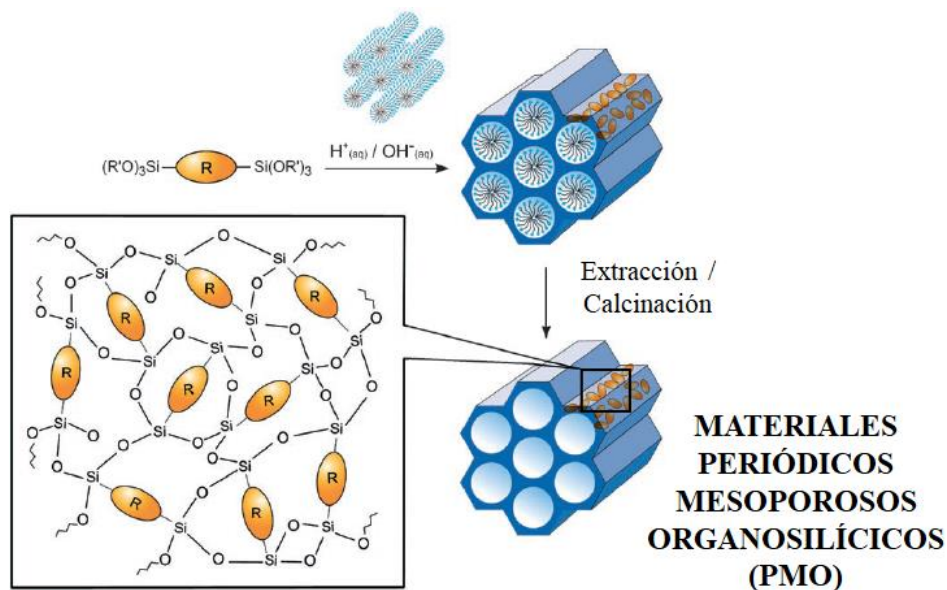


Figura 27. Representación esquemática del proceso de síntesis general de materiales PMOs preparados a partir de unidades orgánicas puenteadas bisililadas $(R'O)_3Si-R-Si(OR')$, donde R es un grupo puente orgánico (adaptado de la referencia ^[329]).

De esta forma, es posible obtener una distribución homogénea de fragmentos orgánicos en la red de canales de sílice dando lugar a estructuras mesoporosas ordenadas con distribuciones estrechas de tamaño de poro, elevadas áreas superficiales, paredes porosas con gran grosor y elevados volúmenes de poro, resultando en una estructura porosa con poros abiertos completamente accesibles para posibles modificaciones superficiales. Por ello, la composición y naturaleza de los componentes orgánicos integrados en las paredes silíceas se puede modular simplemente variando el precursor disilánico y/o mediante modificación in situ o post-síntesis del puente orgánico, lo que permite modificar el carácter hidrófobo/hidrófilo de los materiales resultantes, entre otras propiedades fisicoquímicas. En base a esto, se evitan los problemas mencionados de los dos procedimientos de síntesis (“grafting” y co-condensación) comentados anteriormente, como la distribución no homogénea de los grupos funcionales, el bajo contenido de materia orgánica, la influencia del contenido orgánico en el ordenamiento estructural, el estrechamiento de los poros, las diferentes cinéticas de reacción de los precursores mezclados, etc.

Diversos parámetros de síntesis afectan a la formación, la morfología, las propiedades y la estructura de los materiales PMOs: el tipo de agente director de estructura (catiónico, aniónico o no iónico), la naturaleza del precursor organosilícico, la concentración del surfactante (micelar o cristal líquido), las especies inorgánicas, el pH (ácido o básico), la temperatura (baja temperatura o hidrotermal), la agitación, los tiempos de síntesis, los aditivos (sales inorgánicas como haluros de sodio (NaF, NaCl, NaBr, NaI), haluros de potasio (KF, KCl, KBr, KI) y sulfatos alcalinos (Na₂SO₄, K₂SO₄), y moléculas orgánicas que actúan como moléculas expansivas o co-disolventes), el orden de mezclado, el disolvente (acuoso o no acuoso), el catalizador utilizado para acelerar la hidrólisis, el método de síntesis (autoensamblaje inducido por evaporación o precipitación) y las condiciones establecidas en las etapas de post-tratamientos (extracción, calcinación), entre otras.

La **Tabla 2** y **Tabla 3** muestran una perspectiva general de los agentes directores de estructuras comúnmente utilizados como surfactantes y los precursores organosilícicos más extensamente empleados para la síntesis de PMOs, respectivamente.

Mientras que el agente director de estructura (**Tabla 2**) influye directamente en las propiedades texturales y morfológicas, la naturaleza del precursor organosilícico es considerado un parámetro crucial en la obtención de materiales PMO con funcionalidades específicas a escala molecular aportando la rigidez adecuada para obtener una estructura con elevada estabilidad.

Por tanto, un número limitado de organosilanos puente son adecuados para el desarrollo de estructuras híbridas mesoporosas ordenadas teniendo en cuenta varias particularidades: i) cadena corta o un sistema conjugado que proporcione suficiente rigidez, ii) evitar precursores puenteados orgánicos demasiados largos que puedan ocasionar el colapso de las paredes, iii) la distancia limitada entre dos especies inorgánicas hidrolizables para asegurar un ensamblaje suficiente, iv) asegurar una fuerte interacción surfactante-precursor, y v) la escasa disponibilidad comercial de los precursores organosilícicos, ya que la mayoría tienen que ser sintetizados a escala de laboratorio mediante metodologías que pueden requerir cierta complejidad. Diversos grupos orgánicos puenteados, referibles a metano, etano, benceno, tolueno, tiofeno y p-xileno, entre otros, han sido estudiados.

Tabla 2. Tipos de surfactantes y ejemplos frecuentemente utilizados en síntesis de PMOs.

Tipo de surfactante		Ejemplos	Estructura
Iónicos	Haluros de alquiltrimetilamonio (ATMA)	CTAC/CTAB, Cloruro/bromuro de cetiltrimetilamonio	
		C _n TMACl/Br, Cloruro/bromuro de alquiltrimetilamonio	
		OTAC, Cloruro de octadeciltrimetilamonio	
	Surfactantes catiónicos fluorocarbonados	FC ₄	
	Cloruro de cetilpiridinio	CPCI	
	Surfactantes divalentes	$[(C_nH_{2n+1}N^+(CH_3)_2)(CH_2)_s(N^+(CH_3)_2C_mH_{2m+1})]^{2+}2Br^-$	
No-iónicos	Brij oligoméricos	Brij-30, Éter laurílico de polioxietileno (4)	
		Brij-56, Éter cetílico de polioxietileno (10)	
		Brij-76, Éter estearílico de polioxietileno (10)	
	Triton oligoméricos	Triton-X100, Polioxietileno (10) octilfenil éter	
	Copolímeros en bloque	F127, Pluronic F127 (PEG) ₁₀₀ -(PPG) ₆₅ -(PEG) ₁₀₀	
		P123, Pluronic P123 (PEG) ₂₀ -(PPG) ₇₀ -(PEG) ₂₀	
Binarios	ATMA + Surfactante divalente	C ₁₈ TABr y C ₁₈ -3-1	
	ATMA + Brij oligomérico	(C ₁₈ TMACl) y C ₁₂ (EO) ₄ ; Brij-30	
	ATMA + FC ₄	C ₁₆ TABr y CF ₄	
“Hard and soft templates”	Surfactante y superficie con patrones regulares	C ₁₆ TMACl y sustratos de vidrio fotolitografiados	

En la **Tabla 3**, se ha expuesto una selección genérica de algunos ejemplos representativos, pertenecientes a distintas categorías químicas ^[335]:

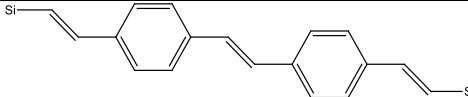
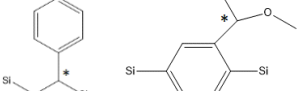
- Grupos alquilenos saturados de cadena corta **(1)**.
- Grupos alquilenos insaturados **(2)**.
- Compuestos multi-sililados cíclicos **(3)** o ramificados **(4)**.
- Compuestos aromáticos **(5)**.
- Grupos aromáticos heterocíclicos **(6)** y policíclicos **(7)**.
- Compuestos aromáticos con sustituyentes que se pueden modificar fácilmente **(8)**, éteres **(9)** y tioéteres **(10)**.
- Unidades con sistemas π conjugados extendidos **(11)** y grupos quirales **(12)**.

Siempre que se emplee un solo tipo de precursor bisililado o multisililado, la formación de PMO pertenece al método de precursores de fuente única conteniendo el 100% de la funcionalidad orgánica puente en las paredes del material. Sin embargo, también es posible llevar a cabo procesos sol-gel mediados por surfactantes con dos o más silsesquioxanos puenteados para dar PMOs en los que se incorporan homogéneamente dos o más grupos orgánicos diferentes. De esta forma, es posible combinar la estrategia de preparación de PMOs con el método de co-condensación empleando mezclas de bis(trialcoxisilil)organosilanos puenteados $[(R'O)_3Si-R-Si(OR')_3]$ y terminales trialcoxisililorganosilanos $[(R'O)_3SiR'']$ en completa analogía con las reacciones de co-condensación de TEOS/TMOS y organosilanos $[(RO)_3SiR'']$.

Los PMOs con doble funcionalidad orgánica resultantes consisten en una combinación de unidades orgánicas puenteados dentro de las paredes y grupos orgánicos terminales cuyos extremos se dirigen a los canales porosos. La modificación posterior de los materiales PMOs también es factible si se elige un precursor organosilícico apropiado aplicando un procedimiento de anclaje (“grafting”) análogo al ya comentado anteriormente en este apartado o mediante reacción química con grupos orgánicos específicos contenidos en el precursor organosilícico puenteado.

Tabla 3. Descripción general de los precursores de organosilíce que se han sido utilizados en la síntesis de PMOs conteniendo el 100% de la funcionalidad orgánica. Átomos terminales de Si: Si = Si(OR)₃ con R = CH₃, C₂H₅ [335].

Tipo de precursor organosilíceo	Estructura
(1) Grupos alquilenos saturados de cadena corta	
(2) Grupos alquilenos insaturados	
(3) Compuestos multi-sililados cíclicos	
(4) Compuestos multi-sililados ramificados	
(5) Compuestos aromáticos	
(6) Grupos aromáticos heterocíclicos	
(7) Grupos aromáticos policíclicos	
(8) Compuestos aromáticos con sustituyentes que se pueden modificar fácilmente	
(9) Éteres	
(10) Tioéteres	

(11) Unidades con sistemas π conjugados extendidos	
(12) Grupos quirales	

Teniendo todo esto en cuenta, cuatro vías de síntesis pueden ser utilizadas para la preparación de materiales PMOs ^[341]: **1)** a partir de un único precursor bis-sililado, $(R'O)_3Si-R-Si(OR')_3$, **2)** a partir de dos precursores bis-sililados con diferentes grupos funcionales, **3)** usando simultáneamente precursores bis-sililados y monosililados, $(R'O)_3SiR''$, y **4)** modificación post-síntesis mediante reacción química del resto orgánico puenteado o aplicando un procedimiento “grafting” empleando precursores monosililados adecuados a través de los grupos silanoles libres (**Figura 28**).

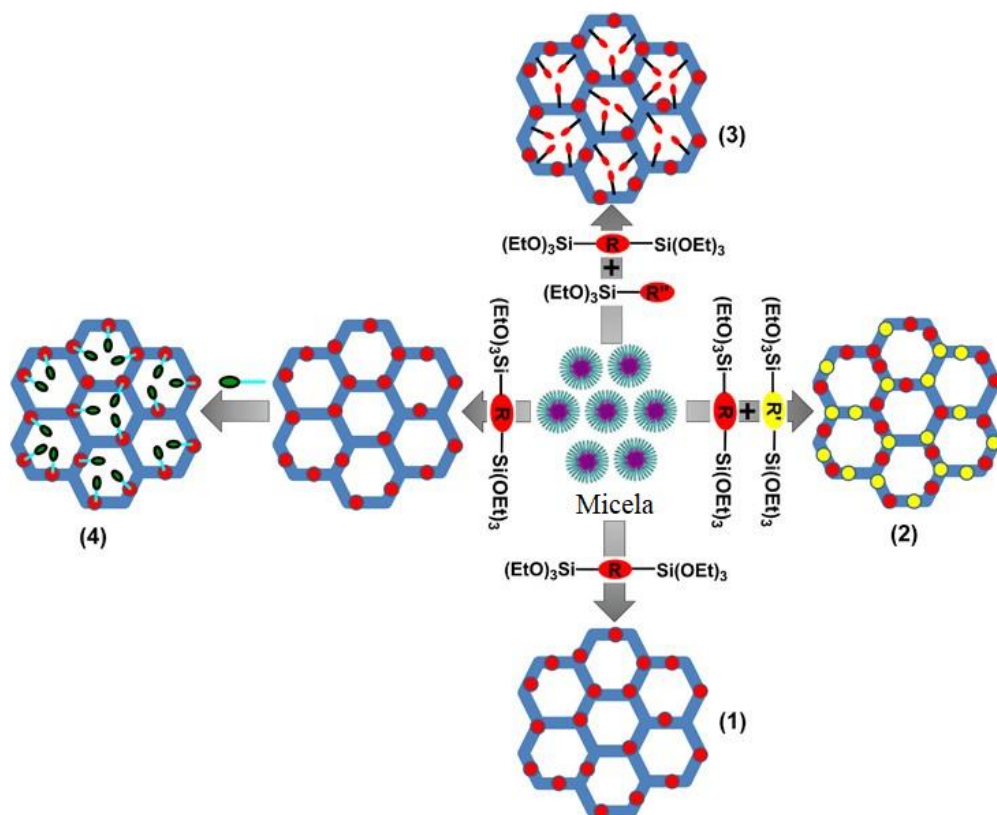


Figura 28. Rutas de síntesis de PMO con grupos funcionales orgánicos en sus estructuras mesoporosas silíceas (adaptado de la referencia ^[341]).

2.3.2. Aplicaciones de los PMOs

El extraordinario avance de las metodologías de síntesis en la Química Orgánica ha promovido el diseño de gran variedad de estructuras mesoporosas PMO con características fisicoquímicas, texturales y morfológicas definidas incorporando una extensa diversidad de grupos orgánicos. Esta enorme versatilidad funcional junto a las interesantes propiedades superficiales y porosas convierte a los materiales PMOs en potenciales candidatos para aplicaciones de creciente interés en la actualidad para industria química y la comunidad científica (**Figura 29**) [140,329,342,343].

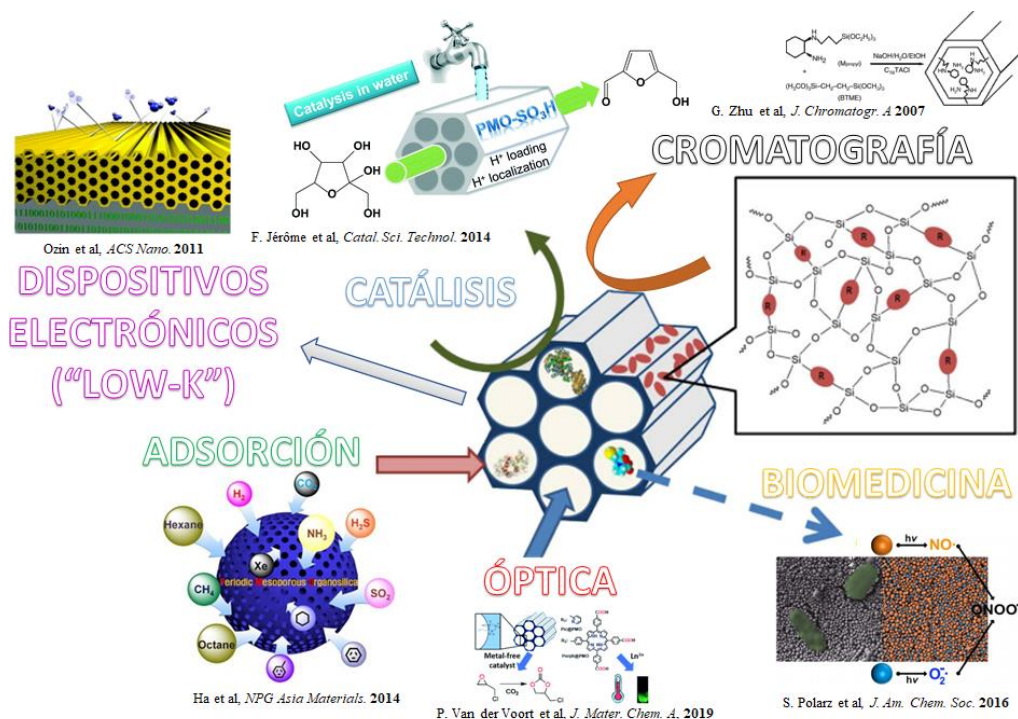


Figura 29. Visión general de las aplicaciones más representativas de los materiales PMOs [341,346–350].

- 1) **Catálisis:** Los PMOs son una clase avanzada de materiales extensamente utilizados como catalizadores heterogéneos o soportes catalíticos debido a sus propiedades únicas [344]. Una de las características más importantes es la presencia de funcionalidades orgánicas completamente insertadas en las paredes de los poros de

la estructura que minimiza cualquier tipo de lixiviación de las funcionalidades orgánicas durante la catálisis, otorgando así mayor estabilidad traducida en un incremento de la vida útil del material. Además, la mesoporosidad particular que poseen permite la difusión de sustratos y productos más grandes dentro y fuera de los poros. La desventaja es que la actividad catalítica de los catalizadores heterogéneos es menor que la de los homogéneos en general, ya que las reacciones tienen lugar en la interfase líquido-sólido o gas-sólido, aunque esto es posible contrarrestarlo si existe una superficie específica elevada. Esta gran área superficial en combinación con una gran cantidad de puentes orgánicos disponibles asegura que muchas funcionalidades sean accesibles para los sustratos de la reacción. Además, los PMO también exhiben cierta hidrofobicidad debido a los puentes orgánicos, lo que puede afectar positivamente a la estabilidad estructural en determinadas condiciones de reacción. En un material PMO se pueden distinguir diferentes tipos de sitios activos catalíticos que dan lugar a diferentes procesos de catálisis: i) catálisis ácida y básica, ii) catálisis asistida por centros metálicos, iii) catálisis asistida por complejos metálicos, iv) catálisis bifuncional, y v) catálisis quiral ^[342]. Las pronunciadas propiedades de absorción de luz y canalización de energía de los PMOs promovidas por las funcionalidades orgánicas incorporadas también permiten su uso en sistemas heterogéneos de fotocatalisis combinados con centros de reacción catalítica fijados en las superficies de los mesoporos. Por tanto, es posible construir sistemas fotocatalíticos jerárquicos basados en PMOs mediante el diseño preciso de la estructura de organosílice, las superficies de las paredes de los poros y los interiores de los canales mesoporosos, que actúan eficientemente en procesos fotocatalíticos de evolución de hidrógeno y reducción de CO₂ ^[343,345].

- 2) **Adsorción:** La gran superficie interna de los PMOs, su excelente accesibilidad a los poros y la posibilidad de funcionalizarlos con diferentes agentes quelantes o complejantes hacen que estos materiales sean ideales para su uso en el área de adsorción. Se han llevado a cabo una gran cantidad de estudios sobre las aplicaciones ambientales de PMOs, en particular abordando la adsorción de metales pesados (cationes, oxianiones y radionúclidos),

contaminantes orgánicos tóxicos e incluso gases (por ejemplo, compuestos orgánicos volátiles) ^[140,342,351,352].

- 3) Cromatografía:** Los materiales PMO con puentes orgánicos simples como metileno, etilideno o 1,4-fenileno benceno claramente poseen una cualidad intrínseca que es de gran importancia en algunas aplicaciones, concretamente a la hidrofobicidad inducida por los grupos orgánicos puente y la elevada estabilidad resultante. Esta propiedad es especialmente útil en cromatografía cuando el PMO se aplica como material de empaquetamiento de columnas en fase normal o reversa ^[140,342,353]. Actualmente, la sílice es empleada principalmente en esta aplicación debido a la posibilidad de ajustar su morfología, porosidad y superficie, y su estabilidad mecánica, aunque como inconveniente cabe mencionar la mala estabilidad hidrolítica, que causa la pérdida de funcionalidad. En este sentido, los PMOs con morfología esférica pueden ser materiales de relleno cromatográfico adecuados para HPLC en fase normal y reversa proporcionando un rango de trabajo de temperatura y pH más amplio debido a su mayor estabilidad e hidrofobicidad. Además, es posible la aplicación de PMOs aplicados como fase estacionaria quiral con intercambio de ligandos en HPLC para la separación de aminoácidos racémicos ^[354].
- 4) Películas con baja constante dieléctrica k :** Las propiedades intrínsecas de los PMOs, como su hidrofobicidad, los convierten en materiales particularmente atractivos para aplicaciones como películas interlaminares aislantes con baja constante dieléctrica incorporadas en dispositivos microelectrónicos ^[342,355]. La creciente densidad de dispositivos e interconexiones exige materiales dieléctricos aislantes con k lo suficientemente baja como para evitar la diafonía y limitar los retrasos de la señal causados por la capacitancia en el interior y en el espacio interlaminar. Se necesitan nuevos materiales con constantes dieléctricas k más bajas (preferiblemente valores $k < 2$) para reducir la constante de tiempo de un circuito RC inducido por cables de interconexión localizados próximamente. Los PMOs tienen una alta porosidad que reduce drásticamente la constante dieléctrica ($k_{aire} \approx 1$). Además, los puentes orgánicos son menos polarizables en comparación con el dióxido de silicio que es considerado el material estándar con baja k ($k = 3.9$), lo que resulta en una disminución adicional de la constante

dieléctrica. En particular, los PMOs con los puentes orgánicos más simples, como el etilideno y el metileno, son extremadamente interesantes para aplicaciones de baja k porque tienen el puente orgánico con menor polarización.

- 5) **Óptica:** La incorporación de unidades orgánicas funcionales (compuestos π -conjugados con grupos cromóforos altamente fluorescentes, grupos antena captadores de luz y especies electroactivas) o metales (generalmente lantánidos emisores de luz) insertados en la estructura de un PMO proporcionando propiedades ópticas sugerentes, incluso en la región de longitud de onda de luz visible, ha atraído gran interés por parte de los investigadores abriendo un nuevo campo en el desarrollo de nuevos sistemas luminiscentes, sensores y materiales de transporte de carga con gran potencial en dispositivos fotovoltaicos, dispositivos emisores de luz y sistemas fotocatalíticos ^[343,356].
- 6) **Biomedicina:** Los materiales PMOs pueden adquirir características óptimas para su empleo en procesos de adsorción/inmovilización/liberación de proteínas, enzimas, aminoácidos y fármacos mediante mecanismos basados en interacciones electrostáticas, interacciones π - π , fuerzas de Van der Waals e hidrofobicidad ^[140,342]. Modulando las propiedades fisicoquímicas (hidrofobia/hidrofilia, morfología, estabilidad mecánica, etc.) a través de la incorporación de diferentes grupos orgánicos funcionales en las paredes de los poros del material para que puedan interactuar con el adsorbato de acuerdo con una o más de las interacciones mencionadas anteriormente, junto con la presencia de mesoporos grandes que permiten la difusión de (bio)moléculas de mayor tamaño en la red porosa, convierte a los PMOs en materiales muy prometedores en aplicaciones emergentes relacionadas con biología, bioquímica y biomedicina ^[357].

Una vez descritas brevemente las aplicaciones principales de los PMOs, se centrará la atención en la aplicación específica que se ha llevado a cabo en la presente Tesis Doctoral, consistente en el diseño de catalizadores heterogéneos PMO decorados con modelos biomiméticos de [FeFe]-hidrogenasa y su aplicación en procesos de producción de hidrógeno mediante fotocatalisis artificial.

2.3.3. PMOs bioinspirados para fotosíntesis artificial

La Naturaleza utiliza la luz solar para generar energía química a través de la fotosíntesis, la cual consiste en reacciones secuenciales en cadena que se llevan a cabo en las membranas tilacoides de algas, bacterias y plantas (**Figura 30**) [358].

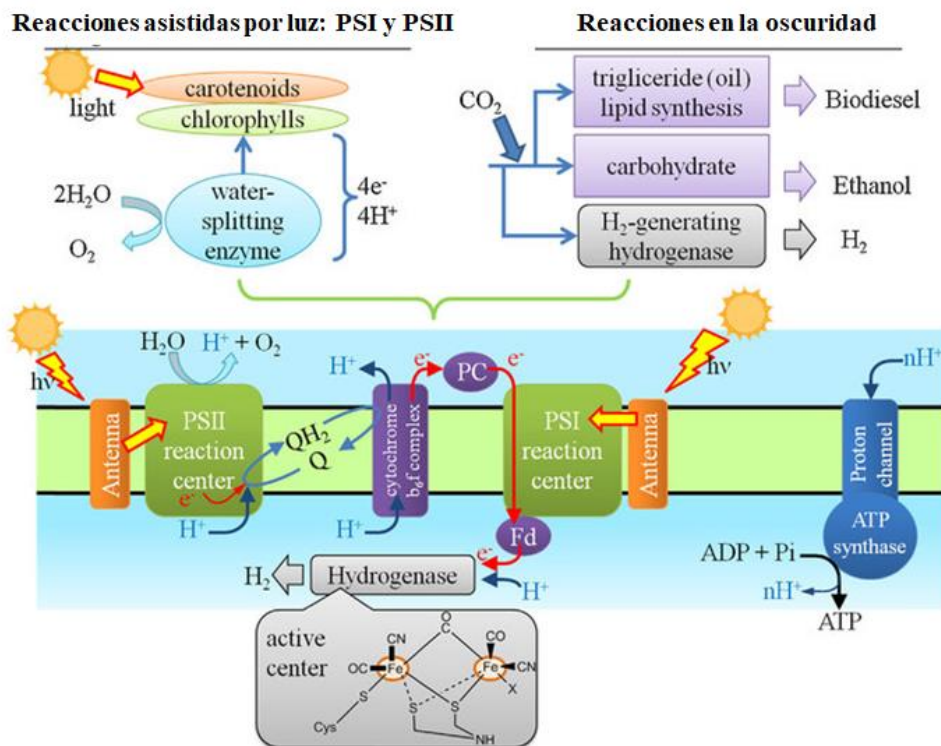


Figura 30. Representación esquemática de los procesos de conversión de energía luminosa por organismos fotosintéticos oxigénicos en la membrana tilacoide (adaptado de la referencia [358]).

Los procesos de captura de fotones procedentes de la luz del Sol por parte de los pigmentos que actúan como moléculas antena (principalmente clorofila y carotenoide), la reducción de $NADP^+$, la formación de ATP y la reacción resultante de división del agua (“*water splitting*”) en moléculas de hidrógeno H_2 y oxígeno O_2 tienen lugar en los fotosistemas I y II (PSI y PSII) de diversos complejos proteicos presentes en organismos oxigénicos [357–359]. El proceso es impulsado por la absorción de fotones de la luz solar

por parte de los complejos captadores de luz de los fotosistemas PSI y PSII. La oxidación del agua impulsada por la luz en PSII genera electrones que pasan a lo largo de una cadena de transporte de electrones a través de plastoquinona (PQ), citocromo b_6/f (cyt b_6/f), plastocianina (PC), PSI y ferredoxina (Fd). La fotoexcitación del complejo antena en PSI activa la transferencia de electrones de la enzima ferredoxina-ADP⁺ oxidorreductasa a NADP⁺ con la subsiguiente formación de NADPH. Los protones liberados en la reacción de evolución de oxígeno (OER) son absorbidos por la ATP sintetasa para producir moléculas de ATP a partir de ADP. El ATP y NADPH que se generan en el proceso proporcionan la energía necesaria para la fijación de CO₂ en el ciclo de Calvin Benson para producir azúcares -combustible vegetal- como la glucosa y el almidón.

Centrando la atención en el fotosistema I donde tiene lugar la reacción de evolución de hidrógeno (HER), cabe resaltar que las metaloenzimas [FeFe]-hidrogenasa localizadas en los cloroplastos de algas verdes unicelulares catalizan la interconversión reversible de protones y electrones en hidrógeno molecular ($2H^+ + 2e^- \rightarrow H_2$) a una velocidad catalítica muy elevada alcanzando la producción de hasta 9000 moléculas de hidrógeno por segundo por molécula de enzima ^[362]. Muchos sistemas de energía sostenible del futuro se basan en el hidrógeno como vector de energía debido a: i) su alta densidad de almacenamiento de energía gravimétrica ($142 \text{ MJ} \cdot \text{kg}^{-1}$), ii) cero emisiones contaminantes produciendo únicamente vapor de agua como subproducto, iii) no presenta toxicidad medioambiental, iv) gran potencial para obtenerse de un recurso abundante como es el agua, v) el hidrógeno es el elemento más abundante del universo aunque solo el 1% está en forma de H₂, y vi) proceso de producción económicamente viable ^[363,364].

El hidrógeno se puede utilizar en presencia de oxígeno para alimentar motores de combustión interna, turbinas de gas o celdas de combustible para generar electricidad. El gas hidrógeno también es esencial para llevar a cabo muchos procesos industriales, pero actualmente se obtiene a escala industrial mediante el reformado de metano con vapor y la gasificación de carbón. Sin embargo, ambos procesos requieren el empleo de combustibles fósiles, altas temperaturas y elevado coste energético. La tercera ruta de generación de hidrógeno es la electrólisis del agua que, aunque actualmente está en vía de desarrollo y requiere mejoras tecnológicas para reducir costes económicos, es considerada la más prometedora y sostenible medioambientalmente en el futuro.

Alternativamente, se considera especialmente atractiva la estrategia basada en el diseño de un sistema impulsado por luz artificial para la generación de combustibles solares a partir de agua en que la absorción de luz es seguida por la separación de electrones y huecos. Los electrones se utilizan en la reacción de formación del combustible catalítico y los huecos son rellenados con electrones implicados en la oxidación del agua. Sin embargo, la absorción de fotones conduce a la separación de pares de electrón-hueco individuales, mientras que tanto la oxidación del agua como la producción de combustible implican reacciones multiprotónicas y multielectrónicas. Por lo tanto, la acumulación de electrones y huecos (separación de carga acumulativa) por absorción sucesiva de fotones es necesaria para completar todas las reacciones catalíticas ^[365].

En base a esto, diseñar un sistema molecular que combine tanto la producción de combustible como la semirreacción de oxidación del agua promoviendo una efectiva separación de cargas inducida por la luz sigue siendo un desafío. Entre otras, se pueden identificar las siguientes dificultades: i) procesos de recombinación de cargas, ii) equilibrar las cinéticas de las dos semirreacciones, y iii) reacciones secundarias indeseables, como, por ejemplo, formación de peróxido en lugar de oxígeno. Para abordar esto, ambas semirreacciones (oxidación de agua o producción de combustible) se han optimizado por separado con el fin de lograr estados separados de carga de alta energía y larga duración, que luego pueden acoplarse a través de un compartimento redox ^[366]. Las semirreacciones independientes pueden ser llevadas a cabo electroquímicamente o fotocatalíticamente mediante el empleo de agentes de sacrificio oxidantes o reductores ^[367]. Respecto a esta última vía, la catálisis fotoquímica emplea un fotosensibilizador y un aceptor o donador de electrones de sacrificio para suministrar los equivalentes redox necesarios para que tengan lugar las reacciones de oxidación del agua y la producción de hidrógeno. Concentrando el interés en el proceso de generación de hidrógeno inducido por luz catalizado por metaloenzimas de tipo [FeFe]-hidrogenasa, es necesario remarcar que la comunidad científica ha invertido grandes esfuerzos en el desarrollo de catalizadores biomiméticos que presenten una actividad similar a las enzimas debido a la baja disponibilidad de hidrogenasas naturales, con el objetivo de diseñar un sistema fotocatalítico artificial para la reducción de protones a moléculas de hidrógeno impulsado por luz ^[368,369]. Para la generación fotocatalítica de hidrógeno catalizada por imitadores del centro activo de [FeFe]-hidrogenasa, se muestra una representación esquemática en la **Figura 31**.

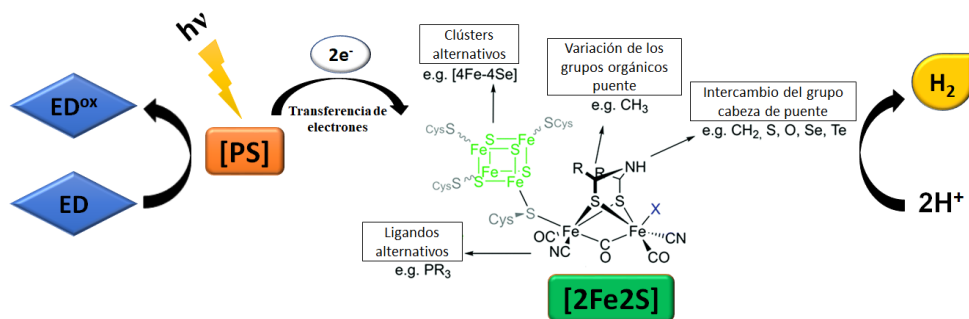


Figura 31. Representación esquemática del mecanismo de producción de hidrógeno impulsado por la luz catalizado por modelos biomiméticos de [FeFe]-hidrogenasa. **ED**: donador de electrones, **PS**: fotosensibilizador y **[2Fe2S]**: sitio activo de dihierro.

La excitación del fotosensibilizador **PS** (complejos metálicos o colorantes orgánicos) inicia el proceso fotocatalítico. La separación de carga fotoinducida del fotosensibilizador excitado (**PS***) proporciona electrones en un proceso de difusión al catalizador **[2Fe2S]** que es responsable de impulsar la reacción de reducción de protones. El donador de electrones de sacrificio **ED** (ejemplos: trietilamina (TEA), trietanolamina (TEOA), ácido etilendiaminotetraacético (EDTA) o ácido ascórbico (AscOH)) debe ser fácilmente oxidable para que el proceso de transferencia de electrones sea termodinámicamente factible y para asegurar una recuperación rápida del **PS** antes de que puedan ocurrir procesos de recombinación de cargas. Este proceso debe repetirse dos veces para acumular dos electrones en el catalizador **[2Fe2S]**, que luego puede reducir dos protones para producir una molécula de **H₂**.

En las últimas décadas, se han realizado grandes esfuerzos para diseñar complejos de dihierro que imiten la estructura y la función de las [FeFe]-hidrogenasas naturales para incluirlos en los esquemas de reacción de producción de hidrógeno inducidos por la luz. Los modelos funcionales de inspiración biológica de las hidrogenasas contienen una primera, una segunda y una tercera esfera de coordinación, cada una de las cuales contribuye al proceso fotocatalítico ^[370,371]. La primera esfera de coordinación describe los ligandos directamente unidos al núcleo de dihierro **[2Fe]** que influyen en las propiedades del centro metálico: sitios de coordinación vacantes para la unión de sustratos, modificación de los potenciales redox, densidad de electrones y obstáculos estéricos para la accesibilidad de los reactivos. Los ligandos de campo fuerte, como el

cianuro (CN) o el monóxido de carbono (CO), están presentes en el centro activo de la enzima para garantizar complejos de bajo espín. La segunda esfera de coordinación incluye grupos funcionales de los ligandos que reaccionan con el sustrato. Desempeñan un papel fundamental en el movimiento de electrones a través del núcleo de cubano [4Fe-4S] y en el traslado de protones a través de los aminoácidos y la cabeza de puente de amina del centro activo. La esfera de coordinación externa de las metaloproteínas tiene unas dimensiones normalmente superiores a 4 Å desde el núcleo metálico de dihierro y abarca todo el andamiaje restante de la [FeFe]-hidrogenasa [372]. Los complejos bioinspirados artificiales de dihierro pueden ajustarse mediante la ingeniería de cada una de estas esferas de coordinación para mejorar el rendimiento de la producción de hidrógeno impulsada por la luz, promoviendo la transferencia eficiente de electrones y protones, la efectiva separación de cargas fotoinducida evitando procesos de recombinación indeseables, la estabilidad y reactividad del catalizador y la solubilidad del complejo de dihierro en soluciones acuosas.

Una de las partes que integran esta Tesis Doctoral es una revisión exhaustiva sobre los catalizadores inspirados en [FeFe]-hidrogenasa para la producción de hidrógeno impulsada por la luz, destacando las tendencias más recientes en este tema donde se proporciona toda la información detallada relacionada con estos sistemas fotocatalíticos (**Capítulo 4.2.1.**). Los diferentes sistemas fueron presentados en grupos siguiendo un orden respecto a la complejidad y el desarrollo cronológico: **1)** Catalizadores inspirados en el centro activo [FeFe]-hidrogenasa ([2Fe2S]) en presencia de PS y ED, **2)** Díadas del modelo de centro activo consistentes en fotosensibilizador-[FeFe]-hidrogenasa [PS-2Fe2S] mediante la incorporación de PS en el sistema catalítico, **3)** Tríadas [ED-PS -2Fe2S] a través de vincular ED a las díadas, **4)** Entidades supramoleculares que integren modelos [2Fe2S] mediante interacción covalente o no covalente, **5)** Ensamblaje de complejos [2Fe2S] en semiconductores inorgánicos, que actúan como fotosensibilizadores, **6)** Modelos biomiméticos de centros activos de [FeFe]-hidrogenasa anclados en soportes heterogéneos, y **7)** Evolución fotoelectroquímica (PEC) de hidrógeno catalizada por fotocátodos que integran catalizadores [2Fe2S].

Dirigiendo el interés específicamente al grupo **6** mencionado anteriormente, el uso de una matriz heterogénea para la inmovilización de grupos [2Fe2S] a través de su esfera de coordinación externa es un enfoque atractivo para aumentar la estabilidad estructural de todos los componentes

de reacción. Estos soportes pueden proporcionar poros o canales adaptables bien ordenados, áreas superficiales internas muy altas, estructuras bien definidas, microambientes electrostáticos y cavidades hidrofóbicas. Los catalizadores [2Fe2S] insolubles en agua se pueden aislar en sitios especialmente diseñados que son accesibles a través de la matriz y capaces de operar de manera eficiente en medios acuosos. El diseño preciso de estas plataformas permite la creación de sistemas fotocatalíticos heterogéneos sólidos con mayor estabilidad, separación simple después de la reacción y reciclaje eficiente para los procesos de producción de hidrógeno inducidos por la luz.

En este aspecto, los tamices moleculares mesoporosos basados en sílice ofrecen: i) capacidad de ajuste del tamaño de poro (2-50 nm), ii) elevada área superficial, iii) síntesis sencilla y generalmente de bajo coste, iv) la generación de un microambiente electrostático, v) estabilidad en medios acuosos, y vi) la capacidad de estabilizar estados de carga separada en procesos catalíticos ^[96,373]. Algunas investigaciones han sido reportadas hasta el momento en el que se hace uso de soportes con naturaleza silícea para la incorporación de modelos biomiméticos [FeFe]-hidrogenasa aplicando los materiales resultantes como catalizadores heterogéneos en reacciones de evolución de hidrógeno. Respecto al empleo de soportes basados en sílices mesoporosas, cabe resaltar la utilización de un tamiz molecular mesoporoso ordenado MCM-41 con capacidad de intercambio catiónico de iones K⁺ para inmovilizar complejos hidrofóbicos [2Fe2S], e incluso diadas [PS-2Fe2S], mejorando así la estabilidad y el rendimiento fotocatalítico del catalizador de dihierro en experimentos fotoquímicos de evolución de hidrógeno empleando una disolución puramente acuosa ^[374,375].

En un enfoque avanzado, los PMOs también han sido utilizados como soportes heterogéneos para experimentos HER. Recientemente, Inagaki y colaboradores diseñaron un sistema fotoquímico heterogéneo mediante el anclaje covalente de un complejo [2Fe2S] unido a un grupo maleimida ubicado en la superficie del poro de un PMO funcionalizado con grupos tioles (SH-PMO) que mostró una elevada actividad fotocatalítica en términos de “*turnover number*” (TON), incluso mayor que la obtenida por el propio complejo en fase homogénea, la cual fue atribuida a la fotoestabilidad en medio acuoso otorgada por la robustez y rigidez de la mesoestructura periódica del PMO ^[376].

En el mismo año, se reportó también el uso de nanopartículas de sílice como soporte sólido para anclar catalizadores de dihierro alcanzando una elevada actividad en la producción de hidrógeno fotocatalítica, aunque se señalaron inconvenientes como la lixiviación y degradación del complejo de dihierro tras varias horas de irradiación [377]. Estos trabajos han puesto de manifiesto que los soportes heterogéneos basados en sílice con complejos de [2Fe2S] inmovilizados proporcionan un incremento en la fotoestabilidad del catalizador y estados de separación de carga de larga duración, factores cruciales para aumentar la actividad de generación de hidrógeno fotocatalítico. Puesto que han sido publicadas un número limitado de investigaciones abordando específicamente esta temática, se hace necesario el diseño y estudio de nuevos sistemas fotoquímicos que integren catalizadores heterogéneos basados en modelos biomiméticos [FeFe]-hidrogenasa soportados en matrices silíceas para seguir avanzando en este campo aplicativo y lograr rendimientos mejorados en la reacción de evolución fotocatalítica de hidrógeno.

2.4. Materiales híbridos basados en grafeno

El carbono es el cuarto elemento más abundante en el Universo y posee una estructura electrónica única que pueden dar lugar a diferentes tipos de hibridación para construir redes sp^3 , sp^2 y sp , posibilitando la formación de alótropos más estables que en cualquier otro elemento presente en la Naturaleza. Entre los alótropos del carbono más extensamente conocidos cabe mencionar el grafito, el diamante, los nanotubos de carbono y el fullereno, cuyas estructuras son expuestas en la **Figura 32**. La forma alotrópica más estable es el grafito, mineral natural muy abundante en el que los enlaces del carbono presentan una hibridación trigonal sp^2 . Otra forma alotrópica del carbono extensamente conocida es el diamante, aunque difiere del grafito en que los enlaces del carbono presentan una hibridación tetraédrica sp^3 [378]. El grafito es un material anisotrópico, por lo que sus propiedades térmicas y eléctricas varían según la dirección en las que son estudiadas. De esta forma, es considerado un excelente conductor térmico y eléctrico en la dirección paralela a las capas de carbono debido al carácter metálico en el plano, mientras que exhibe mala conductividad en la dirección perpendicular a las capas debido a las interacciones débiles de Van der Waals existentes entre ellas [379]. Por su parte, los nanotubos de carbono (*buckytubos*) y fullerenos (*buckybolas*) son formas alotrópicas también muy reconocidas que son diferenciadas del

grafito por sus particulares estructuras en forma de cilindros o esferas huecas, respectivamente, otorgándoles así propiedades fisicoquímicas, mecánicas y conductoras específicas.

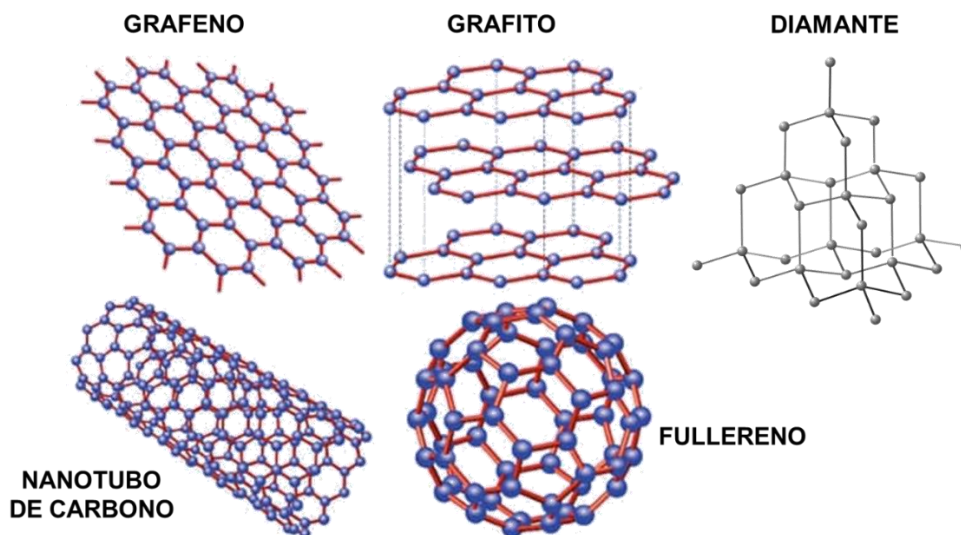


Figura 32. Formas alotrópicas más representativas del carbono: grafeno, grafito, diamante, nanotubo de carbono y fullerenos.

Las capas simples de átomos de carbono fuertemente empaquetadas en una red cristalina de panal bidimensional (2D) se conocen como grafeno (**Figura 32**), término introducido en el año 1994 por los investigadores Boehm, Setton y Stumpp^[380]. El grafeno es un material 2D que consiste en una sola lámina de grafito con un espesor de un átomo de carbono formada por una red de anillos hexagonales de carbonos con hibridación sp^2 , dando como resultado que por cada átomo de carbono quede libre un electrón de su última capa de valencia sin formar enlaces, creando de esta forma una nube electrónica por toda la lámina del grafeno, la cual le confiere una estructura electrónica especial. Es considerada una forma alotrópica del carbono y constituye la unidad 2D elemental básica para construir materiales grafíticos de otras dimensiones como nanotubos de carbono, fullerenos y grafito^[381]. El grafeno fue aislado por primera vez en el año 2004 por Andre Geim y Konstantin Novoselov, quienes desarrollaron un método simple para colocar capas atómicamente gruesas de grafeno en obleas de silicio oxidadas térmicamente (Si/SiO_2) mediante la ruptura mecánica del grafito con cinta adhesiva común^[382]. Sus estudios fundamentales sobre este material revelaron una gama de propiedades

físicas y químicas sobresalientes, cobrando tal importancia esta investigación en términos de innovación científica que hasta fue galardonada con el Premio Nobel de Física en el año 2010. Desde ese momento, el grafeno se ha convertido rápidamente en uno de los materiales más investigados y aplicados en el ámbito científico, siendo objeto de más de 300.000 artículos publicados desde su descubrimiento en el año 2004 hasta el 2022 (fuente de datos: WOS, “*Web of Science*”).

Entre las propiedades más destacadas del grafeno caben destacarse las siguientes: gran superficie específica ($2630 \text{ m}^2 \text{ g}^{-1}$), excelente conductividad electrónica (hasta $2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ a temperatura ambiente) y transmitancia óptica ($\sim 97.7\%$), conductividad térmica extremadamente alta ($5000 \text{ W m}^{-1} \text{ K}^{-1}$), elevadas resistencia mecánica y flexibilidad (módulo de Young $\approx 1 \text{ TPa}$), alta transparencia (2.3% de absorción de luz en el visible e infrarrojo), y notable estabilidad [383]. Generalmente, el término grafeno se refiere a la unidad constitutiva simple, mientras que aquellas formaciones de espesor nanométrico a base de grafeno se denominan nanografenos. En función del número de láminas, podemos clasificar el grafeno de la siguiente manera: i) grafeno monolámina (*single-layer graphene*, **SLG**), ii) grafeno de pocas láminas cuando se obtienen menos de 10 láminas (*few-layer graphene*, **FLG**), y iii) grafeno multiláminas cuando se obtienen más de 10 láminas (*multilayer graphene*, **MLG**) [384].

En la literatura se han descrito varios métodos de obtención de grafeno, que se pueden clasificar principalmente en dos grandes grupos: *bottom-up* y *top-down*:

- a) **Bottom-up**: Se han desarrollado técnicas sintéticas para producir láminas de grafeno de alta calidad (SLG y FLG) a través de un enfoque “*bottom-up*”, como la deposición química de vapor (CVD) y el crecimiento epitaxial en carburo de silicio (SiC) pero el proceso de producción es costoso económicamente y ambos presentan dificultades para obtener las grandes cantidades de grafeno requeridas a nivel industrial.
- b) **Top-down**: En cuanto a los procesos “*top-down*”, la estrategia general consiste en partir del grafito comercial como unidad elemental, para obtener compuestos de grafeno a gran escala. Para ello, se han investigado y mejorado continuamente, tanto a nivel científico como industrial, métodos como la escisión

micromecánica (*Scotch tape*), la exfoliación en fase líquida (*liquid-phase exfoliation*, LPE), la exfoliación mecánica por molienda de bolas, exfoliación asistida por métodos basados en dinámica de fluidos o la exfoliación química (proceso de oxidación y posterior reducción de los grupos funcionales), para obtener grafeno con diferentes tamaños, número de capas y defectos en las lámina [383,385].

En general, existen dos tipos de rutas mecánicas para exfoliar el grafito en láminas de grafeno cuando se llevan a cabo los métodos mencionados anteriormente: fuerza normal y fuerza lateral (**Figura 33**).

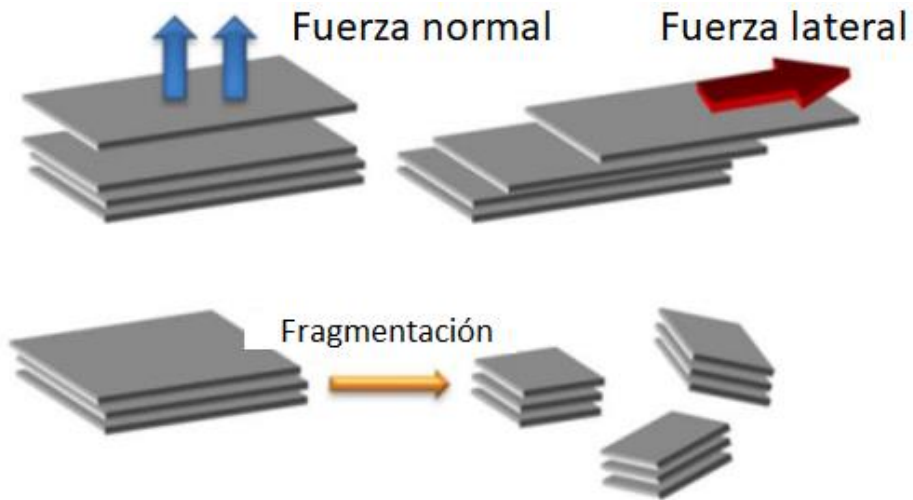


Figura 33. Los dos tipos de rutas mecánicas para exfoliar grafito en láminas de grafeno y la ruta auxiliar de fragmentación.

Se puede ejercer una fuerza normal para superar las fuerzas de Van der Waals cuando se separan dos capas de grafito, como la escisión micromecánica basada en el método de cinta adhesiva o *Scotch tape* ya explicado al inicio de esta sección. A través de la capacidad de autolubricación del grafito en la dirección lateral, también se puede ejercer una fuerza lateral para promover el movimiento relativo entre dos capas de grafito. Otra ruta auxiliar es el efecto de fragmentación durante la exfoliación. La fuerza generada por la técnica de exfoliación también puede fragmentar partículas grandes de grafito o capas de grafeno en otras más pequeñas. Este efecto de fragmentación tiene ventajas e inconvenientes. Por un lado, puede

reducir el tamaño lateral del grafeno, lo cual no es deseable para lograr grafeno de gran área superficial. Por otro lado, facilita la exfoliación porque las partículas de grafito más pequeñas son más fáciles de exfoliar que las más grandes debido a la menor fuerza de las interacciones de Van der Waals entre las capas contenidas en partículas de grafito más pequeñas.

Los métodos LPE se basan en un proceso de exfoliación del grafito llevado a cabo en un solvente específico capaz de vencer las fuerzas de Van der Waals que mantienen unidas las láminas en el grafito. Para ayudar a que la intercalación del solvente entre las capas de grafito supere las fuertes interacciones entre las capas adyacentes, lo que eventualmente conduce a la separación completa de las capas de grafeno, se aplica una fuerza externa. La elección de la fuerza ejercida por una fuente externa y los parámetros de exfoliación utilizados permiten ajustar las características del exfoliado referidas a la calidad, tamaños de láminas resultantes y rendimiento en la obtención de monoláminas de grafeno. Respecto a la fuente externa que promueve el proceso LPE, cabe destacar la LPE asistida por ultrasonidos donde se alcanzan altas temperaturas y presiones en un corto período de tiempo obteniendo grafenos de diferentes tamaños y láminas cuyos rendimientos dependen del tiempo de sonicación, potencia de entrada, condiciones de centrifugación, y tipo de material gráfítico de partida.^[386] En el método de sonicación, la mecánica de exfoliación se origina a partir de la cavitación del líquido, como se ilustra en la **Figura 34**^[387]. En la ruta primaria, las burbujas inducidas por la cavitación se distribuyen alrededor de las escamas de grafito. Cuando estas burbujas colapsan, los microchorros o micro “jets” y las ondas de choque actúan instantáneamente sobre la superficie de grafito, lo que da como resultado ondas de tensión de compresión que se propagan por toda la estructura gráfítica. De acuerdo con la teoría de las ondas de tensión, una vez que la onda de compresión se propaga a la interfaz libre de grafito, una onda de tensión de tracción actuará en sentido contrario. Como tal, el colapso de numerosas microburbujas dará lugar a una intensa tensión de tracción en las láminas de grafito provocando la exfoliación y fragmentación. Un proceso secundario es posible, ya que la tensión de compresión lateral también pueda separar dos capas adyacentes por un efecto de cizalla. Además, los micro “jets” pueden dividir las láminas de grafito justo cuando se

introduce una burbuja colapsada (efecto “cuña”) en la capa intermedia, provocando el proceso de exfoliación y fragmentación de igual forma.



Figura 34. Ilustración del mecanismo mecánico para la exfoliación de grafeno mediante sonicación (adaptado de la referencia ^[387])

Un método también relacionado con LPE asistido por una fuerza impulsora externa es la exfoliación electroquímica de grafito, en la que el grafeno se exfolia aplicando un potencial eléctrico a una celda electroquímica en la que se utiliza grafito como ánodo o cátodo en presencia de un medio que contiene electrolitos ^[388].

La molienda de bolas, una técnica común en la industria para la producción de diferentes tipos de materiales en forma de polvo o para llevar a cabo una extensa variedad de reacciones químicas, es una buena candidata para generar fuerza de corte o cizalla. El mecanismo mecánico de molienda de bolas en la exfoliación de grafeno se puede ilustrar en la **Figura 35** y, a menudo, es llevado a cabo en presencia de un disolvente como N-metil-2-pirrolidona siguiendo una estrategia LPE, denominándose este método exfoliación del grafito con molienda de bolas en fase húmeda (*wet ball milling method*) ^[389], aunque también es posible llevar a cabo este mismo proceso de exfoliación en fase seca sin el uso de

disolventes en el medio de síntesis mediante la mezcla de grafito y sales inorgánicas solubles en agua químicamente inertes (*dry ball milling method*)^[387]. En la mayoría de los instrumentos de molienda de bolas, hay dos formas posibles responsables de los efectos de exfoliación y fragmentación. La principal es la fuerza de cizalla, que se considera una vía mecánica excelente para la exfoliación con el fin de obtener láminas de grafeno aisladas. La ruta secundaria consiste en colisiones o impactos verticales aplicados por las bolas debido a acciones de rodadura. De esta forma, se pueden fragmentar láminas grandes en otras más pequeñas y, en ocasiones, incluso destruir estructuras cristalinas hasta convertirlas en fases amorfas, por lo que se espera minimizar el efecto secundario para obtener láminas de grafeno de mayor calidad estructural^[390].

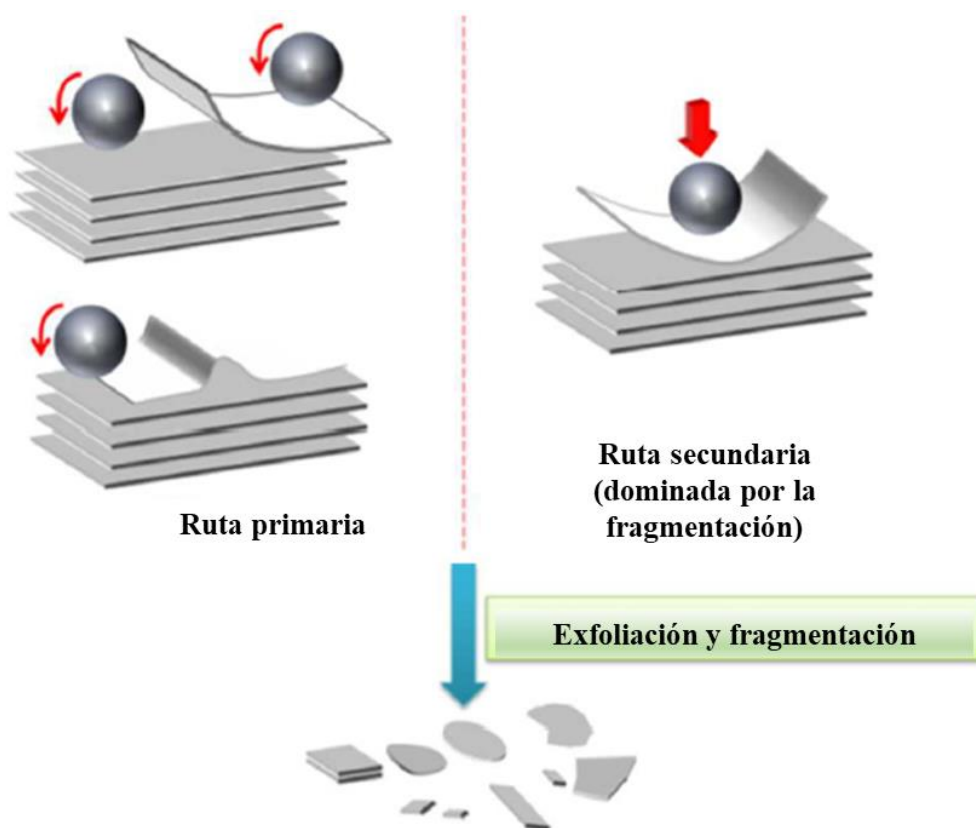


Figura 35. Ilustración del mecanismo mecánico para la exfoliación de grafeno mediante molienda de bolas (adaptado de la referencia^[387])

El método de exfoliación química es extensamente aplicado a gran escala para la producción de grandes volúmenes de grafeno a partir de la obtención del conocido óxido de grafeno (*graphene oxide*, GO) [391]. El GO se puede producir mediante varios métodos, aunque la mayoría de ellos están basados en los protocolos de síntesis propuestos por W. Hummers [392], B. Collins [393] y L. Staudenmaier [394], consistentes en el tratamiento de un grafito comercial con oxidantes fuertes como ácido sulfúrico, nitrato de sodio, agua oxigenada, ácido nítrico, clorato de potasio o permanganato de potasio (**Figura 36, etapa a**). Este proceso de oxidación da como resultado la introducción de grupos funcionales ricos en oxígeno como los grupos epoxi, hidroxilo, carbonilo y carboxilo localizados tanto en el plano basal como en los bordes del GO. El GO producido tiene estructura funcionalizada 2D con elevado grado de desorden y es de color más claro que el grafito, adquiriendo una tonalidad marrón oscura. Durante la oxidación del grafito se rompen las fuerzas intermoleculares de Van der Waals establecidas entre las láminas y la incorporación covalente de los grupos funcionales oxigenados crea defectos en toda su estructura. Además, tiene lugar la pérdida de conjugación estructural durante el proceso, ya que se produce el cambio en la hibridación de los átomos de carbono de trigonal plana sp^2 a tetraédrica sp^3 . Las funcionalidades añadidas y la presencia de carbonos sp^3 hacen que el GO sea hidrofílico, eléctricamente aislante y altamente reactivo, mientras que el grafeno es hidrofóbico, conductor e inerte. La reducción del GO mediante métodos térmicos (solvotérmico en autoclave o microondas), químicos (con agentes reductores como borohidruro de sodio ($NaBH_4$) e hidrazina (N_2H_4)), fotoquímicos o electroquímicos conduce a la eliminación de la mayoría de los grupos oxigenados y produce que la mayoría de los carbonos sp^3 se transformen nuevamente a carbonos con hibridación sp^2 [395]. El material es denominado generalmente óxido de grafeno reducido (*reduced graphene oxide*, rGO), mostrando una distribución de láminas con conformación tridimensional y características intermedias entre el GO y el grafeno prístino, con presencia de un gran número de defectos, una conductividad eléctrica mucho más alta y una reactividad e hidrofilia menor en comparación con el GO (**Figura 36, etapa b**).

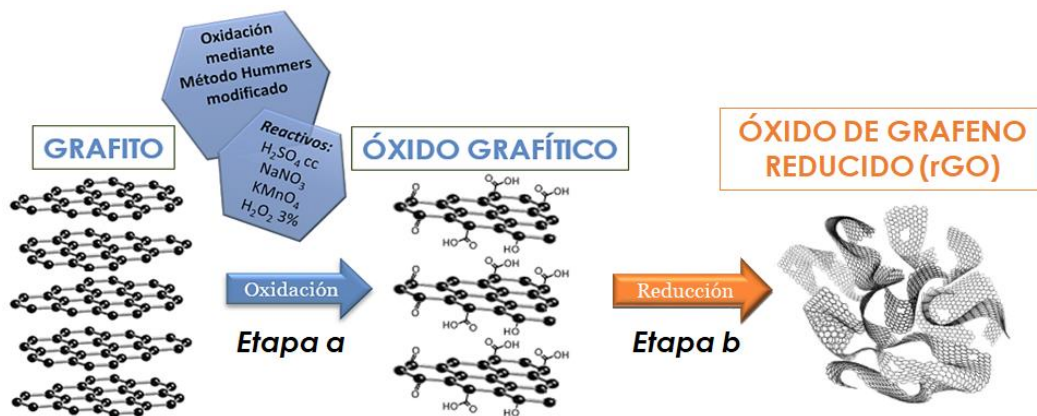


Figura 36. Ilustración del proceso de exfoliación química de GO y la obtención de rGO partiendo de grafito.

Además de las metodologías mencionadas anteriormente, han surgido estrategias de síntesis para la producción de grafeno basadas en la dinámica de fluidos (*vortex fluidic film*, *pressure driven fluid dynamics* y *mixer driven fluid dynamics*)^[396]. Dentro de la dinámica de fluidos en condiciones suaves o intensas, las láminas de grafito pueden moverse con el líquido y, por lo tanto, pueden exfoliarse repetidamente en diferentes posiciones. Esta característica es intrínsecamente diferente de la sonicación y la molienda de bolas, lo que la convierte en una técnica potencialmente eficiente para la producción escalable de grafeno.

Otras técnicas recientemente implementadas para la exfoliación de grafito en láminas de grafeno han sido empleadas entre las que cabe citar la detonación inducida por ondas de choque potentes y energía térmica para una exfoliación violenta y de alta energía, exfoliación asistida por fluidos supercríticos como el CO_2 , exfoliación de grafito asistida por descargas de plasma y ablación por láser, entre otras [387,397].

Las propiedades fisicoquímicas y mecánicas excepcionales junto con la excelente conductividad eléctrica, la transparencia y la flexibilidad de las láminas del grafeno han motivado su incorporación en una multitud de aplicaciones de gran interés científico e industrial^[395,398–402]:

- Biosensores y dispositivos optoelectrónicos (diodos orgánicos emisores de luz (OLED), dispositivos fotovoltaicos orgánicos (OPV) y pantallas táctiles).

- Dispositivos fotónicos (células solares, fotodetectores, moduladores ópticos, controladores de polarización óptica, etc.)
- Supercondensadores y baterías (litio-ion, litio-azufre, sodio ion, etc.) y
- Biomedicina.
- Aplicaciones de anticorrosión y lubricación.
- (Foto/electro)catálisis y celdas de combustible.
- Aplicaciones mecánicas y reológicas, pinturas y revestimientos.
- Aplicaciones para la remediación medioambiental (adsorción y separación selectiva de gases, membranas para la purificación de agua, etc.).
- Bioimagen y transistores de alta frecuencia.

En los últimos años, la comunidad científica comenzó a preguntarse qué podría pasar si se combina este privilegiado material con otros materiales o moléculas con diferentes características para formar materiales o materiales híbrido basados en grafeno ^[383]. La implementación del enfoque híbrido del grafeno no solo permitió mejorar el rendimiento en los campos aplicativos anteriormente mencionados, sino que también allanó el camino para su uso en una variedad más amplia de aplicaciones.

Los híbridos se obtienen mediante el acoplamiento de dos o más materiales que comparten dimensiones similares en una pequeña escala nanométrica, donde predominan las interacciones químicas y/o electrónicas. La proximidad de los componentes en el híbrido, que están íntimamente conectados e interactúan entre sí a través de interacciones covalentes o no covalentes, y sus dimensiones similares producen una gran área interfacial permitiendo llevar a cabo procesos de transferencia de energía y de electrones o reacciones químicas superficiales. El efecto sinérgico de ambos componentes hace que el híbrido presente nuevas propiedades mecánicas, térmicas, eléctricas y electrónicas que conducen a rendimientos mejorados y mayor versatilidad en determinadas aplicaciones respecto a los componentes individuales.

Seguidamente, se van a describir en líneas generales las dos áreas de aplicación abordadas en esta Tesis Doctoral, **fotoluminiscencia** y **electrocatalisis**, así como las estrategias de síntesis empleadas para el diseño de los materiales híbridos basados en grafeno que han sido desarrolladas en los correspondientes trabajos de investigación que integran la presente memoria.

2.4.1 Materiales híbridos basados en grafeno como materiales luminiscentes

La posibilidad de impartir propiedades fotónicas al grafeno es un desafío en la actualidad, ya que es un semiconductor de banda prohibida cero y, por tanto, no presenta prácticamente luminiscencia ^[403]. Por ello, la incorporación de características luminiscentes a compuestos de naturaleza grafénica mediante la funcionalización de su estructura con moléculas específicas es un área de creciente interés debido a que los nanomateriales emisores tienen muchas potenciales aplicaciones, incluidas la detección, la bioimagen, optoelectrónica, células fotovoltaicas y la fotocatalisis, entre otras. En la actualidad existen dos estrategias generales para producir materiales luminiscentes basados en grafeno. La primera implica la existencia de sitios aislados sp^2 sin interacciones de tipo π , como ocurre en algunos rGOs, mientras que la segunda se origina por la presencia de defectos, como ocurre en los quantum dots de carbono (QDs) ^[404]. Estos nanomateriales exhiben emisiones localizadas en las regiones azul y verde del espectro electromagnético. Las estrategias anteriores se basan fundamentalmente en la introducción de defectos en las láminas de grafeno, por lo que inevitablemente darán lugar a materiales con propiedades reducidas. Una limitación a tener en cuenta a la hora de diseñar materiales híbridos basados en grafeno es que, al igual que el grafito, el propio grafeno no es fácil de someter a procesos de funcionalización, a diferencia de su correspondiente óxido, que presenta elevada reactividad.

Como alternativa para paliar este inconveniente, surgen las reacciones de tipo Diels-Alder introducidas por Otto Diels y Kurt Alder en 1928 ^[405], las cuales han cobrado enorme relevancia en la historia de la Química Orgánica. Estas reacciones consisten en una cicloadición [4+2] de un dieno conjugado y un dienófilo sustituido (generalmente un alqueno o un alquino) dando lugar a un aducto cíclico (sistema basado en un (hetero)ciclohexeno) (**Figura 37a**). Según los efectos electrónicos del sustituyente sobre el dieno y el dienófilo, las reacciones de Diels-Alder se pueden clasificar como de demanda de electrones normal (el dieno rico en electrones reacciona con el dienófilo deficiente en electrones) o demanda de electrones inversa (iEDDA, el dieno deficiente en electrones reacciona con dienófilos ricos en electrones) (**Figura 37b**). En este contexto, las unidades de 3,6-di(2-piridil)piridazina han recibido gran atención como ligandos para la coordinación de centros metálicos y la química

supramolecular ^[406]. Estos ligandos se pueden sintetizar mediante una reacción de Diels-Alder de demanda inversa de electrones entre la correspondiente 3,6-di(2-piridil)-1,2,4,5-tetrazina (como dieno) y alquinos o alquenos (como dienófilos) ^[407]. Como se muestra en el esquema representado en la **Figura 37c**, una tetrazina sustituida y derivados de alquenos o alquinos se someten a una cicloadición de Diels-Alder de demanda electrónica inversa seguida de una reacción de retro-Diels-Alder para dar el producto de dihidropiridazina y liberar N₂ ^[408]. Esta reacción procede rápidamente a temperatura ambiente en ambientes acuosos sin requerir la presencia de un catalizador y, generalmente, muestra elevados rendimientos. Un posterior tratamiento de oxidación con agentes oxidantes como nitrito de sodio (NaNO₂) o 2,3-dicloro-5,6-dicianobenzoquinona (DDQ) produce la aromatización del anillo de dihidropiridazina dando lugar a las unidades de piridazina correspondientes.

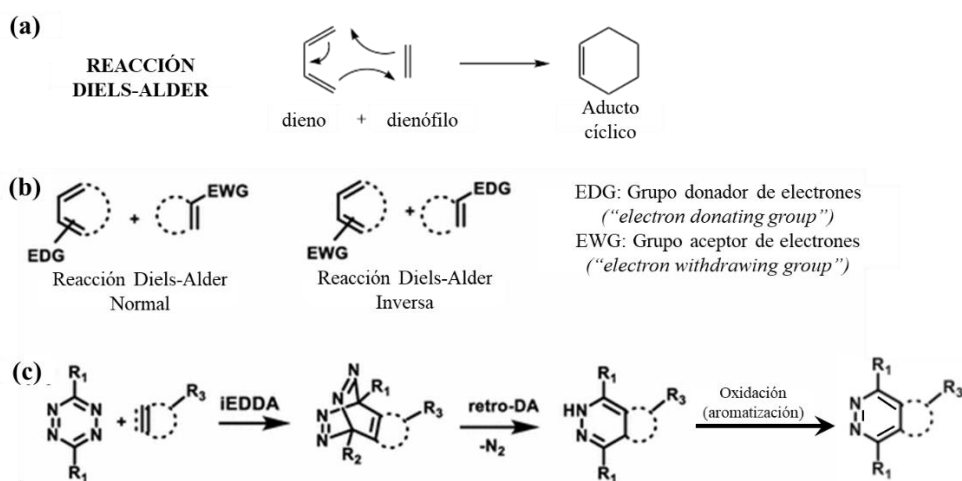


Figura 37. a) Ejemplo representativo de reacción Diels-Alder entre el 1,3-butadieno y el etileno para la obtención de ciclohexeno, b) Reacciones de Diels-Alder de demanda de electrones normal y de demanda de electrones inversa (iEDDA), y c) Esquema de reacción entre tetrazinas sustituidas y derivados de alquenos para dar lugar a la formación de unidades de tipo piridazina (adaptado de la referencia ^[408]).

De esta forma, la preparación de materiales híbridos orgánico-inorgánicos mediante reacciones hetero-Diels-Alder se hace posible seleccionando este tipo de moléculas orgánicas nitrogenadas y el dienófilo adecuado que asegure la efectividad de la reacción. Por tanto, en los últimos años se han explorado las propiedades de emisión de diferentes

organosílices mediante su funcionalización con complejos de lantánidos vía ligandos superficiales de dipiridilpiridazina. Estos aductos superficiales fueron generados por reacción de Diels-Alder según el mecanismo de demanda de electrones inversa anteriormente comentado [408] entre los dobles enlaces C=C incorporados en la estructura de la organosílice (dienófilo) y 3,6-di(2-piridil)-1,2,4,5-tetrazina, cuya nomenclatura abreviada es dptz (dieno). En particular, se demostró que estos aductos superficiales son ligandos que: i) sensibilizaron adecuadamente iones de europio [409], ii) proporcionaron materiales híbridos emisores de infrarrojo cercano (NIR) al formar complejos con iones de lantánidos (Ln) emisores de NIR (Nd^{3+} , Er^{3+} , Yb^{3+}) [410], y iii) fueron capaces de actuar como un termómetro luminiscente óptico cuando se incorporan iones $\text{Eu}^{3+}/\text{Tb}^{3+}$ [411].

De estos trabajos se pueden extraer dos rutas sintéticas para la incorporación de aductos de tipo dipiridilpiridazina en materiales PMO como puede observarse en la **Figura 38**. La **estrategia 1** consiste en la reacción Diels Alder iEDDA entre el doble enlace de los grupos etileno puente insertados en la pared de un PMO y moléculas dptz, mientras que la **estrategia 2** basada en la misma reactividad, pero este caso, los dobles enlaces se encuentra localizados en el grupo vinilo colgante de la pared del material PMO.

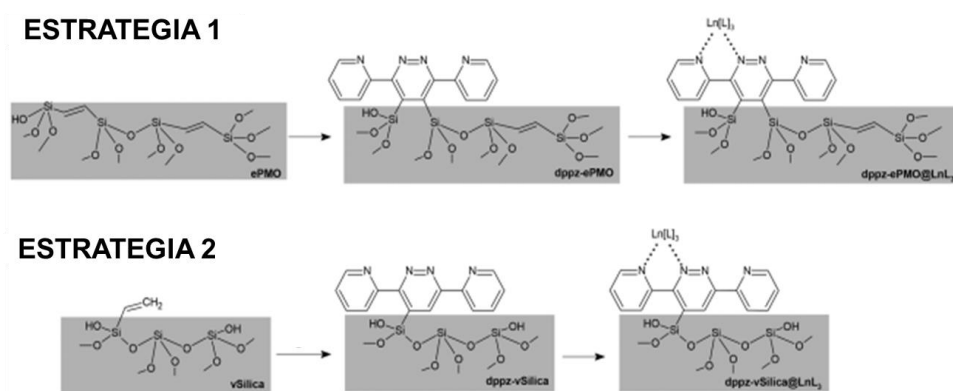


Figura 38. Esquema de rutas de síntesis diseñadas para la incorporación de aductos dipiridilpiridazina en materiales PMO mediante reacciones Diels-Alder de tipo iEDDA (adaptado de la referencia [410]).

Situando a los grafenos dentro de esta temática, cabe mencionar inicialmente que los grafenos dopados con nitrógeno son obtenidos generalmente mediante dos estrategias: síntesis directa y postratamiento.

Independientemente del procedimiento de dopaje, se generan diferentes tipos de nitrógeno en diferentes lugares y, por lo tanto, los sitios específicos para la coordinación de metales están mal definidos ^[412].

Hace una década aproximadamente, Haddon et al. ^[413,414] reportaron que tanto el grafito como el grafeno pueden actuar como dienos o dienófilos en la reacción de Diels-Alder. En particular, se investigó su comportamiento como dienófilos utilizando 9-metilantraceno, 9,10-dimetilantraceno y 2,3-dimetoxi-1,3-butadieno, todos ellos dienos ricos en electrones. Un estudio computacional posterior reveló que estas reacciones de cicloadición no tenían lugar en los enlaces internos del grafeno sino específicamente en los bordes de las láminas ^[415].

Asimismo, Schirmacher et al. ^[416] demostraron la eficacia de la reacción de Diels-Alder con un material de matriz carbonosa y un compuesto a base de tetrazina capaz de funcionalizar nanotubos de carbono de pared simple con 3,6-diclorotetrazina conjugada con nanopartículas de oro. De manera similar, informaron más tarde sobre la reacción de Diels-Alder entre clorotetrazinas sustituidas y grafito pirolítico altamente orientado (HOPG) en condiciones suaves ^[417].

Teniendo en cuenta que los derivados de dipiridilpiridazina son ligandos excelentes para la coordinación de diferentes metales y las extraordinarias aplicaciones de los materiales conteniendo Ln, se prevé potencialmente atractiva de cara al futuro el diseño de una ruta sintética para la preparación de materiales híbridos basados en grafeno integrando aductos superficiales de tipo dipiridilpiridazina (dppz) mediante reacciones Diels-Alder que sean capaces de coordinar complejos metálicos mostrando propiedades inéditas en el campo de la luminiscencia.

2.4.2 Materiales híbridos basados en grafeno para electrocatalisis

A modo de introducción para enfatizar la enorme importancia del empleo de híbridos basados en grafeno en aplicaciones electrocatalíticas, es de crucial relevancia establecer el punto de partida de esta temática en las grandes preocupaciones energéticas que afectan a la sociedad mundial. Ante el inminente agotamiento de los combustibles fósiles, el aumento exponencial de emisiones de dióxido de carbono y el calentamiento global, la comunidad científica ha llevado a cabo tremendos esfuerzos en buscar

fuentes de energía y recursos energéticos alternativos sostenibles medioambientalmente y de bajo coste. La abundancia de hidrógeno en el universo y la relativamente fácil producción de gas H_2 a partir del agua por electrólisis lo convierten en un portador de energía ideal, como ya se ha comentado en el apartado anterior de esta sección introductoria.

El avance de la denominada “economía del hidrógeno” depende directamente del diseño de nuevos materiales que actúen eficientemente como electrocatalizadores en la reacción de división del agua (*water splitting*) en hidrógeno y oxígeno empleando electricidad procedente de fuentes de energía renovables como la solar o la eólica, así como en las reacciones involucradas en los procesos llevados a cabo en celdas de combustible donde el hidrógeno producido previamente es utilizado como combustible para generar electricidad ^[418].

Por ello, las reacciones de evolución (OER) y de reducción (ORR) de oxígeno tienen un papel clave en el rendimiento general de estos dispositivos tecnológicos de conversión y almacenamiento de energía renovable donde están involucradas ambas reacciones, incluyendo electrolizadores de agua, celdas de combustible y baterías recargables metal-aire ^[419,420]. Específicamente, en la electrólisis del agua se llevan a cabo la reacción OER en el ánodo de la celda electrolítica y la reacción de evolución de hidrógeno (HER) en el cátodo ^[421]. Por su parte, en las celdas de combustible tienen lugar las reacciones de oxidación electroquímica del combustible (hidrógeno y alcoholes) (HOR y AOR) y la reacción de reducción de oxígeno (ORR) en el ánodo y el cátodo, respectivamente ^[422]. En el caso de las baterías recargables metal-aire se llevan a cabo las reacciones ORR y OER en el electrodo catódico de aire durante los ciclos de carga y descarga, respectivamente ^[423]. Para evidenciar con mayor claridad las reacciones electrocatalíticas llevadas a cabo en estos tres dispositivos de conversión energética, en la **Figura 39** se muestran representaciones de cada uno de ellos.

Todas las reacciones electroquímicas llevadas a cabo en estos dispositivos están intervenidas por electrocatalizadores, por tanto, la electrocatálisis es la clave en la aplicación exitosa de estas tecnologías de conversión de energía. Una ventaja evidente de la electrocatálisis es que los electrocatalizadores pueden reducir las barreras de energía de las reacciones electroquímicas para permitir que ocurran bajo potenciales eléctricos más pequeños, lo que lleva a un menor consumo de energía durante el proceso de conversión. Además, el uso de electrocatalizadores puede permitir un

fácil control de las vías y velocidades de reacción para producir productos determinados.

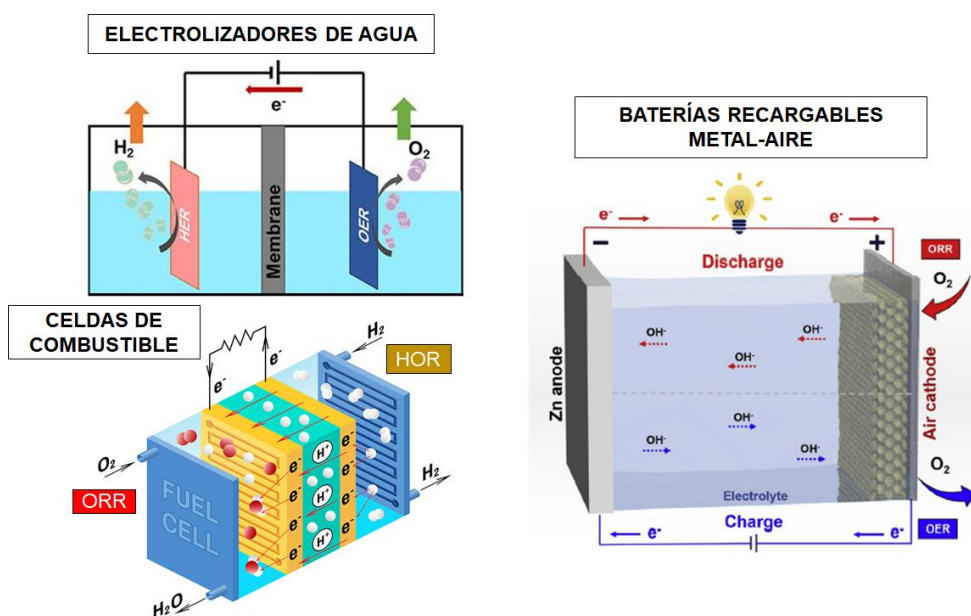


Figura 39. Representación de los dispositivos de conversión de energía en los que se encuentran implicadas las reacciones ORR y OER: electrolizadores de agua, celdas de combustible y baterías metal-aire (adaptado de la referencia ^[423]).

En general, las reacciones electroquímicas ocurren en la interfaz entre los electrocatalizadores y los reactivos en solución en las que la superficie de los electrocatalizadores interactúa con los reactivos disueltos. Aquí, el rendimiento de los electrocatalizadores está determinado principalmente por factores como la composición química, la estructura cristalina, la microestructura y la macromorfología, y estos parámetros tienen una influencia directa en el rendimiento catalítico, lo que significa que las interfaces catalíticamente activas son vitales para lograr una alta eficiencia en el proceso electrocatalítico. Una consideración clave de la catálisis interfacial es la capacidad de adsorción y desorción de los intermedios de reacción por parte del catalizador. Por ello, un catalizador ideal debe poseer energía de adsorción y desorción adecuada para los intermedios con objeto de facilitar las reacciones electrocatalíticas. Otras consideraciones incluyen una buena conductividad electrónica, rápida transferencia de masa, alta durabilidad y benignidad ambiental.

Debido a esto, no solo es importante la actividad intrínseca de los catalizadores, sino que la estructura de estos también es fundamental para lograr procesos catalíticos eficientes. Por ello, el principal objetivo en la búsqueda de nuevos electrocatalizadores se centra en el diseño y la síntesis sostenible de materiales que muestren alta actividad, alta selectividad y extensa durabilidad en procesos de electrocatálisis. Por lo tanto, las investigaciones sobre la relación entre la estructura del catalizador y el rendimiento electrocatalítico son vitales debido a que las estructuras interfaciales tienen influencia directa sobre la eficiencia y la selectividad electroquímicas.

Hasta la fecha, los catalizadores basados en Pt/Pd y Ru/Ir se han considerado como los catalizadores comerciales de referencia para los procesos ORR y OER, respectivamente, por sus altos rendimientos mostrados en estas reacciones electroquímicas ^[424]. Sin embargo, el elevado coste económico, la escasa disponibilidad y baja estabilidad limitan el uso de estos metales nobles a escala industrial. Por estas razones, el diseño de catalizadores libres de metales nobles que muestren un rendimiento mejorado frente a las reacciones críticas involucradas en estos procesos electrocatalíticos, concretamente ORR y OER, es fundamental para progresar con rapidez en la anteriormente mencionada economía del hidrógeno y, por consiguiente, en el desarrollo de dispositivos de conversión de energía. Es por esto por lo que se han realizado grandes esfuerzos han sido dedicados en la preparación de nuevos electrocatalizadores libres de metales nobles a bajo coste que muestren actividad bifuncional mejorada y elevada estabilidad en las reacciones ORR y OER debido a su amplia aplicabilidad en una extensa variedad de tecnologías electroquímicas avanzadas de energías renovables.

Los electrocatalizadores basados en materiales carbonosos son considerados muy prometedores para los procesos electrocatalíticos mencionados anteriormente, debido a su buena estabilidad, alta área superficial, excelente conductividad eléctrica y flexibilidad para la introducción de dopantes ^[425,426]. Sin embargo, la mayoría de los materiales grafíticos 2D poseen poca o ninguna actividad electrocatalítica. Concretamente, el grafeno no posee actividad electrocatalítica debido a su superficie inerte. Sin embargo, sus estructura electrónica químicamente inerte pueden activarse a través de varios enfoques, incluido el dopaje de heteroátomos, la formación e ingeniería de defectos, la ingeniería de deformaciones, la intercalación de iones y la interacción interfacial, pueden

mejorar el rendimiento catalítico de los compuestos de grafeno a través de diferentes mecanismos ^[419].

Por tanto, los materiales basados en grafeno son de particular interés debido a sus privilegiadas propiedades ya descritas a lo largo de esta sección que los convierten en candidatos ideales como electrocatalizadores en dispositivos de almacenamiento y conversión de energía debido a las siguientes ventajas ^[427]: i) sus extraordinarias propiedades eléctricas y ópticas permiten un rendimiento potencialmente elevado como portadores de electrones en aplicaciones electroquímicas, ii) las buenas propiedades mecánicas y térmicas dotan a los materiales grafénicos de una excepcional estabilidad térmica y mecánica que puede ser importante en dispositivos electrónicos o sistemas electrocatalíticos que implican la liberación de calor como los explicados previamente, y iii) el desarrollo de métodos de preparación simples y de bajo costo también simplifica el procesamiento de materiales basados en grafeno y, por lo tanto, favorece sus aplicaciones tecnológicas en el sector industrial.

Estos materiales híbridos basados en grafeno tienen el potencial de manifestar no solo propiedades únicas de sus componentes individuales, sino también propiedades físicas y químicas novedosas que surgen del efecto sinérgico entre el grafeno y las nanoestructuras acopladas, lo que eventualmente resulta en una mayor mejora en el rendimiento. Estas propiedades prometedoras, junto con la facilidad de procesamiento y funcionalización, hacen que los materiales funcionales basados en grafeno sean candidatos ideales para una variedad de aplicaciones energéticas.

Por tanto, un tema candente en electrocatálisis es el dopaje adecuado de materiales basados en carbono, específicamente en grafeno, con heteroátomos (p. ej., N, S, P) y metales de transición (p. ej., Fe o Co) para obtener estructuras electrónicas y geométricas óptimas que muestren actividad electroquímica superior en determinados procesos electrocatalíticos ^[428-430].

El dopaje de grafeno con átomos de nitrógeno (N) ha experimentado un progreso excepcional y han demostrado ser materiales muy prometedores en el área de la electrocatálisis ^[431]. Se pueden introducir en el grafeno tres tipos de especies de N, incluido el N-grafítico o N-cuaternario, el N-piridínico y el N-pirrólico, cada uno de los cuales afecta su distribución de carga atómica de manera diferente. Los resultados teóricos sobre el efecto del dopaje de N en el grafeno han revelado que tanto

la carga atómica como la densidad de espín determinan las propiedades catalíticas del material ^[431]. En consecuencia, los mecanismos a través de los cuales el grafeno dopado con N logra una mejora de la actividad también difieren según la naturaleza de las especies de N presentes ^[432]. Es, por lo tanto, muy importante determinar la correlación entre la configuración de enlaces de nitrógeno en el grafeno y la actividad electrocatalítica. Las especies de nitrógeno piridínico y cuaternario se consideran generalmente como los componentes electrocatalíticamente activos del grafeno dopado con N.

A pesar de la actividad ORR superior en medios alcalinos, el rendimiento electrocatalítico del grafeno dopado con N es generalmente pobre en medios ácidos, quizás debido a la presencia de sitios superficiales inactivos ^[427]. Se ha demostrado que los materiales basados en carbono pueden exhibir una alta actividad ORR en medios ácidos mediante la adición de especies metálicas y la formación de estructuras de coordinación entre el nitrógeno y metales de transición. Luego, esta idea se extendió al grafeno con sitios activos incorporados para la coordinación de metales de transición como Fe y Co. Se esperaba que los materiales híbridos basados en grafeno con metales de transición coordinados a través de los N insertados en la estructura grafénica condujeran a un mejor rendimiento en diferentes procesos electrocatalíticos como las reacciones ORR y OER.

Más concretamente, los cálculos teóricos llevados a cabo mediante la teoría del funcional de la densidad (DFT) sugirieron que el dopaje conjunto de Fe y N en forma de posibles sitios de FeN₄ en un sustrato grafítico podría ser tan activo como el Pt para la adsorción de O₂ y la posterior ruptura del enlace O=O durante la ORR ^[433,434]. En este sentido, los grupos funcionales que contienen nitrógeno en una matriz grafítica también juegan un papel fundamental en el rendimiento y la conductividad electrónica de los procesos electrocatalíticos ^[435–437]. De hecho, el N-piridínico mejora el potencial de inicio (del inglés *onset potential*), mientras que el N-grafítico mejora en gran medida la densidad de corriente limitante para la reacción ORR en materiales carbonosos y grafénicos dopados con N ^[432,438]. Además, las especies de N-piridínico son responsables de coordinar los átomos de Fe para generar sitios activos FeN₄ que, junto con el efecto sinérgico de las especies de N-grafítico, contribuyen a mejorar la actividad electrocatalítica de la ORR ^[439–442].

Por otro lado, los cálculos DFT han confirmado que estas especies de N-grafítico creadas en grafeno dopado con N mostraron un

sobrepotencial bajo y se identificaron como los sitios activos óptimos para OER electrocatalítica ^[443], mientras que la reactividad de las especies coordinadas de FeN₄ en estructuras basadas en carbono contribuye positivamente reduciendo barreras potenciales y mejorando la actividad electrocatalítica OER ^[444].

En principio, los electrocatalizadores Fe-N/C de alto rendimiento deben diseñarse mediante la disposición adecuada de átomos de N y Fe para formar sitios óptimos FeN₄ dispersos uniformemente en la estructura gráfica ^[445,446]. Además, estudios computacionales han corroborado que la estructura de carbono local que rodea el sitio activo FeN₄ juega un papel clave en la determinación de las propiedades catalíticas finales, específicamente, ya que si el centro FeN₄ se encuentra ubicado en el borde de la lámina mostrara una actividad electrocatalítica superior al centro activo localizado en el plano ^[447,448].

La preparación de este tipo de material basado en carbono se basa principalmente en dos estrategias diferentes: el método de plantilla de sacrificio utilizando estructuras de tipo MOFs ^[449,450] o soportes de sílice ^[451,452], y la incorporación de sitios activos de FeN₄ en matrices de carbono como nanotubos de carbono, grafeno o carbón activado ^[447,453,454]. En general, todos estos estudios han informado que los materiales basados en carbón conteniendo átomos de N se pueden preparar mediante procesos de dopaje empleando amoníaco, aminas o compuestos orgánicos que contienen N. Frecuentemente, estas síntesis son llevadas a cabo mediante tratamiento térmico simultáneo de una sal de hierro, un precursor de nitrógeno y un soporte de carbono, estableciendo condiciones de alta temperatura. En consecuencia, las especies resultantes de N presentes en esos materiales son en su mayoría impredecibles y se caracterizan a posteriori utilizando diferentes técnicas.

Por este motivo, el horizonte en la ingeniería de materiales híbridos basados en grafeno se centra en la funcionalización de láminas de grafeno con determinadas moléculas nitrogenadas creando aductos superficiales específicamente localizados en los bordes para, posteriormente, coordinar átomos de Fe generando sitios activos FeN₄ altamente enriquecidos en los bordes de láminas de grafeno adyacentes, lo que se prevé una estrategia especialmente innovadora y prometedora para alcanzar rendimientos electrocatalíticos superiores en reacciones ORR y OER (**Figura 40**).

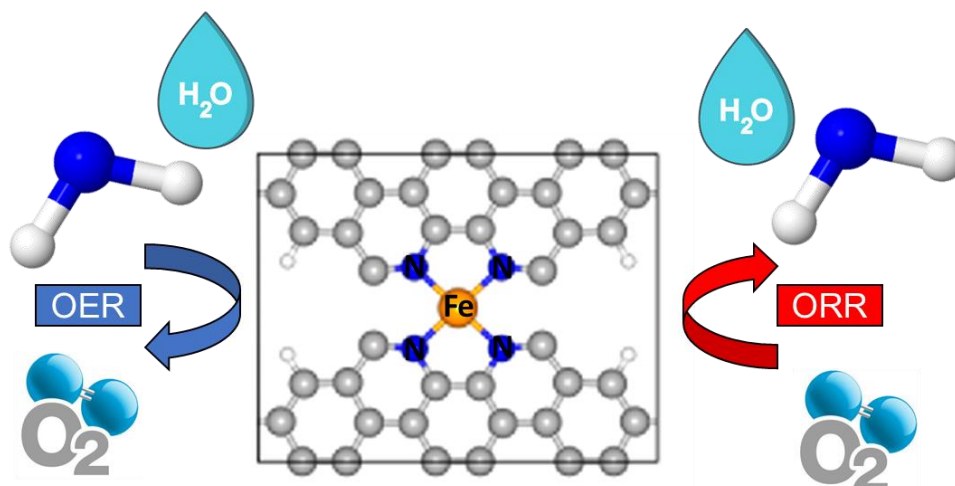


Figura 40. Representación de un composite híbrido basado en grafeno con sitios FeN₄ generados específicamente en los bordes de dos láminas de grafeno adyacentes y su aplicación en los procesos electrocatalíticos ORR y OER.

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Capítulo 3

Hipótesis y Objetivos

La presente Tesis Doctoral se ha realizado planteando una serie de objetivos y estrategias, en sintonía con las líneas de investigación llevadas a cabo por el Grupo de Investigación FQM-346 “*Catálisis Orgánica y Materiales Nanoestructurados*” de la Universidad de Córdoba en el desarrollo de los Proyectos y Ayudas de Investigación que tiene encomendados. Específicamente, el objetivo principal de esta Tesis se basa en *diseñar y caracterizar nuevos materiales híbridos orgánicos-inorgánicos con propiedades fisicoquímicas mejoradas y evaluarlos en aplicaciones de interés en el ámbito de la Química Fina y la Energía.*

A continuación, se describen los objetivos específicos establecidos, enmarcados en cada una de las secciones de resultados que constituyen esta Memoria, partiendo de determinadas hipótesis, que son consecuencia de una exhaustiva revisión del estado del arte sobre el tema en cuestión, para lograr la consecución de cada uno de ellos:

- **Sección 1: Polímeros de coordinación-Metal Organic Frameworks (MOFs)**

- ◆ **Antecedente 1**

Los polímeros de coordinación son materiales híbridos compuestos por ligandos orgánicos y nodos metálicos. Entre las diferentes moléculas orgánicas utilizadas para la preparación de polímeros de coordinación, los ácidos málico y tartárico son ligandos prometedores porque son productos naturales abundantes y en su estructura, además de dos grupos carboxilato, contienen grupos hidroxilo que pueden proporcionar múltiples modos de coordinación. Tanto estos ácidos como sus derivados son considerados

fuentes de estereocentros simples y económicas para trabajos en procesos quirales.

Los polímeros de coordinación de zirconio son particularmente atractivos porque generalmente exhiben una alta estabilidad debido a la fuerza significativa de los enlaces Zr-O. Por otro lado, tanto los sitios ácidos de Lewis como los de Brønsted presentes en este tipo de materiales pueden resultar muy atractivos para ser utilizados en aplicaciones catalíticas. La posibilidad de incorporar quiralidad en estos polímeros de coordinación a través de ligandos basados en malatos y tartratos es una estrategia particularmente interesante porque proporcionaría materiales capaces de actuar como catalizadores enantioselectivos. El centro ácido desencadenaría la reacción proporcionando la activación necesaria y el centro quiral cercano ejercería el control de la enantioselectividad.

La cianosililación de compuestos carbonílicos con trimetilsilanocarbonitrilo es una reacción orgánica interesante que da lugar a cianohidrinas quirales, las cuales son intermediarios útiles para la síntesis de una amplia variedad de compuestos, como α -hidroxiácidos, α -hidroxicetonas, β -hidroxiaminas, α -aminonitrilos y β -aminoalcoholes, entre otros. Se conocen un gran número de catalizadores diferentes activos para esta reacción, incluidos los ácidos de Lewis. Además, el carbono sp^2 del grupo carbonilo, tras la adición, se transforma en un estereocentro sp^3 , por lo que la síntesis de cianohidrinas quirales es un proceso extraordinariamente interesante por sí mismo, y por los productos quirales que pueden derivarse de ellas. Por ello, se ha investigado intensamente este aspecto, sobre todo, en el campo de la catálisis homogénea. La conversión y la enantioselectividad son muy sensibles a la naturaleza del sustrato, al catalizador y, en general, a las condiciones de reacción. Esto sucede tanto en la catálisis homogénea como heterogénea. La mayoría de los

catalizadores homogéneos se basan en los denominados “ligandos privilegiados” como bloques de construcción quirales, que generalmente contienen metales coordinados muy costosos económicamente. Aunque la mayoría de estos ligandos están disponibles comercialmente, su alto coste impide su uso generalizado en la industria. Por ello, la búsqueda de nuevos materiales preparados a coste reducido a partir de compuestos ampliamente disponibles que sean capaces de actuar como catalizadores heterogéneos activos y altamente enantioselectivos, continúa siendo un desafío para la comunidad científica.

❖ **Hipótesis 1**

De acuerdo con los antecedentes planteados, se considera que los polímeros de coordinación construidos a partir de ligandos orgánicos portadores de estereocentros podrían actuar como catalizadores heterogéneos quirales con óptima enantioselectividad.

♣ **Objetivo 1**

Para ello, el objetivo se basa en sintetizar polímeros de coordinación basados en zirconio que incluyan ligandos orgánicos quirales procedentes de productos naturales sencillos y derivados: ácido L-tartárico, ácido dibenzoil-L-tartárico y ácido L-málico. La influencia de la metodología de síntesis (reactor tipo batch o autoclave), la relación estequiométrica metal-ligando, el disolvente, la temperatura y la adición de un agente modulante para promover cristalinidad estructural serán los parámetros fundamentales de estudio en el proceso de síntesis.

Después de una caracterización exhaustiva mediante diferentes técnicas instrumentales, se aplicarán como catalizadores heterogéneos en la

reacción de cianosilación asimétrica de benzaldehído con cianuro de trimetilsililo, evaluando diferentes variables importantes que afectan a la actividad catalítica resultante como son la temperatura, el disolvente, la adición de promotor y el uso de otros sustratos, específicamente benzaldehídos *p*-sustituídos. Además, se evaluará la estereoquímica de las cianohidrinas quirales obtenidas del benzaldehído. Los resultados relacionados con este objetivo constituyen el argumento del artículo *“Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions”* que ha sido publicado en la revista *“Applied Catalysis A: General”*.

◆ Antecedente 2

Los llamados metal-organic frameworks (MOFs) o redes metal-orgánicas son una clase de polímeros de coordinación caracterizados por su porosidad y cristalinidad elevadas. Son, por tanto, materiales de gran interés por la gran cantidad de aplicaciones industriales en las que pueden tener un papel muy relevante, como el almacenamiento y separación de gases, procesos de adsorción global o selectiva, suministro y liberación controlada de fármacos, catálisis y energía, entre otras.

La experiencia obtenida previamente en el estudio de los polímeros de coordinación, y el enorme interés general que estos materiales han despertado en la comunidad científica, nos animó a incluir a los MOFs entre las investigaciones realizadas en esta Tesis y experimentar con ellos nuevos retos y aplicaciones originales.

Una de las rutas de síntesis más utilizadas para obtener partículas MOF implica el uso de condiciones solvotérmicas que, aunque exhiben buenos rendimientos hacia el producto obtenido, requiere períodos

relativamente largos de calentamiento y altas temperaturas. La metodología asistida por ultrasonidos se postula como una alternativa atractiva para disminuir los tiempos de síntesis y la energía térmica gastada en el proceso, aunque ha sido escasamente utilizada para la preparación de MOFs.

Los MOFs de hierro (III) han mostrado características muy interesantes debido a su carácter inocuo en la salud humana permitiendo su viabilidad para la administración de fármacos. Algunos MOFs basados en hierro de la serie Fe-MIL88 han sido sintetizados por ultrasonidos, pero se obtuvieron con una baja cristalinidad estructural y morfologías poco definidas. Entre estos materiales, el MIL-88A posee un marco flexible 3D basado en trímeros oxocéntricos de octaedros de hierro (III) conectados por dianiones de fumarato. Esta disposición proporciona una gran superficie específica y una alta porosidad, convirtiéndolos así en un candidato de interés para muchas aplicaciones, entre las que cabe destacar la adsorción de gases.

Concretamente, la adsorción de etileno se postula como una opción de enorme proyección en el sector de la industria agroalimentaria, puesto que la maduración de la fruta es un problema post-cosecha debido a la generación de etileno como resultado de su proceso metabólico endógeno. Por tanto, el exceso de etileno almacenado en el propio envase de las frutas produce cambios irreversibles que conducen a una rápida pérdida de calidad y deterioro del producto si no se consume en un corto período de tiempo. En consecuencia, la captura y eliminación de etileno durante el proceso de envasado son operaciones necesarias que tienen una gran demanda con el objetivo de ralentizar la maduración empleando materiales inocuos que no comprometan el valor nutricional de las frutas.

Por otro lado, la aplicación de materiales porosos basados en MOFs en procesos de conversión y almacenamiento de energía ha atraído una enorme atención de los investigadores, específicamente en la tecnología de baterías Litio-Azufre (Li-S). Estos materiales son considerados excelentes hospedadores de azufre y muestran gran capacidad de confinamiento de los polisulfuros generados en los procesos de carga/descarga, reduciendo así el indeseable efecto “shuttle” que provoca una pérdida irreversible de material activo. De esta forma, se considera una opción prometedora el uso de estos materiales en el componente catódico de celdas Li-S para mejorar su estabilidad en condiciones de reuso cíclico prolongado.

❖ **Hipótesis 2**

Considerando las relevantes características fisicoquímicas y texturales del MOF MIL-88A, esta hipótesis radica en que la selección y optimización de una metodología de síntesis basada en el uso de ultrasonidos podría reducir los tiempos de síntesis comúnmente requeridos en condiciones solvotermales preservando su elevada cristalinidad y área superficial. Entre el extenso abanico de aplicaciones que ofrecen los MOFs, se vaticina que, atendiendo a sus propiedades estructurales y la funcionalidad incorporada, las partículas de MIL-88A pueden ser excelentes candidatas para ser utilizadas en el campo de adsorción y energía.

♣ **Objetivo 2**

Fundamentado en la hipótesis anterior, este objetivo consiste en sintetizar partículas cristalinas del MOF MIL-88A empleando una metodología asistida por ultrasonidos a tiempos cortos de síntesis y

aplicarlas en procesos de adsorción de etileno y en sistemas de almacenamiento de energía basados en la tecnología de las baterías Li-S.

La experimentación realizada sobre la síntesis, la caracterización y las singularidades de los materiales obtenidos, así como sus aplicaciones, han constituido los argumentos de los siguientes artículos, que han sido publicados en dos revistas de alto impacto dentro de esta temática: *“Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents”*, publicado en la revista *“Ultrasonics Sonochemistry”*, y *“MIL-88A Metal-Organic Framework as a stable sulfur-host cathode for long-cycle Li-S batteries”* publicado en la revista *“Nanomaterials”* y llevado a cabo en colaboración con el Grupo de Investigación FQM-175 *“Química Inorgánica”* del Departamento de Química Inorgánica e Ingeniería Química de la Universidad de Córdoba.

- **Sección 2: Materiales híbridos orgánico-inorgánicos basados en sílice-Periodic Mesoporous Organosilicas (PMOs)**

- ◆ **Antecedente 3**

La actual crisis energética producida por el inminente agotamiento de las fuentes de energía no renovables ha llevado a la comunidad científica a realizar numerosas investigaciones con el objetivo de encontrar formas de energía alternativas inagotables y respetuosas con el medio ambiente. Una economía mundial basada en hidrógeno como portador energético podría garantizar una energía renovable ambientalmente sostenible, segura y rentable para el siglo XXI. La energía solar aplicada a la descomposición química de un sustrato abundante como es el agua está en constante auge

como estrategia clave para la obtención de hidrógeno. Las enzimas [FeFe]-hidrogenasa, presentes en bacterias anaerobias y algas verdes, son la clase más eficiente de catalizadores biológicos para la evolución de hidrógeno. Por tanto, la actividad de estas metaloenzimas hidrogenasas naturales ha sido una enorme fuente de inspiración para el diseño de sistemas catalíticos sintéticos que lleven a cabo el proceso de reducción de protones para producir moléculas de hidrógeno mediante fotosíntesis artificial.

Las reacciones bimoleculares en las que se produce transferencia de electrones entre catalizadores biomiméticos basados en [2Fe2S]-hidrogenasa y fotosensibilizadores adecuados en presencia de un donador de electrones, han sido investigados ampliamente. El uso de una matriz heterogénea para la inmovilización de complejos biomiméticos [2Fe2S] a través de su esfera de coordinación externa es un enfoque atractivo para aumentar la estabilidad estructural de todos los componentes de la reacción. Estos soportes pueden proporcionar poros o canales modulables bien ordenados, áreas superficiales muy elevadas, estructuras bien definidas, microambientes electrostáticos y cavidades hidrofóbicas. Los catalizadores [2Fe2S] insolubles en agua se pueden aislar en sitios especialmente diseñados que son accesibles a través de la matriz y capaces de operar de manera eficiente en medios completamente acuosos.

Los organosílices periódicas mesoporosas (PMO) son una clase de materiales híbridos orgánico-inorgánicos basados en sílice preparados mediante la combinación de un surfactante y un silsesquioxano como precursor de organosílice. Los PMO exhiben el ordenamiento estructural típico de las sílices mesoporosas y áreas superficiales elevadas. La gran variedad de procedimientos sintéticos reportados para la preparación de PMOs proporciona una extensa gama de funcionalidades pudiendo ser utilizados en una amplia diversidad de aplicaciones, como catálisis,

adsorción, cromatografía y biomedicina, entre otros. Por ello, este tipo de materiales proporcionan una matriz sólida suficientemente robusta y rígida como para estabilizar los complejos biomiméticos inmovilizados conteniendo el sitio activo [2Fe2S].

❖ **Hipótesis 3**

Justificada en los antecedentes previamente descritos, la hipótesis de esta sección reside en que la incorporación de análogos del centro activo de las enzimas [FeFe]-hidrogenasa en materiales de tipo PMO podría conducir a catalizadores heterogéneos biomiméticos con actividad en procesos de fotosíntesis artificial, particularmente la reacción de evolución de hidrógeno asistida por luz solar.

♣ **Objetivo 3**

Por tanto, este objetivo se centra en estudiar la reacción catalítica de producción de hidrógeno promovida por luz utilizando sistemas biomiméticos basados en el sitio activo [FeFe]-hidrogenasa. La estancia realizada durante 6 meses en el Grupo de Investigación “*Synthetic Molecular Chemistry*” del Departamento de Química de la Universidad de Uppsala (Suecia) bajo la supervisión del profesor Dr. Sascha Ott, y en colaboración con el Grupo de Investigación “*Molecular Devices for Artificial Photosynthesis*” del Departamento de Química Física de la Universidad de Uppsala (Suecia) liderado por el profesor Dr. Haining Tian, ha sido fundamental para completar este objetivo.

La investigación se abordará en dos etapas secuenciales, que consistirán en:

1) Realizar un trabajo de revisión bibliográfica exhaustivo sobre catalizadores inspirados en modelos biomiméticos de [FeFe]-hidrogenasa aplicados en la producción fotocatalítica de hidrógeno.

2) Llevar a cabo la síntesis de complejos imitadores del sitio activo de [FeFe]-hidrogenasa incorporados en soportes heterogéneos hidroxilados, específicamente organosílices periódicas mesoporosas (PMOs), y aplicarlos en procesos fotocatalíticos de generación de hidrógeno en fase heterogénea.

Este objetivo se ha plasmado en la publicación de dos artículos científicos: *“Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production”* publicado en la revista *“Coordination Chemistry Reviews”*, y *“Hydroxyl-decorated diiron complex as a [FeFe]-hydrogenase active site model complex: Light-driven photocatalytic activity and heterogenization on ethylene-bridged periodic mesoporous organosilica”* publicado en la revista *“Catalysts”*.

• **Sección 3: Materiales híbridos basados en grafeno**

◆ **Antecedente 4**

Los materiales basados en grafeno tendrán un impacto tecnológico destacado en el futuro por su disponibilidad y excelentes propiedades mecánicas, térmicas, eléctricas y electrónicas. Se han reportado muchos métodos para obtener grafeno, aunque para la obtención de nanoláminas de grafeno es habitual el empleo de la metodología de exfoliación en fase líquida partiendo de grafito comercial disperso en determinados disolventes orgánicos (N-metilpirrolidona, dimetilformamida, o-diclorobenceno o piridina, entre otros) mediante la aplicación de ultrasonidos. Este método de síntesis tiene diferentes ventajas con respecto a los métodos

convencionales de producción de grafeno: no se requieren agentes oxidantes fuertes, se reduce el tiempo de síntesis y se obtienen grafenos no funcionalizados y no oxidados en una única etapa.

Además de las técnicas de caracterización comúnmente utilizadas para estudiar las propiedades estructurales y morfológicas, el análisis del tamaño de partícula de las nanoláminas de grafeno se postula como un elemento clave, pues muchas características fisicoquímicas de los nanomateriales dependen del tamaño. Este parámetro es fundamental ya que la síntesis a nivel de laboratorio debe ser monitorizada para la posterior obtención de productos nanotecnológicos a gran escala. En los últimos años, tres técnicas han atraído enorme interés entre la comunidad científica para la caracterización de la distribución del tamaño de partícula de los nanomateriales: la dispersión dinámica de la luz (DLS), el análisis de seguimiento de nanopartículas (NTA) y el fraccionamiento en flujo mediante campo de flujo asimétrico (AF4). Por tanto, el conocimiento del tamaño de partícula mediante estas técnicas durante la síntesis de nanomateriales será crucial para ver sus posibilidades de aplicación en diversos sectores industriales, como la nanomedicina, la nanoalimentación, la nanoenergía o la nanocosmética.

❖ **Hipótesis 4**

Se considera que la caracterización de la distribución del tamaño de partícula de materiales basados en grafeno mediante diferentes técnicas, algunas de ellas novedosas, podría proporcionar a la comunidad científica información adicional valiosa sobre el comportamiento de las láminas de grafeno en suspensión acuosa, lo que resulta de esencial importancia en aplicaciones biológicas y biomédicas.

♣ **Objetivo 4**

Soportado en la hipótesis anterior, el presente objetivo consiste en sintetizar materiales de naturaleza grafénica, concretamente nanoláminas de grafeno (GNS), mediante exfoliación de grafito y caracterizarlos detalladamente, en particular mediante un estudio comparativo exhaustivo de su distribución de tamaño de partícula aplicando diferentes técnicas analíticas como DLS, NTA y AF4.

La consecución de este objetivo se ha reflejado en el artículo “*A comparative study of particle size distribution of graphene nanosheets synthesized by an ultrasound-assisted method*”, publicado en la revista “*Nanomaterials*” y desarrollado en colaboración con el Grupo de Investigación FQM-175 “*Química Inorgánica*” del Departamento de Química Inorgánica e Ingeniería Química de la Universidad de Córdoba y el Instituto Universitario de Nanoquímica (IUNAN) de la Universidad de Córdoba.

♦ **Antecedente 5**

Los materiales basados en grafeno son utilizados en una amplia variedad de ámbitos científicos e industriales, habiendo despertado un enorme interés entre la comunidad investigadora.

Específicamente, los nanomateriales emisores de luz tienen aplicaciones potenciales en muchas áreas, incluidas la detección, la bioimagen y la fotocatalisis, entre otras. Sin embargo, la posibilidad de brindar propiedades fotónicas al grafeno es actualmente un desafío que despierta gran interés, ya que es un semiconductor que tiene una banda prohibida cero y, por lo tanto, prácticamente no presenta luminiscencia. En la actualidad existen dos estrategias generales para producir materiales

luminiscentes con estructura grafénica: i) la existencia de sitios aislados sp^2 sin interacciones π , como ocurre en algunos óxidos de grafeno reducidos, y ii) la presencia de defectos, como ocurre en los denominados “carbon quantum dots” que exhiben emisiones concentradas en las regiones azul y verde. Las unidades de 3,6-di(2-piridil)piridazina han recibido gran atención como ligandos para la coordinación y la química supramolecular. Estos ligandos se pueden sintetizar mediante una reacción de Diels-Alder entre 3,6-di(2-piridil)-1,2,4,5-tetrazina (dieno) y alquinos o alquenos (dienófilos). Los materiales híbridos orgánico-inorgánicos también se han funcionalizado mediante reacciones hetero-Diels-Alder. Además, recientes estudios han informado que tanto el grafito como el grafeno pueden actuar como dienos y dienófilos en la reacción de Diels-Alder. Teniendo en cuenta que los derivados de dipiridilpiridazina son excelentes ligandos para la coordinación de diferentes metales con propiedades fotoluminiscentes, el diseño de materiales híbridos basados en grafeno que incorporen la reactividad anteriormente mencionada se postula como una estrategia potencialmente atractiva para la obtención de materiales emisores de luz en un determinado rango del espectro electromagnético.

Por otro lado, la creciente demanda de energías renovables, limpias y sostenibles para contrarrestar el agotamiento de los combustibles fósiles y reducir las emisiones de CO_2 , así como mitigar el calentamiento global, ha llevado a la comunidad científica a prestar gran atención al desarrollo de fuentes de energía y sistemas de almacenamiento energético alternativos eficientes. La abundancia de hidrógeno en el universo y su producción por electrólisis a partir de agua, lo convierten en un portador de energía ideal. Sin embargo, el uso de la electricidad procedente de fuentes de energía renovables (como la energía solar o eólica) para dividir el agua en hidrógeno y oxígeno y, posteriormente, emplear el hidrógeno producido en pilas de

combustible, requiere el desarrollo de electrocatalizadores sostenibles y preparados a bajo coste que muestren elevada actividad en los procesos electrocatalíticos involucrados en estas reacciones. En este sentido, los electrocatalizadores bifuncionales para la reacción de reducción de oxígeno (ORR) y la reacción de evolución de oxígeno (OER) son de creciente interés debido a su extensa aplicabilidad en una amplia variedad de tecnologías basadas en energías renovables, como baterías recargables de metal-aire, “*water splitting*” o celdas de combustible reversibles. Hasta la fecha, los catalizadores basados en Pt y Ru/Ir se consideran principalmente los catalizadores comerciales de referencia para las reacciones ORR y OER, respectivamente. Debido al elevado coste económico requerido para la producción de este tipo de catalizadores, la búsqueda de materiales carentes de metales nobles que muestren un rendimiento mejorado en las reacciones críticas involucradas en estos procesos electrocatalíticos es crucial para el rápido avance de la economía del hidrógeno. Los materiales híbridos basados en carbón son materiales prometedores para ser utilizados en los procesos electrocatalíticos mencionados anteriormente debido a su buena estabilidad, excelente conductividad eléctrica y flexibilidad para la introducción de dopantes. En consecuencia, un tema candente en electrocatálisis se centra en el dopaje adecuado de materiales a base de carbono con heteroátomos (p. ej., N, S, P) y metales de transición (p. ej., Fe o Co) para obtener estructuras electrónicas y geométricas óptimas.

❖ Hipótesis 5

Fundamentado en los antecedentes anteriormente expuestos, se asume la funcionalización de las láminas de grafeno con unidades de dipiridilpiridazina mediante reacciones de Diels-Alder, incorporándoles así

sitios de coordinación para diferentes metales, que resultarían en materiales híbridos basados en grafenos con nuevas propiedades y aplicaciones.

♣ **Objetivo 5**

Una vez adquirida experiencia en la síntesis y caracterización de grafeno (**Objetivo 4**), se propuso como nuevo objetivo preparar materiales híbridos basados en grafeno mediante la funcionalización de sus láminas con unidades orgánicas de dipiridilpiridazina a través de reacciones de cicloadición de tipo Diels-Alder, llevar a cabo la coordinación de diferentes metales y estudiar su aplicación como materiales luminiscentes y catalíticos.

Los resultados derivados de este objetivo han quedado recogidos en dos artículos científicos diferentes publicados en revistas científicas de alto impacto en la temática correspondiente: *“Luminescent graphene-based materials via europium complexation on dipyriddyridazine-functionalized graphene sheets”* publicado en la revista *“Chemistry-A European Journal”* en colaboración con el Grupo de Investigación del Dr. Pascal Van Der Voort, director del Centro de Materiales Ordenados, Organometálicos y Catálisis (COMOC, Center for Ordered Materials, Organometallics and Catalysis) de la Universidad de Gante (Bélgica), y *“Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN₄ sites for ORR and OER electrocatalysis”* publicado en la revista *“Sustainable Energy & Fuels”* en colaboración con los Grupos de Investigación FQM-175 *“Química Inorgánica”* del Departamento de Química Inorgánica e Ingeniería Química y FQM-204 del Departamento de Química Física de la Universidad de Córdoba, y el personal investigador del Instituto de Microscopía Electrónica y Materiales (IMEYMAT) de la Universidad de Cádiz.

Capítulo 4

*Técnicas instrumentales
para la caracterización de
materiales híbridos*

Los materiales híbridos orgánico-inorgánicos sintetizados en esta tesis han sido caracterizados mediante diferentes técnicas instrumentales para estudiar sus diferentes características y propiedades:

4.1. Caracterización estructural.

- 4.1.1. Difracción de Rayos X (XRD).*
- 4.1.2. Espectroscopía Raman.*
- 4.1.3. Espectroscopia Ultravioleta-Visible (UV-Vis).*
- 4.1.4. Espectroscopia infrarroja con dispositivo de reflectancia total atenuada (FTIR-ATR).*
- 4.1.5. Espectroscopía fotoelectrónica de Rayos X (XPS).*
- 4.1.6. Resonancia magnética nuclear (RMN).*

4.2. Caracterización textural.

- 4.2.1. Porosimetría de adsorción-desorción de nitrógeno.*

4.3. Caracterización morfológica.

- 4.3.1. Microscopía electrónica de barrido (SEM).*
- 4.3.2. Microscopía electrónica de transmisión (TEM).*

4.4. Análisis de la distribución de tamaño de partícula.

- 4.4.1. Dispersión dinámica de la luz (DLS).*
- 4.4.2. Análisis de seguimiento de nanopartículas (NTA).*
- 4.4.3. Fraccionamiento de flujo de campo de flujo asimétrico (AF4).*

4.5. Composición química.

- 4.5.1. Análisis elemental (EA).*
- 4.5.2. Análisis termogravimétrico (TGA).*
- 4.5.3. Espectrometría de masas con plasma de acoplamiento inductivo (ICP-MS).*

Estas técnicas de caracterización empleadas en la presente Tesis Doctorales serán descritas con detalle a continuación junto con las condiciones de operación usadas en cada una de ellas.

4.1. Caracterización estructural

4.1.1 Difracción de Rayos X (XRD)

Fundamento de la técnica

La difracción de rayos X (X-Ray Diffraction, XRD) se basa en la incidencia de un haz de rayos X con una determinada longitud de onda y ángulo sobre la superficie plana de un material cristalino. La interacción resultante produce una dispersión de parte de este haz en todas las direcciones a causa de los electrones asociados a los átomos que se encuentra en el trayecto, mientras que el resto del haz de rayos X puede dispersarse elásticamente en ciertas direcciones mediante interferencia constructiva, dando lugar al fenómeno físico de difracción de rayos X. La respuesta obtenida queda materializada en forma de espectros comúnmente conocidos como difractogramas, los cuáles proporcionan la información necesaria para estudiar la estructura de los materiales, ya que cada sólido cristalino tiene un patrón único (huella dactilar). En base a esto, esta técnica da información sobre la disposición ordenada de los átomos en la estructura cristalina siempre regida por las condiciones establecidas por la Ley de Bragg ^[1] que relaciona la longitud de onda de incidencia y la distancia interatómica con el ángulo de incidencia del haz difractado:

$$n\lambda = 2d_{hkl} \cdot \text{sen}\theta \quad [1]$$

Esta ecuación establece la relación entre el espaciado entre planos dentro de la red cristalina (d), la longitud de onda de los rayos X (λ) y el ángulo formado entre los rayos incidentes y los planos de dispersión del material (θ), siendo n un número entero que indica el orden de la reflexión producida.

Otro parámetro de gran interés que puede ser calculado a partir de un difractograma es el tamaño de cristalito, definido como el tamaño del dominio donde se difractan de manera coherente los rayos X. La ecuación de Scherrer ^[2] relaciona, mediante la constante K que depende de la forma de los cristales, la longitud de onda (λ) y el ángulo de difracción (θ) con la anchura a la mitad del pico (β) de la reflexión (hkl) para obtener el tamaño del cristalito (L):

$$L = \frac{K\lambda}{\beta \cos \theta} \quad [2]$$

Esta técnica ha sido de gran utilidad para evaluar el grado de cristalinidad de los polímeros de coordinación quirales basados en ácido málico y tartárico. Los materiales híbridos orgánico-inorgánicos de tipo MOF muestran picos característicos a diferentes ángulos de difracción que permiten la correcta identificación de las distintas fases cristalinas presentes en la red metal-orgánica sintetizada, en este caso la MIL-88A. La disposición regular de los poros en los materiales mesoestructurados produce reflexiones que se manifiestan como señales a bajos ángulos de difracción. Por ello, los materiales periódicos mesoporosos organosilícicos con mesoestructuras tipo SBA-15 de simetría $p6mm$ muestran unos difractogramas fácilmente identificables debido al ordenamiento bidimensional de sus canales, proporcionando únicamente reflexiones $hk0$. En la **Figura 1** se representa la estructura hexagonal de una SBA-15 y su difractograma de rayos X. El grado de ordenamiento estructural puede ser evaluado mediante la relación de intensidades de las señales de difracción d_{100} y d_{110} , siendo mayor la cristalinidad cuanto mayor sea la relación I_{110}/I_{100} .

La ley de Bragg anteriormente descrita permite la obtención de la distancia interplanar en la dirección cristalográfica (100) en estos materiales, calculándose a partir de ella el valor de la celda unidad a_0 por medio de la ecuación.

$$a_0 = \frac{2d_{100}}{\sqrt{3}} \quad [3]$$

Este valor representa la distancia entre los centros de dos poros contiguos en esa dirección que, combinándose con el diámetro de poro (d_p) obtenido por los análisis de las isothermas de adsorción-desorción de nitrógeno, permite determinar el grosor de pared (e) aplicando la ecuación [4].

$$e = a_0 - d_p \quad [4]$$

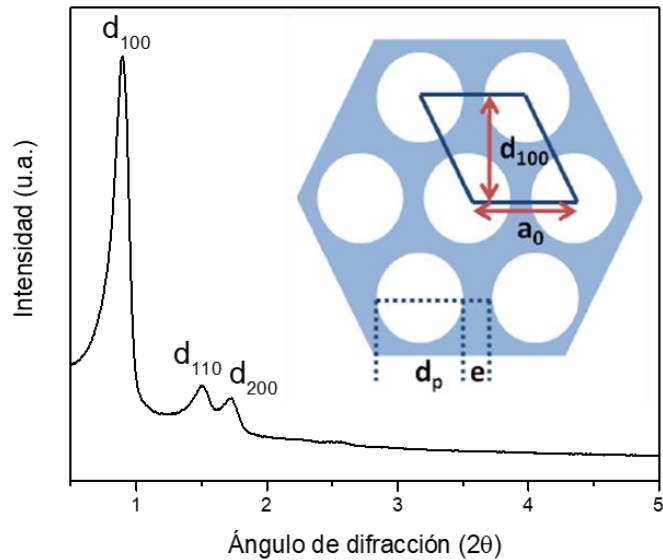


Figura 1. Difractograma de un material mesoporoso SBA-15 junto con su estructura de canales hexagonales.

Los materiales basados en grafeno suelen mostrar un pico de difracción ancho bien definido correspondiente al plano (002). La anchura a la mitad del pico (002), llamada también FWHM, es de gran interés para calcular el tamaño del cristalito en esta dirección cristalográfica, de tal manera que cuanto mayor sea esta anchura, más pequeño será el cristalito y menor el número de láminas apiladas en esta dirección.

La **Figura 2** muestra un esquema de la difracción de rayos X y el equipo instrumental utilizado:

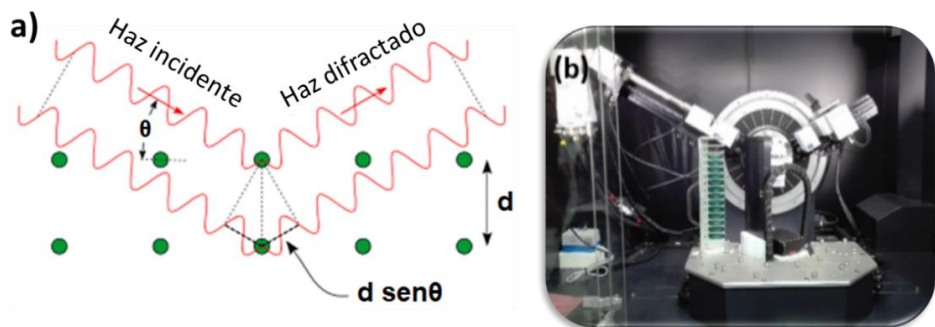


Figura 2. a) Esquema del proceso de difracción de rayos X y b) equipo experimental XRD empleado.

Metodología experimental

Los difractogramas de rayos X han sido obtenidos con un difractómetro Bruker D8 Discover A25 del Instituto Universitario de Nanoquímica (IUNAN) de la Universidad de Córdoba, equipado con un monocromador primario de Germanio y una radiación de $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$). Los difractogramas se registraron estableciendo diferentes condiciones en cuanto al intervalo de barrido de ángulo 2θ , tamaño y duración de paso, según el material híbrido orgánico-inorgánico caracterizado.

Los difractogramas fueron registrados con la ayuda del software DiffractPlus BASIC 4.0. Adicionalmente, se utilizó el programa EVA MFC Applications 4.0 para el análisis y el tratamiento de los difractogramas.

4.1.2 Espectroscopia Raman

Fundamento de la técnica

En 1928, el físico indio Chandrasekhara Venkata Raman descubrió el fenómeno de dispersión inelástica de la luz, conocido como el efecto Raman y, por este motivo, le fue otorgado el premio Nobel en Física en el año 1930. Dicho efecto explica el cambio en la longitud de onda de una pequeña fracción de la radiación dispersada por moléculas, que tiene una frecuencia diferente de la del haz incidente. Este cambio en la longitud de onda depende de la estructura química de las moléculas responsables de la dispersión ^[3].

La irradiación de una molécula con una luz monocromática siempre da como resultado dos tipos de dispersión de luz, elástica e inelástica. En la dispersión elástica, no ocurre ningún cambio en la frecuencia del fotón, esto es, sin ningún cambio en su longitud de onda y energía. Por el contrario, la dispersión inelástica es acompañada por un cambio en la frecuencia del fotón debido a la excitación o desactivación de las vibraciones moleculares en las que el fotón puede perder o ganar una cierta cantidad de energía ^[4].

En función de esto, pueden ocurrir tres tipos de fenómenos:

- i. En primer lugar, cuando la luz incide sobre una molécula, puede interactuar con la molécula, pero el intercambio neto de energía (E) es cero, por lo que la frecuencia de la luz dispersa es la misma que

la de la luz incidente ($E=E_0$). Este proceso se conoce como dispersión de Rayleigh.

- ii. En segundo lugar, la luz puede interactuar con la molécula y el intercambio neto de energía es la energía de una vibración molecular. Las moléculas en un estado vibracional excitado ($v=1$) pueden absorber un fotón de energía $h\nu_{ex}$ y a continuación volver a emitir un fotón de energía $h(\nu_{ex} + \nu_v)$. En este caso, la radiación difundida es de frecuencia más alta que la radiación de excitación, por lo que la frecuencia de la luz dispersada será mayor que la de la luz incidente ($E = E_0 + E_v$). Esto es conocido como dispersión Raman anti-Stokes.
- iii. En tercer lugar, una molécula en el nivel vibracional fundamental ($v = 0$) puede absorber un fotón de energía $h\nu_{ex}$ y volver a emitir un fotón de energía $h(\nu_{ex} - \nu_v)$. En este caso, la radiación difundida es de frecuencia más baja que la radiación de excitación ($E = E_0 - E_v$). Este proceso se conoce como dispersión Raman Stokes.

Con el propósito de comprender estos fenómenos se expone el siguiente esquema para observar las transiciones energéticas que se producen con cada uno de ellos (**Figura 3**).

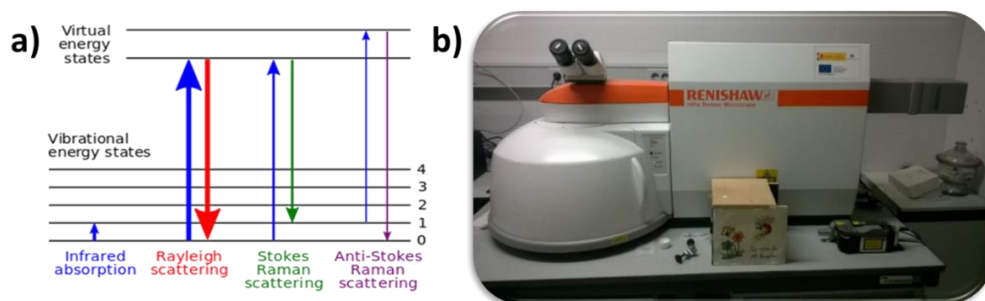


Figura 3. a) Mecanismo de las transiciones energéticas Rayleigh y Raman, y b) espectrómetro Raman utilizado para la medida de muestras.

Teniendo en cuenta el fundamento teórico de esta técnica, es posible tener conocimiento de las vibraciones moleculares que proporcionan información sobre la estructura y los grupos funcionales presentes en la molécula permitiendo el análisis cuantitativo y cualitativo de los compuestos híbridos orgánico-inorgánicos sintetizados.

Metodología experimental

Los espectros Raman de las muestras han sido registrados en un espectrómetro Raman Renishaw (InVia Raman Microscope) equipado con un microscopio Leica con varias lentes, monocromadores, filtros, un detector CCD y dos videocámaras. Los espectros fueron obtenidos por excitación con un láser de Nd:YAG (Neodimio:Granate de Aluminio Itrio) que emite a 532 nm y una rejilla de 1200 líneas mm^{-1} . Este equipo pertenece al Departamento de Química Orgánica de la Universidad de Córdoba, grupo FQM-346: Catálisis Orgánica y Materiales Nanoestructurados. La potencia del láser, tiempo de exposición y número total de acumuladas fueron parámetros ajustados según el material híbrido orgánico-inorgánico medido con el objetivo de aumentar la relación señal/ruido. Previamente al análisis, las muestras se han pulverizado hasta conseguir un tamaño de partícula suficientemente pequeño. Una pequeña porción de ese polvo de sólido es colocada sobre un portamuestras de vidrio y extendido hasta conseguir que la superficie expuesta fuera plana y uniforme. Los espectros fueron registrados en diferentes intervalos de número de onda según el compuesto analizado.

4.1.3 Espectroscopia Ultravioleta-Visible (UV-vis)

Fundamento de la técnica

La espectroscopía Ultravioleta-Visible (UV-Vis) es una técnica que proporciona información sobre la estructura electrónica y composición de la muestra analizada. Su fundamento se basa en la absorción de radiación electromagnética por parte de los grupos cromóforos a una determinada longitud de onda relacionándose proporcionalmente la cantidad de luz absorbida con la concentración total del compuesto estudiado: Ley de Lambert-Beer ($A = \varepsilon \cdot c \cdot l$, siendo A la absorbancia, ε el coeficiente de extinción molar, c la concentración y l la longitud de paso de la cubeta). Este proceso ocurre generalmente en dos etapas comenzando con la excitación electrónica de una determinada molécula, como consecuencia de la promoción de un electrón desde un estado basal a uno excitado, seguida de una relajación, liberando la energía absorbida mediante mecanismos de vibración o rotación hasta el estado fundamental. Cada molécula tiene una serie de estados excitados (o bandas) que la distingue del resto de moléculas,

por lo que la absorción a distintas longitudes de onda de una molécula (su espectro de absorción) constituye una señal de identidad de la misma. Las longitudes de onda utilizadas en esta espectroscopia de absorción se encuentran comprendidas en las regiones del ultravioleta (UV cercano, de 195-400 nm) y el visible (400-780 nm). Las bandas que aparecen en un espectro UV-Vis son anchas, ya que se superponen transiciones vibracionales y electrónicas. Generalmente, la excitación corresponde a los electrones de enlace, lo que las bandas de absorción pueden correlacionarse con los tipos de enlaces permitiendo la identificación de grupos funcionales presentes en la molécula. En la **Figura 4** se muestra el diagrama de niveles de energía general para una molécula y los espectrofotómetros utilizados para la caracterización de muestras líquidas y sólidas.



Figura 4. a) Diagrama de niveles de energía en una molécula que explican el fundamento de la espectroscopia UV-Vis, b) espectrofotómetro UV-Vis utilizado para la medida de muestras líquidas (ZUZI 4260/50) y c) espectrofotómetro UV-Vis utilizado para la medida de muestras sólidas (Perkin Elmer Lambda 650S).

Metodología experimental

De forma general, un espectrofotómetro UV-Vis consta de una fuente de energía radiante (lámpara de deuterio y tungsteno), un monocromador para seleccionar radiaciones de diferente longitud de onda, un compartimento de muestras, un detector de luz, un amplificador convertidor de las señales luminosas en señales eléctricas y un sistema de lectura de datos. Las muestras en fase líquida fueron medidas con un instrumento de doble haz UV/Vis modelo ZUZI 4260/50 en un rango de longitud de onda de 250-700 nm. En cambio, las muestras sólidas se analizaron con un espectrómetro UV-Vis de reflectancia difusa modelo Perkin Elmer Lambda 650S UV/Vis en un rango de longitud de onda de 250–700 nm. El tratamiento de los espectros UV-Vis obtenidos fue llevado a cabo empleando el software UV-Vis Analyst (Auxilab), suministrado por el fabricante del equipo.

4.1.4 Espectroscopia infrarroja con dispositivo de reflectancia total atenuada (FTIR-ATR)

Fundamento de la técnica

La espectroscopía infrarroja (IR) se basa en la absorción de luz en la región infrarroja del espectro electromagnético generando transiciones vibracionales moleculares características de los enlaces químicos presentes en la muestra analizada. Esta absorción se mide en función de la longitud de onda, generalmente, en el intervalo de 4000 a 600 cm^{-1} . El resultado es un espectro que sirve como una característica "huella digital molecular" utilizada comúnmente para identificar muestras orgánicas e inorgánicas y, en nuestro caso materiales híbridos orgánico-inorgánicos.

La espectroscopia infrarroja por transformada de Fourier (FT-IR) permite recoger los datos espectrales de todas las longitudes de onda en una sola medición. Como puede ser observado en el esquema de la **Figura 5a**, que representa la configuración de un espectrofotómetro FT-IR, una fuente continua genera luz IR en una amplia gama de longitudes de onda infrarrojas, pasa a través de un interferómetro y luego se dirige a la muestra obteniendo un interferograma, que necesita ser convertido en un espectro IR mediante la transformada de Fourier.

La espectroscopia infrarroja FTIR incorporando un dispositivo de reflectancia total atenuada (FTIR-ATR) ha superado a muchas otras técnicas de muestreo, ya que generalmente no es destructiva, muy fácil de preparar/aplicar las muestras y es muy adecuada para analizar sólidos y líquidos. Esta técnica se basa en que la luz infrarroja pasa a través de un cristal de un determinado material (diamante, ZnSe o germanio) e interactúa con la muestra, que se presiona con dicho cristal obteniendo un espectro que muestra todas las características específicas de la muestra, aunque la relación señal/ruido podría diferir de un espectro de transmisión tradicional debido a los efectos físicos. La **Figura 5b** muestra el equipo instrumental FTIR-ATR empleado para la medida de los diferentes complejos, precursores y materiales híbridos orgánicos-inorgánicos reportados en esta memoria.

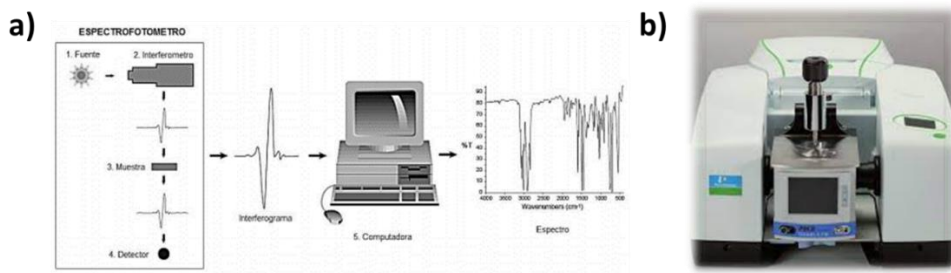


Figura 5. a) Configuración básica de un espectrofotómetro FTIR, y b) equipo FTIR-ATR utilizado.

Metodología experimental

Los espectros FTIR-ATR se registraron en un espectrofotómetro FTIR modelo PerkinElmer equipado con un accesorio de reflectancia total atenuada ATR modelo Pike GladiATR provisto de un cristal de diamante monolítico con un rango de número de onda entre 400-4000 cm^{-1} y una resolución de 10 cm^{-1} , estableciéndose un total de 20 acumuladas por medida. Las muestras líquidas analizadas correspondieron a complejos organometálicos y precursores organosilícicos disueltos en solventes orgánicos y, por tanto, fueron desechadas después de llevar a cabo la medición. Sin embargo, los materiales híbridos orgánico-inorgánicos fueron recuperados una vez obtenido el espectro FTIR-ATR correspondiente.

4.1.5 Espectroscopia fotoelectrónica de Rayos X (XPS)

Fundamento de la técnica

La técnica de espectroscopia fotoelectrónica de rayos X (X-Ray photoelectron spectroscopy, XPS), desarrollada por el físico sueco K. Siegbahn y su grupo de investigación a mediados de la década de los 60, se fundamenta en hacer incidir un haz de rayos X sobre la superficie de una muestra para llevar a cabo el estudio de la energía cinética y el número de electrones que escapan de la estructura de los átomos parcialmente ionizados en condiciones de alto vacío (efecto fotoelectrónico).

El registro de las energías cinéticas y el número de estos fotoelectrones que escapan de la parte superior del material analizado proporcionan información acerca de la distribución y población de los niveles de energía electrónicos, por lo que es posible la determinación de los elementos presentes en la muestra, sus estados químicos y en qué cantidades están presentes ^[5]. El proceso fotoelectrónico es extremadamente rápido (10^{-16} s), y su física básica se describe mediante la ecuación de Einstein:

$$E_B = h\nu - KE \quad [5]$$

donde E_B es la energía de enlace del electrón en el átomo, $h\nu$ es la energía de la fuente de rayos X, y KE es la energía cinética del electrón detectado que es medida por el espectrómetro de XPS ^[6].

Es una técnica de caracterización superficial que permite obtener información tanto cualitativa como cuantitativa sobre la composición química superficial de sólidos y sobre la estructura electrónica de todas las especies químicas en superficie, excepto H y He, con una capacidad de penetración de unos 10-12 nm (100-120 Å).

En XPS las fuentes de rayos X más comunes son la de Al $K\alpha$ (1486.6 eV) y la de Mg $K\alpha$ (1253.6 eV). Un espectro XPS representa en el eje horizontal la energía de enlace (eV) y en el eje vertical la intensidad o cuentas medidas, proporcionando así información sobre el entorno químico y estado de oxidación de los elementos analizados.

El entorno químico de los átomos afecta a la fortaleza con la que los electrones están enlazados. Los átomos asociados con diferentes entornos químicos producen señales con pequeñas diferencias en las energías de enlace, las cuales se deben al grado de fortaleza del enlace químico.

De manera simultánea (o independientemente) al registrar un espectro XPS también tendremos señales Auger que aportan información sobre la composición de las capas superficiales. Los distintos estados químicos con energías de enlace similares englobados en una curva pueden ser deconvolucionados usando programas informáticos de ajuste de picos para identificar y calcular el porcentaje de cada contribución.

En la **Figura 6** se muestra el diagrama del proceso de emisión fotoelectrónico y el equipo XPS empleado.

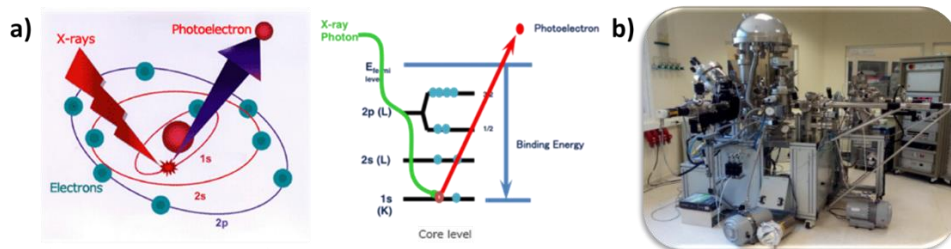


Figura 6. a) Diagrama del proceso fotoelectrónico y b) equipo XPS utilizado.

Metodología experimental

El equipo instrumental de espectroscopía de fotoelectrones de rayos X (XPS) empleado se encuentra disponible en el Servicio Central de Apoyo a la Investigación (SCAI) de la Universidad de Córdoba y consta de un espectrómetro SPECS mod. PHOIBOS 150 MCD, una fuente de rayos X con ánodos de Mg y Al, una fuente monocromática de Al y Ag y un detector multicanal. Adicionalmente, el sistema posee un cañón de iones Ar⁺ para poder realizar perfiles de profundidad. Las muestras fueron preparadas en forma de pastillas, sometiéndose a ultra-alto vacío previamente a la medida experimental. Los espectros obtenidos se analizaron con el software CasaXPS proporcionado por el SCAI. Los valores de energía de enlace se referenciaron a la señal del carbono adventicio C1s (284.8 eV). La energía de enlace fue determinada mediante el ajuste de las curvas de fondo de tipo Shirley y las curvas de Gauss-Lorentz.

4.1.6 Resonancia magnética nuclear (RMN)

Fundamento de la técnica

La espectroscopia de resonancia magnética nuclear (Nuclear Magnetic Resonance, NMR) es una técnica utilizada frecuentemente en Química Orgánica para la determinación y análisis cuantitativo de estructuras moleculares, así como en estudios cinéticos y termodinámicos. Se fundamenta en la interacción del momento magnético nuclear producido por un campo magnético externo con los núcleos magnéticos de las moléculas generando diferentes niveles energéticos ^[7]. Aquellos átomos que poseen un espín nuclear distinto a cero presentan diferentes estados energéticos bajo un campo magnético externo, de forma que irradiando a

una frecuencia adecuada se genera la resonancia entre dos estados, manifestada por una absorción dependiente del entorno de los núcleos atómicos. Los núcleos con espín nuclear igual a 1/2, carecen de un momento cuadrupolar eléctrico que produce un ensanchamiento de las señales de NMR y, por lo tanto, una baja definición espectral [8].

Un espectrómetro de RMN común posee un imán, con el que se obtiene un campo magnético muy preciso, un transmisor de radiofrecuencias (RF), que es sea capaz de emitir ondas de una frecuencia muy precisa, un detector que mide la energía absorbida por la muestra, y un registrador, que imprime los datos que surgen del detector. Los núcleos comúnmente analizados son: ^1H , ^{13}C , ^{15}N , ^{19}F y ^{31}P . Los más utilizados en química orgánica son el hidrógeno (^1H) y el carbono-13 (^{13}C), principales componentes de las moléculas orgánicas, aunque en el análisis de materiales también son empleados otros como el ^{27}Al , en el caso de estudiar aluminofosfatos, o ^{29}Si , en el caso de analizar materiales basados en sílice.

En la **Figura 7** se muestra un esquema con los diferentes componentes del sistema para llevar a cabo la obtención de datos mediante esta técnica y uno de los equipos RMN basado en el giro de ángulo mágico utilizados para medir principalmente muestras sólidas (RMN-MAS).

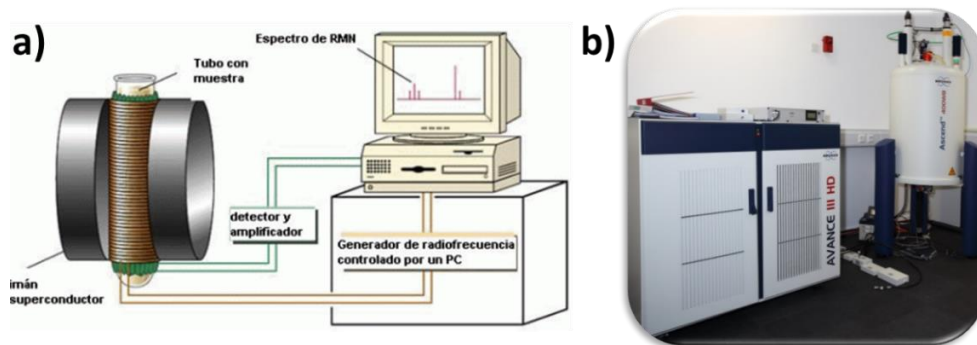


Figura 7. a) Esquema del sistema instrumental de resonancia magnética nuclear y b) equipo RMN-MAS empleado.

Metodología experimental

Los espectros NMR de muestras sólidas se han realizado a temperatura ambiente, con un espectrómetro multinuclear Bruker Avance III HD 400WB, con transformada de Fourier y campo magnético externo de 9.4 T. Con el fin de obtener una resolución espectral óptima fue empleada

la técnica “MAS” (Magic Angle Spinning) llevada a cabo con rotores de dióxido de circonio que son girados, alrededor del ángulo mágico con una frecuencia de 12 kHz. La cantidad de muestra colocada en el rotor es de unos 200 mg con un volumen aproximado de 0.35 cm³. Se han realizado ensayos en blanco con el rotor para comprobar su contribución a los espectros, que en todos los casos fue nula.

Los datos obtenidos ¹³C CP/MAS NMR, utilizando las técnicas de giro de ángulo mágico y polarización cruzada, fueron adquiridos a una frecuencia de 100.61 MHz a temperatura ambiente realizando un total de 1500 acumuladas. El pulso de excitación y el tiempo de relajación fueron de 3.6 μs y 2 s, respectivamente. El desplazamiento químico fue medido tomando como referencia un patrón de tetrametilsilano (TMS) a 0 ppm. Los espectros obtenidos fueron procesados mediante el software informático de la empresa Bruker denominado TopSpin elucidando de las estructuras de los diferentes compuestos sólidos híbridos orgánico-inorgánicos.

Las muestras líquidas fueron analizadas a temperatura ambiente empleando un equipo de RMN modelo Bruker Avance III 300 MHz NMR, estableciendo una frecuencia de 300 MHz y realizando 500 acumuladas. Previamente a la realización de las medidas, los complejos y precursores sintetizados fueron disueltos en cloroformo deuterado (CDCl₃). Se registraron espectros ¹H-NMR, ¹³C-NMR y ¹³C DEPT-NMR para lograr una caracterización molecular detallada de los compuestos. Los desplazamientos químicos obtenidos en cada espectro fueron estudiados tomando como referencia el patrón interno de tetrametilsilano (TMS) a 0 ppm. El software libre empleado para la identificación y cuantificación de las señales espectrales fue MestReNova (MNova, Mesterelab Research S. L.).

4.2. Caracterización textural

4.2.1 Isotermas de adsorción-desorción de nitrógeno

Fundamento de la técnica

La técnica de adsorción-desorción de nitrógeno es la más habitual en la determinación de áreas superficiales, distribución de tamaño y volumen de poro de materiales sólidos. La fisisorción de gases se produce cuando un

gas se pone en contacto con un sólido, previamente desgasificado a una determinada temperatura, originándose fuerzas de Van der Waals que pueden ser de tipo London o de tipo dipolo-dipolo, con energías que van de 1 a 5 kJ mol⁻¹. Por ello, los adsorbatos empleados son, principalmente, nitrógeno, argón, dióxido de carbono e incluso hidrocarburos como etileno. La caracterización de la estructura porosa de los sólidos mediante esta técnica se lleva a cabo mediante la medida de los siguientes parámetros: superficie específica (S , m² g⁻¹), volumen acumulado de poro (V_p , cm³ g⁻¹), diámetro medio de poro (d_p , Å) y distribución de tamaño de poro ($d V_p/d d_p = f[d_p]$).

Esta técnica se basa en que las fuerzas de cohesión de los átomos del interior de un sólido se encuentran compensadas; sin embargo, en la superficie existe una resultante de las fuerzas no nula y dirigida hacia el interior que se denomina fuerza de cohesión superficial que es la responsable de la fisisorción en los sólidos. La interacción del gas con la superficie de un sólido produce un equilibrio entre las moléculas adsorbidas y las moléculas en fase gaseosa, que depende de la presión del gas y de la temperatura. La relación entre las moléculas de gas adsorbidas (moles por gramo de adsorbente) y la presión relativa P/P_0 en el intervalo $0 < P/P_0 < 1$ (donde, P = presión de vapor de equilibrio del adsorbato, P_0 = presión de vapor del adsorbato líquido puro), a temperatura constante, se representa en una isoterma de adsorción ^[9].

Las curvas de adsorción-desorción de nitrógeno reflejan un proceso de adsorción y un proceso de desorción proporcionando en conjunto la característica forma de isoterma. Cuando el camino de desorción no coincide con el de adsorción se produce un ciclo de histéresis debido a una interacción del adsorbato dentro de los poros del material en un determinado rango de presión relativa.

Según la forma de las isotermas obtenidas, la IUPAC reconoce seis tipos de sólidos diferentes (**Figura 8**) ^[10]. Esta clasificación se basa en las diferentes interacciones que puede tener el sólido con el adsorbato y, por tanto, está relacionada con la porosidad del adsorbente.

A continuación, se expone la descripción fundamental de cada tipo de isoterma ^[11]:

- **Tipo I:** Se caracteriza por la adsorción en monocapa y se refiere, generalmente, a procesos de quimisorción. La adsorción muestra un aumento rápido a presiones relativas bajas y finalmente alcanza una

meseta a elevados valores de presión. Esta isoterma reversible es característica de sólidos microporosos que tienen superficies externas relativamente pequeñas y se ajusta al modelo matemático descrito por Langmuir.

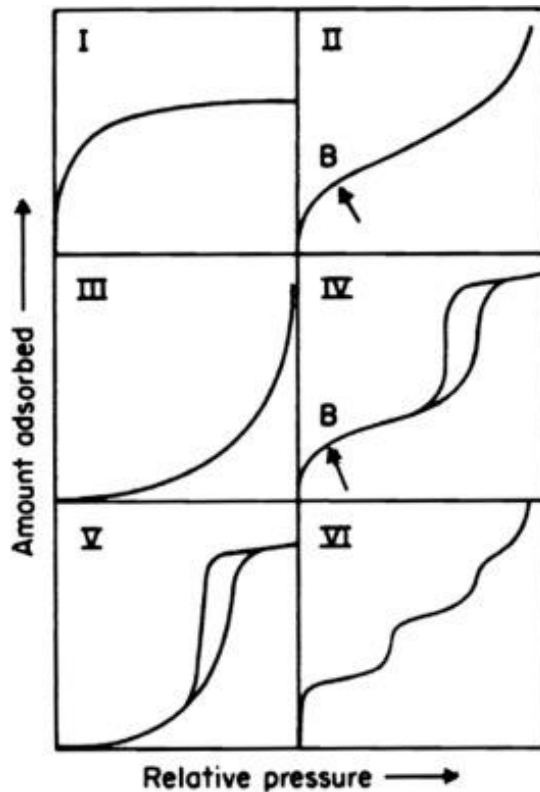


Figura 8. Clasificación de isothermas de adsorción según la IUPAC.

- **Tipo II:** Esta isoterma exhibe adsorción multicapa y, por lo tanto, no existe la meseta de absorción observada en la isoterma tipo I. La adsorción continúa aumentando incluso cuando la presión relativa está cerca de la unidad. El punto de inflexión corresponde con el recubrimiento total de la monocapa y el comienzo de la adsorción en multicapas. Se trata de un perfil frecuente de procesos de adsorción física en el que debe predominar la afinidad del adsorbato por el adsorbente. Esta isoterma también es reversible y, por lo general, los sólidos macroporosos o no porosos muestran ese tipo de comportamiento.

- **Tipo III:** Es otro tipo de isoterma reversible y la curva de adsorción es convexa en todo el rango de presión relativa. Estas isothermas son obtenidas para sólidos macroporosos o no porosos en las que las interacciones adsorbato-adsorbente son relativamente débiles. Así, el adsorbato tiene una afinidad similar por el adsorbente y por sí mismo, produciendo un recubrimiento desigual de monocapas y multicapas.
- **Tipo IV:** Caracterizada por la presencia de una histéresis que se atribuye al llenado/vaciado de los mesoporos por condensación capilar. La rama inferior de la histéresis representa la medición por adición progresiva de gas al adsorbente y la rama superior representa la medición por extracción progresiva. Esta isoterma puede considerarse como una combinación de isothermas de adsorción de tipo I y tipo II. La adsorción aumenta bastante con la presión dentro de la región de baja presión y luego se somete a adsorción monocapa-multicapa. La condensación en el mesoporo domina cuando la presión se acerca a la presión de saturación.
- **Tipo V:** Esta isoterma en forma de S muestra también un ciclo de histéresis. Esta curva isotérmica se diferencia por la baja adsorción inicial, atribuida a la adsorción sobre la superficie no polar o débilmente polar de los poros seguida de un aumento brusco de la adsorción a mayores valores de presiones relativas donde tiene lugar la condensación capilar en los poros.
- **Tipo VI:** Similar al tipo II, el tipo VI exhibe adsorción multicapa en una superficie no porosa uniforme, pero en este tipo la adsorción ocurre en etapas. La altura del escalón representa la capacidad de monocapa para cada capa adsorbida, y casi permanece constante para dos o tres capas adsorbidas. La nitidez de los pasos depende del sistema, la energía de adsorción y la temperatura.

Los sólidos mesoporosos presentan un comportamiento singular en la fisorción de gases debido a sus estructuras interconectadas de poros de diferentes formas y tamaños. De esta forma, las isothermas de este tipo de materiales presentan diferentes ciclos de histéresis que han sido clasificados por la IUPAC como se describe a continuación (**Figura 9**)^[12]:

- **Histéresis HI:** Este tipo de histéresis a menudo se asocia con materiales porosos que consisten en canales de poro cilíndricos bien

definidos o aglomerados de esferas uniformes mostrando las ramas de adsorción-desorción paralelas y casi verticales.

- **Histéresis H2:** Tiene forma triangular y se atribuye a materiales que a menudo están desordenados donde la distribución del tamaño y la forma de los poros no está bien definida presentando una rama de desorción completamente vertical. Tal comportamiento se achaca a los efectos de conectividad porosa, los cuales se consideran el resultado de la presencia de poros con bocas estrechas (“ink-bottle pores”).
- **Histéresis H3:** Los materiales que dan lugar a la histéresis H3 tienen partículas en forma de platos (“platelike”). La isoterma con histéresis de este tipo no muestran ninguna adsorción limitante a P/P_0 alta, lo cual se atribuye a materiales con agregados no rígidos de partículas en forma de placa.
- **Histéresis H4:** Este tipo se caracteriza por mostrar las ramas de adsorción-desorción paralelas y casi horizontales, asociándose a poros estrechos en forma de hendidura o rendija y a la presencia de microporosidad.

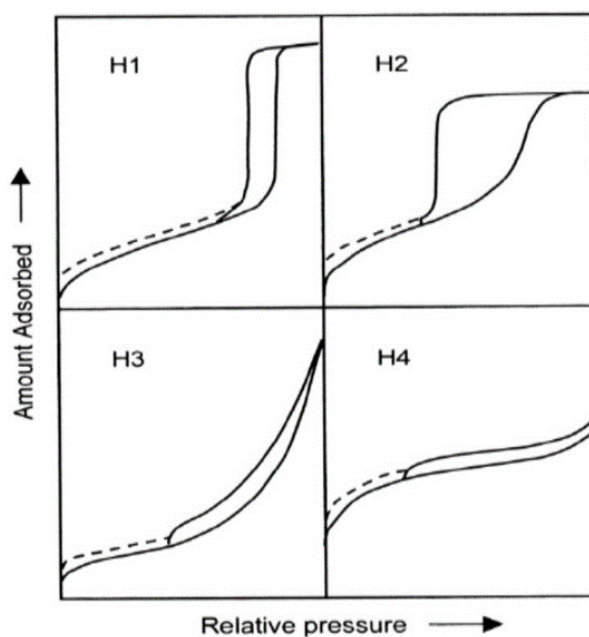


Figura 9. Clasificación establecida por la IUPAC de los tipos de histéresis.

Numerosos métodos de cálculo han sido desarrollados para determinar los parámetros texturales de materiales sólidos mediante esta técnica como la superficie específica, el volumen y diámetro de poro.

Entre ellos, el método BET es frecuentemente utilizado para la obtención de la superficie específica, el método BJH para el volumen y distribución de tamaño de poros y los métodos DFT y t-plot para el análisis de sólidos microporosos.

- **El método BET (Brunauer, Emmet y Teller; 1939)** está basado en la consideración de las fuerzas de atracción de Van der Waals como únicas responsables del proceso de adsorción, de forma que, conocida la cantidad de gas adsorbido necesario para formar una monocapa y el área que ocupa una de estas moléculas adsorbidas, es posible estimar el área del sólido ^[13].
- Esta teoría considera que: No existen sitios preferenciales de adsorción (es decir, todos los sitios tienen la misma energía superficial) y no existen interacciones laterales entre moléculas adsorbidas. Para calcular la cantidad de gas adsorbido necesario para la formación de una monocapa, se utiliza la siguiente ecuación:

$$\frac{P}{n(P_0 - P)} = \frac{1}{n_a C} + \frac{C - 1}{n_a C} x \frac{P}{P_0} \quad [6]$$

donde C es una constante que está relacionada con el calor de adsorción de la primera monocapa. De la representación de P/n(P₀-P) frente a la presión relativa obtenemos 1/Cn_a como ordenada en el origen y (C-1)/Cn_a como pendiente. A partir de estos valores podemos calcular C y n_a.

- **El método BJH (Barrer, Joyner y Halenda)** es el más utilizado para el cálculo de volumen y distribución de mesoporos (2-50 nm). Dicho método se desarrolla basándose en la ecuación de Kelvin ^[14] suponiendo que los poros son cilíndricos y que la cantidad de adsorbato en equilibrio con la fase vapor se produce mediante adsorción física en las paredes y condensación capilar (en los mesoporos a presiones relativas superiores a 0.4).
- **El método de la teoría del funcional de la densidad (DFT)** es empleado para el cálculo del volumen y distribución de tamaños de microporo. El modelo teórico puede ser utilizado desde los ultramicroporos hasta los macroporos, siendo la limitación inferior

el tamaño de la molécula que actúa como adsorbato, y la limitación superior viene dada por la dificultad que presenta el llevar a cabo las medidas cerca del nivel de saturación. Este método ha adquirido una relevancia importante en los últimos años, sobre todo en el análisis de materiales microporosos, como carbones, zeolitas o redes metal-orgánicas ^[15].

- **El método t-plot (B. C. Lippens y J. H. de Boer, 1965)** se fundamenta en que el espesor medio (t) de la capa de adsorción puede ser calculado a partir del volumen de adsorbato (V_a) que se adsorbe sobre una superficie sólida (S):

$$t = V_a/S \quad [7]$$

Representando t en función de la presión relativa para sólidos no porosos se obtiene una curva común indicando que el espesor de la capa es independiente del sólido, y depende principalmente de la presión relativa y del ordenamiento geométrico de las moléculas en la capa. Esta es la base del método t-plot ^[16] ampliamente utilizado en el cálculo de la superficie externa y microporosidad de materiales. En sólidos macroporosos, el volumen adsorbido por unidad de superficie (t) frente a la presión sigue una curva independiente del sólido. Por lo tanto, representando el volumen adsorbido, V_a , en un material con meso y/o macroporos frente a t , se obtiene una línea recta que pasa por el origen. La pendiente m es directamente proporcional al área superficial S . Si existe microporosidad, la adsorción en la superficie disminuye y, por tanto, decrece la pendiente de la curva- t . Cuando los microporos están completamente llenos, aparece una línea recta con la pendiente correspondiente a la superficie externa. Si el sólido contiene mesoporos, se observa una desviación de la linealidad hacia arriba debido a la condensación capilar.

En la **Figura 10** se muestra un esquema del proceso de fisisorción sobre la superficie de un sólido y el equipo de porosimetría de adsorción-desorción de nitrógeno empleado.

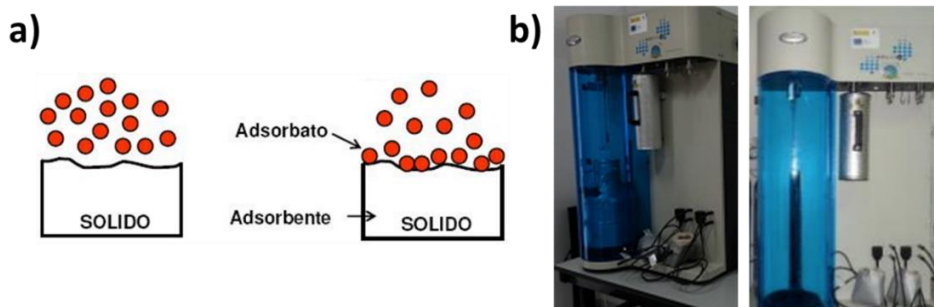


Figura 10. a) Esquema del proceso de fisisorción de un adsorbato sobre un sólido y b) equipo de porosimetría utilizado.

Metodología experimental

Las isothermas de adsorción-desorción de nitrógeno se han determinado a la temperatura de ebullición del nitrógeno líquido (77 K, -196 °C) utilizando el sistema instrumental automático modelo Autosorb-iQ-2 MP/XR (Quantachrome Instruments Autosorb iQ/ASiQwin), perteneciente al Instituto Universitario de Nanoquímica (IUNAN) de la Universidad de Córdoba.

Es un analizador multi-estación que incorpora dos estaciones para la medida del área superficial, el volumen de poro y, la distribución de tamaño de poros, incluyendo ultramicroporos. Actualmente, incluye los accesorios necesarios para realizar ensayos de adsorción con nitrógeno y etileno, así como vapores de distinta naturaleza. En ambos casos, previamente a las medidas, todas las muestras se desgasificaron a 0.1 Pa y una temperatura dependiente del material analizado. Las isothermas de adsorción obtenidas muestran la cantidad de N₂ adsorbido en función de la presión relativa (P/P₀).

El cálculo del área superficial realizado por el equipo se hizo utilizando el método BET. Para la distribución del tamaño de poro, se han empleado los métodos DFT en el caso de los sólidos microporosos y el método BJH para los sólidos mesoporosos. El método t-plot ha sido utilizado para el cálculo del volumen de micro y mesoporos de los sólidos empleados. Adicionalmente, el sistema de adsorción de etileno ha sido utilizado para evaluar la capacidad de adsorción de diferentes redes metal-orgánicas empleando una corriente de C₂H₄ a 0 °C.

4.3. Caracterización morfológica

4.3.1 Microscopía Electrónica de Barrido (SEM)

Fundamento de la técnica

La microscopía electrónica de barrido (SEM) se fundamenta en el bombardeo de un haz focalizado de electrones sobre una muestra situada en una columna de alto vacío. Cuando el haz primario de electrones entra en contacto con la superficie de la muestra, una parte de ellos es reflejada de la superficie, pero el resto penetra algunas capas atómicas, siguiendo una trayectoria muy diferente de una recta, antes de volver a emerger a la superficie. Modulando la acción de estos electrones es posible obtener la imagen deseada de las partículas que conforman el material. Las señales producidas por la interacción entre los átomos y el haz electrónico son captadas por diferentes tipos de detectores, convertidas en señales electrónicas y amplificadas proporcionando información de gran importancia para la caracterización de muestras ^[17]. Las emisiones generadas pueden ser: electrones secundarios (SE), que proporcionan imágenes topográficas superficiales, electrones retrodispersados (BSE), que proporcionan imágenes en escala de grises, permitiendo la diferenciación de diversos elementos constituyentes de la muestra según sus números atómicos y rayos X dispersados (EDS), que permiten un análisis cualitativo y semicuantitativo de los elementos presentes en las muestras. Es una técnica con un excelente poder de resolución (3,5 nm y 300.000x) que, unido a la gran profundidad de campo y al efecto de sombreado, proporciona una herramienta de un alto potencial a la hora de realizar análisis tridimensionales de estructuras. De esta forma, es posible llevar a cabo una caracterización detallada de la morfología de materiales y la topología de sus superficies permitiendo obtener información sobre el tamaño y forma de partículas. La **Figura 11** muestra un esquema del microscopio electrónico de barrido y sus componentes principales, así como el equipo utilizado.

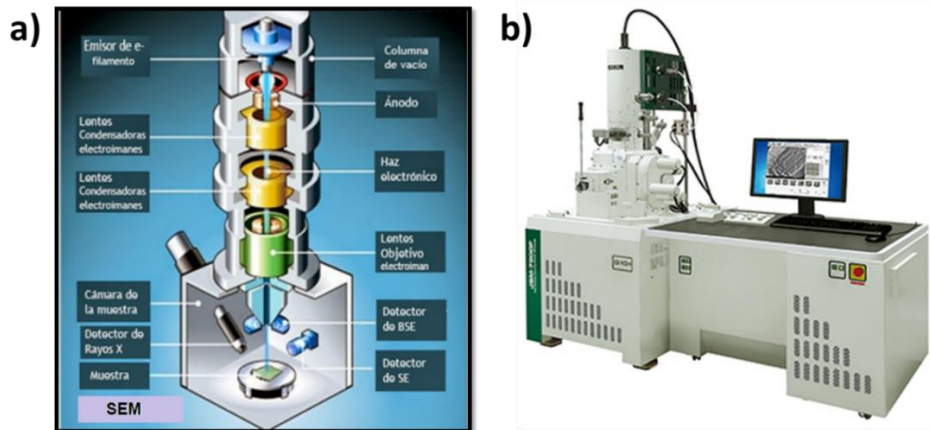


Figura 11. a) Esquema de los componentes de un microscopio electrónico de barrido y b) equipo SEM JEOL JSM 7800F empleado.

Metodología experimental

Las muestras, en forma de polvo sólido, fueron colocadas en un portamuestras de cobre, las cuáles fueron depositadas sobre un adhesivo conductor (carbón u oro) de doble cara e introducida en el equipo aplicando vacío para evitar interferencias entre los electrones generados y la humedad o el aire. El equipo instrumental de microscopía electrónica de barrido utilizado fue un modelo JEOL JSM 7800F perteneciente a los Servicios Centrales de Apoyo a la Investigación (SCAI) de la Universidad de Córdoba.

4.3.2. Microscopía Electrónica de Transmisión (TEM)

Fundamento de la técnica

La microscopía electrónica de transmisión es una técnica basada en la irradiación de una muestra delgada con un haz de electrones de densidad de corriente uniforme, cuya energía está dentro del rango de 80 a 200 keV. Cuando los electrones colisionan con la muestra, en función de su grosor y del tipo de átomos que la forman, parte de ellos son dispersados selectivamente, otra parte de ellos son transmitidos y otra parte da lugar a interacciones que producen distintos fenómenos como emisión de luz, electrones secundarios y Auger, rayos X, etc. Todos ellos son conducidos y

modulados por lentes para formar una imagen final sobre una CCD (Charge-Coupled Device) que puede tener miles de aumentos con una definición inalcanzable para cualquier otro instrumento. La información que se obtiene es una imagen con distintas intensidades de gris que se corresponden al grado de dispersión de los electrones incidentes. Las imágenes obtenidas son habitualmente empleadas para obtener información sobre la naturaleza de la muestra (morfología, composición, estructura cristalina, estructura electrónica, etc.)^[18].

En esta técnica, se emplea la transmisión/dispersión de los electrones para generar imágenes, la difracción de los electrones para obtener información acerca de la estructura cristalina y la emisión de rayos-X para conocer la composición elemental de la muestra (análisis EDX, Energy-dispersive X-ray spectroscopy). Para que se pueda producir la transmisión de los electrones a través de la muestra es necesario que ésta sea preparada en una capa delgada, es decir, transparente a los electrones, normalmente de un grosor inferior a 100 nm, ya que cuanto menor sea el espesor de la muestra, mejor calidad de imágenes será posible obtener.

En el ámbito práctico, es una técnica muy potente en la caracterización de materiales basados en grafeno, ya que permite observar monoláminas o multiláminas dependiendo del nivel de exfoliación llevado a cabo partiendo de un grafito comercial, así como sus tamaños e imperfecciones. Además, es una técnica de gran utilidad en la caracterización morfológica de materiales híbridos orgánico-inorgánicos. La **Figura 12** muestra un esquema de los componentes principales de un microscopio electrónico de transmisión y el equipo instrumental empleado.

Metodología experimental

Para la preparación de la muestra se utiliza 2-propanol como dispersante y se mantiene 2-3 minutos sometido a ultrasonidos para evitar que las partículas se aglomeren. Después, se depositan unas gotas de la dispersión sobre una rejilla de cobre con recubrimiento de carbón dejándose secar una noche a temperatura ambiente. El equipo instrumental utilizado es un modelo JEOL JEM 1400 de alta resolución (Akishima, Tokyo, Japan), de los Servicios Centrales de Apoyo a la Investigación (SCAI) de la Universidad de Córdoba, operando a un voltaje de aceleración de 120 kV.

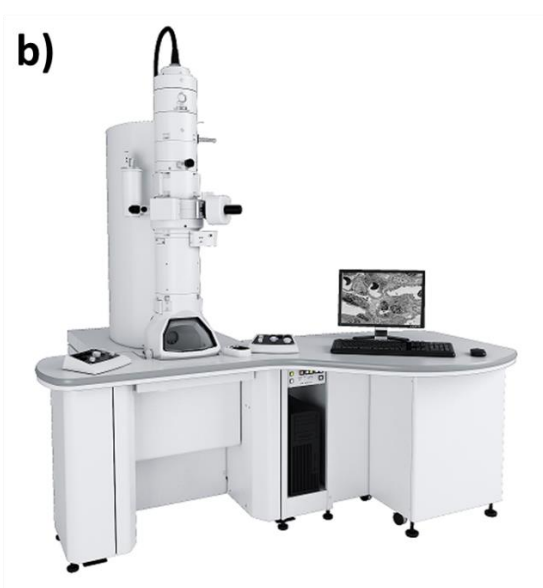
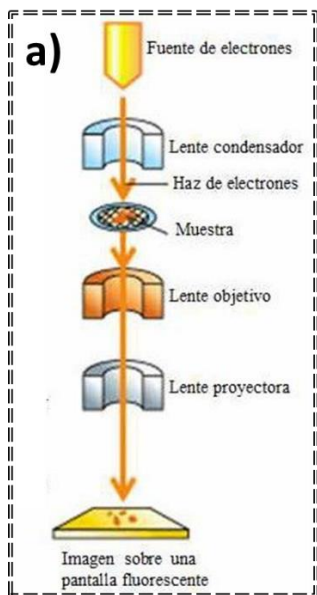


Figura 12. (a) Esquema de un microscopio electrónico de transmisión (TEM) y (b) equipo TEM utilizado.

4.4. Análisis de la distribución de tamaño de partícula

Las técnicas de análisis de la distribución de tamaño de partícula han sido empleadas para llevar a cabo el estudio de los materiales basados en grafenos obtenidos en uno de los trabajos de investigación reportados en esta Tesis Doctoral. A continuación, se va a proceder a la descripción de los fundamentos básicos y características principales de cada una de ellas.

4.4.1. Dispersión dinámica de la luz (DLS)

Fundamento de la técnica

La dispersión dinámica de la luz (Dynamic Light Scattering, DLS) es una técnica no invasiva aplicada fundamentalmente para la medición in situ de la distribución de tamaños de partículas dispersas en un líquido, generalmente, en la región submicrométrica. El movimiento Browniano de las partículas o moléculas en suspensión hace que la luz láser se disperse con diferentes intensidades. Del análisis de estas fluctuaciones de intensidad, relacionadas directamente con los coeficientes de difusión

rotacional y traslacional, se obtiene la velocidad del movimiento browniano y, por lo tanto, el tamaño de partícula utilizando la ecuación de Stokes-Einstein (ecuación [8]), obteniendo el parámetro comúnmente conocido como diámetro hidrodinámico (D_h) [19].

$$D_h = \frac{K_B T}{3\pi\eta_0 D_t} \quad [8]$$

Esta tecnología ofrece un análisis de tamaño de partícula rápido (1-2 minutos) en el ambiente nativo del material, presenta una configuración sencilla y automatizada, permite la medición de tamaños de partículas inferiores a 1 nm y con pesos moleculares < 1000 Da, se requieren volúmenes bajos (< 2 μ L) y es una técnica no destructiva.

La **Figura 13** muestra un esquema del proceso de dispersión dinámica de la luz y el equipo instrumental utilizado.

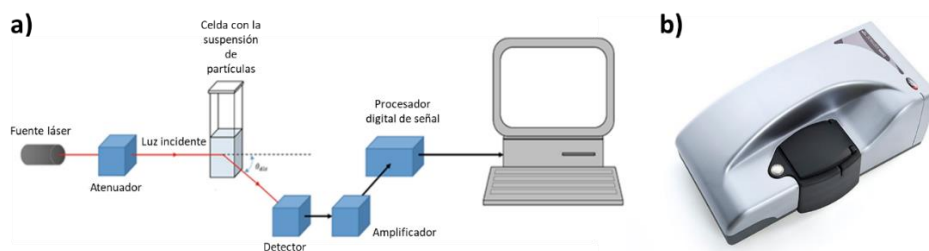


Figura 13. (a) Esquema de la técnica instrumental de dispersión dinámica de la luz [20] y (b) equipo DLS utilizado.

Metodología experimental

Los tamaños de partícula de los materiales basados en grafeno se midieron en un equipo Zetasizer ZSP (Malvern Instrument Ltd., Worcestershire, Reino Unido) a 25 °C basado en velocimetría láser Doppler y dispersión dinámica de luz (DLS).

La preparación de muestra fue llevada a cabo mediante la homogeneización de una suspensión del material a medir usando una sonda de ultrasonidos durante 5 minutos. El análisis se realizó por triplicado para calcular parámetros estadísticos como la media muestral y desviación estándar.

4.4.2. Análisis de seguimiento de nanopartículas (NTA)

Fundamento de la técnica

El análisis de seguimiento de nanopartículas (Nanoparticle Tracking Analysis, NTA) es una técnica analítica relativamente novedosa empleada para la caracterización de la distribución de tamaños de partícula de una muestra en suspensión líquida. Al igual que DLS, utiliza las propiedades tanto de dispersión de luz como de movimiento browniano para obtener el diámetro hidrodinámico mediante la ecuación de Stokes-Einstein (ecuación [8]).

La característica más importante de esta técnica que la diferencia del resto destinadas al mismo fin es que permite la visualización y grabación en tiempo real de nanopartículas individuales durante la medición, combinando un dispositivo de carga acoplada con un microscopio de dispersión de luz láser. Adicionalmente, proporciona información relevante relativa a la concentración de partículas en suspensión, grado de agregación y seguimiento de partículas marcadas con moléculas fluorescentes.

En base a lo anteriormente expuesto, esta técnica permite la medición simultánea de múltiples características que ahorran tiempo y volúmenes de muestras requiriendo una sencilla preparación de muestra, lo que la hace de especial interés en el campo de biomedicina y nanotoxicología.

La **Figura 14** muestra un esquema del análisis de seguimiento de nanopartículas y el equipo instrumental empleado.

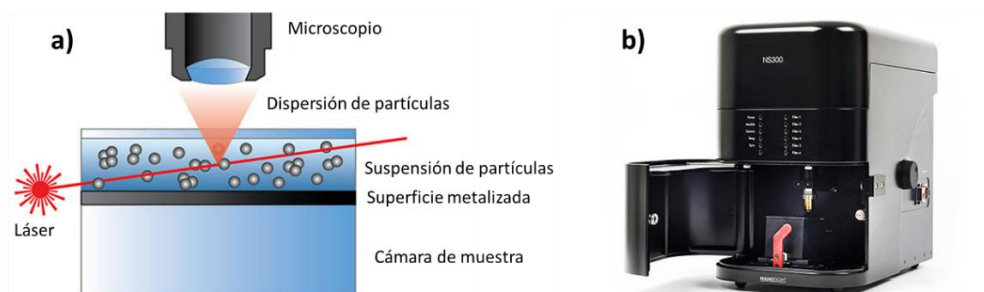


Figura 14. (a) Esquema de la técnica instrumental de análisis de seguimiento de nanopartículas y (b) equipo NTA utilizado.

Metodología experimental

Las mediciones de NTA se realizaron en un equipo instrumental NanoSight NS300 (Malvern Panalytical Ltd., Malvern, Reino Unido), equipado con una cámara de muestra y un láser de 488 nm.

La preparación de muestras se llevó a cabo suspendiendo 1 mg de material en 1 ml de agua. Antes del análisis, la suspensión se homogeneizó durante 3 minutos en un baño ultrasónico. Finalmente, las muestras fueron inyectadas en la cámara de muestra con jeringas estériles.

4.4.3. Fraccionamiento en flujo mediante campo de flujo asimétrico (AF4)

Fundamento de la técnica

El fraccionamiento de flujo de campo de flujo asimétrico (Asymmetric Flow Field-Flow Fractionation, AF4) es una de las técnicas de mayor potencial para el fraccionamiento y caracterización de nanopartículas debido a su elevada precisión y el amplio rango de tamaños que pueden ser analizados (2 nm - 1 μ m).

El principio de separación del método AF4 se muestra esquemáticamente en la **Figura 15a**. Es considerado un método cromatográfico consistente en el transporte de muestra propulsada por un líquido portador siguiendo un flujo laminar parabólico combinado con la aplicación de un flujo cruzado (crossflow) que ejerce una fuerza en dirección perpendicular sobre todo el canal. De esta forma, los componentes de la muestra se mueven hacia una membrana de ultrafiltración que funciona como una pared de acumulación, donde dichos componentes quedan confinados en una capa fina concentrada. La retención se origina por un equilibrio entre el movimiento de difusión de las partículas y la fuerza del campo generado. En base a esto, la separación de partículas se lleva a cabo según sus coeficientes de difusión, que son inversamente proporcionales al tiempo de elución. Por tanto, las partículas de menor tamaño, con mayores coeficientes de difusión y más cercanas al centro del canal, serán eluidas antes que las más grandes, que quedan más retenidas en la membrana semipermeable del canal ^[21,22].

La obtención de una capacidad efectiva de separación experimental se consigue a través de una optimización muy cuidadosa de las condiciones de operación: la composición del portador, la membrana y sus propiedades superficiales, las dimensiones del canal y el campo externo. Esta técnica presenta numerosas ventajas como su gran versatilidad, resolución y la capacidad de ser acoplada a distintos detectores en línea (UV-Vis, ICP-MS, etc.).

La **Figura 15** muestra un esquema del principio de separación de partículas mediante esta técnica y el equipo instrumental empleado.

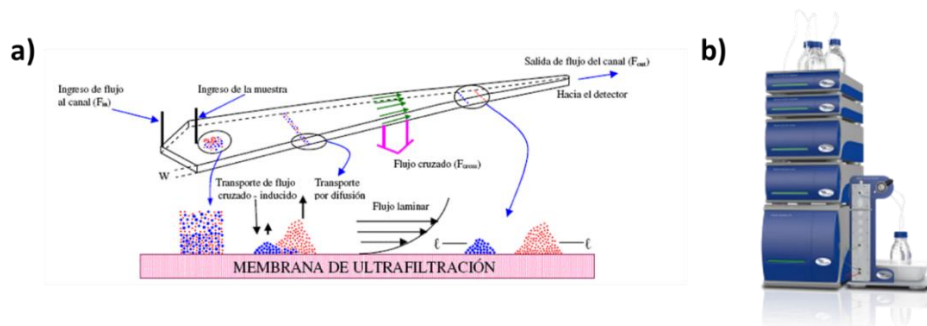


Figura 15. (a) Esquema del método de separación mediante fraccionamiento de flujo de campo de flujo asimétrico y (b) equipo AF4 utilizado.

Metodología experimental

El sistema AF4 (AF2000, Postnova Analytics, Landsberg am Lech, Alemania) acoplado en línea a un detector MALS de 21 ángulos (PN3621, Postnova Analytics, Landsberg am Lech, Alemania) y una matriz de diodos UV-Vis (PN3241 Postnova Analytics).

Los detectores MALS fueron calibrados utilizando un monómero de albúmina de suero bovino y se normalizaron con respecto a un detector de 90° que mide un estándar de poli (estirenosulfonato) de sodio (PSS). El canal AF4 fue de forma trapecoidal, 350 μm de espesor (definido por un espaciador), 29.8 cm de largo (entrada a salida) y una anchura máxima de 2 cm.

Todas las inyecciones se llevaron a cabo por triplicado con un muestreador automático (PN5300, Postnova Analytics) empleando diferentes tipos de membranas.

4.5. Composición Química

4.5.1. Análisis Elemental (EA)

Fundamento de la técnica

La técnica de análisis elemental o CHNS está basada en la determinación y rápida de carbono, nitrógeno, hidrógeno, oxígeno y azufre mediante un proceso de combustión en muestras orgánicas e inorgánicas, convirtiendo los elementos antes mencionados en gases simples (CO_2 , N_2 , H_2O y SO_2) para conseguir una determinación cuantitativa en términos de porcentaje en peso.

Los gases generados son arrastrados por una corriente inerte de He hasta una columna cromatográfica donde se procede a su separación y detección mediante un detector de conductividad térmica.

En la **Figura 16** se muestra el proceso de combustión en un analizador elemental y el equipo instrumental empleado.

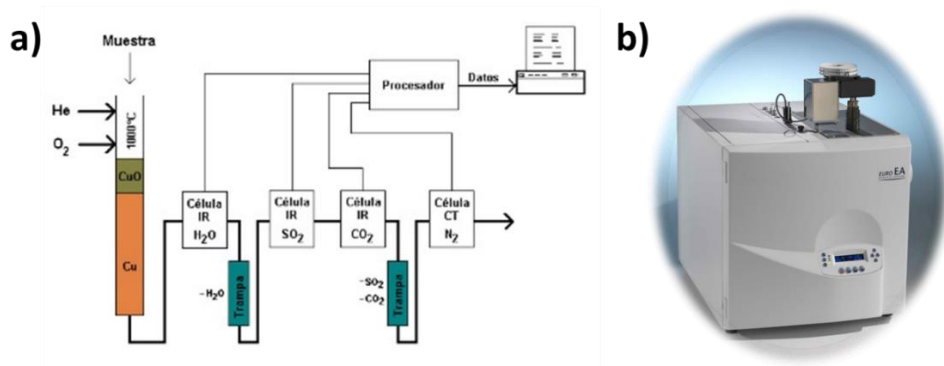


Figura 16. a) Esquema del proceso de análisis elemental de CHNS y b) el equipo EA utilizado.

Metodología experimental

El instrumento empleado es un analizador elemental Eurovector EA 3000 perteneciente a la Unidad de Espectroscopia NIR/MIR del Servicio Central de Apoyo a la Investigación (SCAI) de la Universidad de Córdoba. Este instrumento puede analizar de forma simultánea los elementos C, H, N y S.

Antes de cada análisis se lleva a cabo un calibrado con una muestra patrón con porcentajes certificados de estos elementos, proporcionados por el propio fabricante. El software utilizado para el análisis de los resultados es Callidus versión 2E3.

4.5.2. Análisis Termogravimétrico (TGA)

Fundamento de la técnica

El análisis termogravimétrico (Thermogravimetric analysis, TGA) se usa para caracterizar las propiedades físicas y químicas de los materiales en función de la temperatura aplicando una atmósfera controlada de forma precisa. Por tanto, TGA es una técnica basada en el control de la masa de un sólido mientras es sometida a un programa de temperatura controlado en una atmósfera específica estática o dinámica con un caudal determinado, siendo los gases más utilizados nitrógeno, oxígeno, argón y dióxido de carbono [23].

Esta técnica suministra información de una amplia variedad de investigaciones químicas: calcinación, actividad catalítica, quimisorción, descomposición, cinéticas, reacciones en estado sólido, adsorción-desorción, estabilidad térmica, etc. Una característica fundamental del TGA es que sólo permite detectar procesos en los que se produce una variación de masa, tales como descomposición, sublimación, reducción o absorción.

El procedimiento de medida consiste en colocar la muestra pulverizada en el interior de una electrobalanza de alta sensibilidad. Una vez cerrada, se hace pasar un determinado flujo de gas a través de la muestra y se empieza a calentar mediante una rampa programada de temperatura. El instrumento puede constar de un ordenador que registra en continuo la temperatura, la pérdida de peso y el flujo de calor. Conforme ocurre algún proceso de tipo térmico que modifique el peso del sólido se observará una variación en la curva y un máximo o un mínimo en el flujo de calor, según se absorba (endotérmico) o lo desprenda (exotérmico) en dicho proceso.

Los instrumentos comerciales actuales empleados en termogravimetría constan de: una balanza analítica de alta precisión, un horno, un sistema de gas de purga para proporcionar una atmósfera inerte y un microprocesador para el control del instrumento y la adquisición y visualización de datos.

En la **Figura 17** se muestra el proceso de análisis termogravimétrico y el equipo instrumental TGA utilizado.

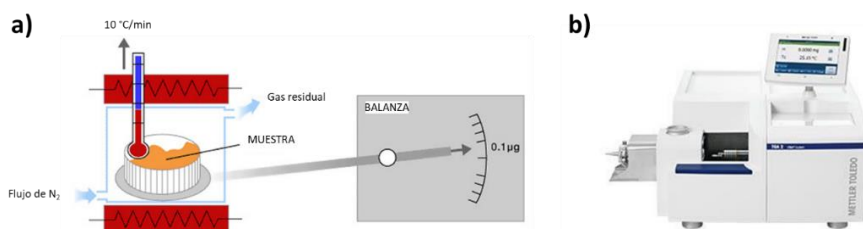


Figura 17. a) Esquema del proceso de análisis termogravimétrico en una muestra y b) el equipo TGA empleado.

Metodología experimental

Las muestras son introducidas en polvo (10-20 mg) en un portamuestras de alúmina de 100 µL y se calientan en un intervalo de temperatura determinado utilizando la rampa deseada con un flujo de oxígeno o nitrógeno según el material híbrido orgánico-inorgánico analizado. Antes de realizar las medidas se realiza un ensayo en blanco con el portamuestras vacío, que se considera la línea de base, la cual se sustrae posteriormente en todos los análisis.

El equipo instrumental utilizado fue un modelo TGA/DSC 1 Star System Mettler Toledo, perteneciente al grupo FQM-175 del Departamento de Química Inorgánica de la Universidad de Córdoba. Las condiciones empleadas en las medidas dependen de la muestra a analizar y del tipo de información que se pretende obtener. Por ello, estas condiciones son indicadas convenientemente en el capítulo para cada análisis realizado.

4.5.3. Espectrometría de masas con plasma de acoplamiento inductivo (ICP-MS)

Fundamento de la técnica

La Espectrometría de Masas con fuente de Plasma de Acoplamiento Inductivo (Inductively Coupled Plasma Mass Spectrometry, ICP-MS) es una técnica de análisis inorgánico elemental e isotópico de gran relevancia en la caracterización de materiales híbridos orgánico-inorgánicos que permite determinar y cuantificar la mayoría de los elementos de la tabla periódica (a excepción de H, C, N, O, F y los gases nobles) en un rango

dinámico lineal de concentración entre ppt (ng/L) – ppm (mg/L), lo que la hace ideal para el análisis de trazas de diferentes elementos.

En cuanto a sus características principales, cabe mencionar su bajo límite de detección, elevado grado de selectividad y una buena precisión y exactitud. En primer lugar, la muestra es sometida a un proceso de digestión, comúnmente en medio ácido (fluorhídrico, sulfúrico y clorhídrico), y, posteriormente, la disolución obtenida del sólido digerido se diluye en un determinado volumen. A continuación, la muestra líquida a analizar es transformada en un fino aerosol que es dirigido hacia la antorcha donde se ha generado un plasma de Ar (10.000 K), donde se producen procesos de desolvatación, vaporización, atomización e ionización. Los iones generados pasan al espectrómetro de masas y son focalizados hacia el analizador de tipo cuadrupolo, donde son separados según su relación masa/carga (m/z) [24].

En la **Figura 18** se muestra el proceso de análisis mediante espectrometría de masas con plasma de acoplamiento inductivo y el equipo instrumental ICP-MS utilizado.

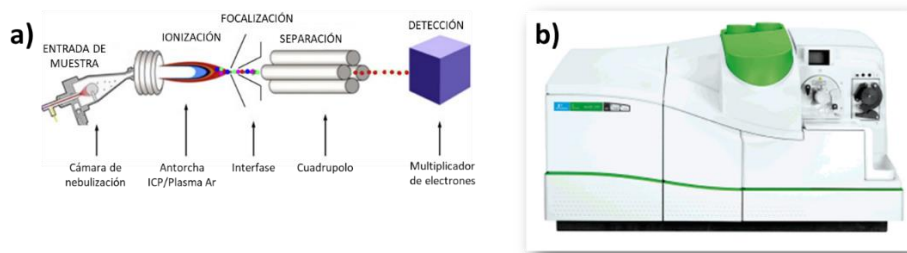


Figura 18. a) Esquema del proceso de análisis de muestra mediante espectrometría de masas con fuente de plasma de acoplamiento inductivo y b) el equipo ICP-MS empleado.

Metodología experimental

Los materiales híbridos orgánico-inorgánicos fueron analizados por el personal del Servicio Central de Apoyo a la Investigación (SCAI) de la Universidad de Córdoba en un equipo instrumental Perkin-Elmer Nexion 350X equipado con sistema de introducción de muestras, ionización por plasma de argón y detección de iones tipo cuadrupolo. Dispone de celdas de colisión/reacción para la eliminación de algunas interferencias poliatómicas. El cuadrupolo simple es un espectrómetro de masas de baja

resolución adecuado para llevar a cabo análisis semicuantitativo y cuantitativo. Previamente al análisis, los sólidos son sometidos a un proceso de digestión durante 24 h que puede llevarse a cabo en un Microondas Ultrawave (Milestone) o un Digestor SPB (Perkin-Elmer). Para la calibración se utilizan estándares de espectroscopia atómica PE PurePlus (Perkin-Elmer). El análisis cuantitativo se ha realizado mediante las correspondientes rectas de calibrado. El porcentaje final calculado para cada elemento cuantificado corresponde a la media aritmética de tres mediciones para asegurar la reproducibilidad del análisis.

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Chapter 5

Results and

Discussion

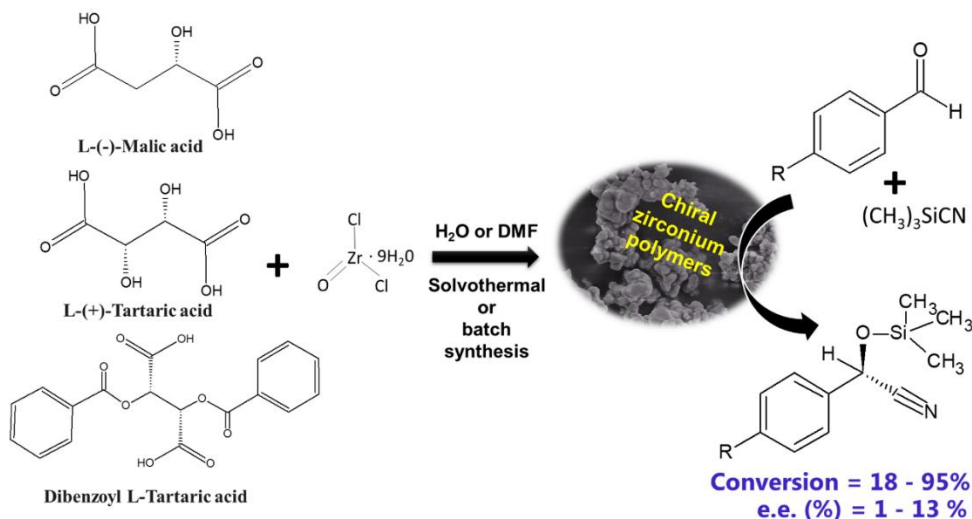
5.1. Section 1: Coordination Polymers - Metal Organic Frameworks (MOFs)

5.1.1. Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions

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Published in *Applied Catalysis A: General*

Applied Catalysis A: General, 2019, vol. 585, p. 117190

DOI: <https://doi.org/10.1016/j.apcata.2019.117190>

Abstract

The synthesis of chiral materials is a great challenge. This work describes the synthesis of Zr-based coordination polymers composed of chiral ligands derived from natural products. L-tartaric acid, dibenzoyl-L-tartaric acid and L-malic acid were selected as ligands from the chiral pool. Their reaction with zirconium oxychloride gave rise to several materials that were characterized by different techniques, such as XRD, Raman spectroscopy, ^{13}C MAS NMR, TGA and N_2 adsorption/desorption isotherms. Significant structural and textural properties have been observed depending on the ligand, the synthesis procedure and the metal to ligand ratio. These polymers were used for the first time as catalysts in the cyanosilylation of benzaldehyde with trimethylsilyl cyanide and their activity was compared with that of UiO-66. Different reaction parameters and reusability were studied for this asymmetric reaction. Some of the reported materials were very active in this reaction and provided a remarkable enantioselectivity depending on the reaction conditions.

Keywords: Coordination polymers, Zr(IV) complexes, Chiral linkers, Cyanosilylation reaction, Enantioselectivity, Heterogenous catalysis

5.1.1.1. Introduction

Coordination polymers are hybrid materials composed of organic linkers and metal nodes [1, 2]. Among different organic ligands used for the preparation of coordination polymers, malic and tartaric acids are promising linkers because they are readily abundant natural products and, besides two carboxylate groups, contains hydroxyl groups which can provide multiple coordination modes. In addition, both acids and their derivatives are simple and inexpensive chiral sources [3, 4]. Numerous coordination polymers and metal organic frameworks composed of malic and tartaric acids have been synthesized in the last years. Thus, for example, Williams et al. [5] reported two new indium tartrates, one of them with a microporous 3D framework with a channel size of ca. 6 Å and Del Castillo et al. [6] described cadmium tartrates with open frameworks. Metal tartrates exhibit interesting applications such as antiferromagnetic coupling by manganese coordination polymers [3], photoluminescence by some rare-earth MOFs (La, Sm, Eu, Tb and Dy) [4] and ferroelectricity by cerium coordination polymers [7], among others. Metal malates of a variety of metal ions have also been synthesized [8]. For instance, the crystal structure of several chiral and achiral malates of Sr(II), Cu(II), Pb(II), Co(II), Ni(II), Mg(II), Zn(II) and Cd(II) have been reported in the last years [9-12].

Zirconium coordination polymers are particularly attractive because they generally exhibit a high stability due to the significant strength of Zr-O bonds. An example is UiO-66, which is a Zr-terephthalate based MOF, a versatile material for catalytic applications [13]. Both Lewis and Brønsted sites present in this material can act complementary to each other, making it very attractive for catalysis [14]. Even, the strength of the Lewis acid sites can be modulated changing the electronic character of groups bound to the linker [15]. Also, the important role of the accessibility of substrates to internal active sites was revealed by comparison of the catalytic activity of UiO-66 and UiO-67, the latter containing biphenyl-4,4'-dicarboxylate ligands [16]. Other Zr-based MOFs have been used as catalysts, i.e. a bimetallic Zr(Ti)-naphthalendicarboxylate MOFs [17], which was active in Lewis acid catalyzed reactions, such as Meerwein-Ponndorf-Verley and isomerization of α -pinene oxide, among others.

The first example of chiral catalysis with a MOF was reported by Kim et al. [18] This material was synthesized from a pyridyl derivative of tartaric acid and Zn(II). The enantiomeric excess in the transesterification of 2,4-dinitrophenyl acetate with 1-phenyl-2-propanol was 8%. Later, the

coordination polymer Ni(L-asp)bipy_{0.5}, with L-asp = L-aspartate and bipy = 4,4'-dipyridyl, provided enantiomeric excess between +17% and -6% in the methanolysis of *cis*-2,3-epoxybutane [19]. A chiral Cu(II) coordination polymer based on binaphthyl units was essayed as catalyst in the cyanosilylation of benzaldehyde but it exhibited very low activity [20]. No results on the enantioselectivity of this process were provided.

The cyanosilylation of carbonyl compounds with TMSCN is an interesting organic reaction that gives rise to cyanohydrins, which are useful intermediates for the synthesis of a wide variety of compounds, such as α -hydroxyacids, α -hydroxyketones, β -hydroxyamines, α -aminonitriles and β -aminoalcohols, among others. A great number of different catalysts are active, including Lewis acids. In addition, the sp² carbon of the carbonyl group is transformed into a sp³ stereogenic center and so the asymmetric cyanohydrins synthesis has been intensively pursued. Nevertheless, conversion and enantioselectivity are very sensible to the substrate, the catalyst and the reaction conditions [21]. Most homogeneous catalysts are based on privileged ligands as chiral building blocks, which usually work with coordinated expensive metals. Although most of these ligands are commercially available, their high cost prevents their general use in industry.

Even though several coordination polymers based on tartaric acid and malic acid has been reported (*vide supra*), to the best of our knowledge, materials containing them or very simple readily available derivatives have not been ever used as heterogeneous catalysts. Furthermore, the use of zirconium as metal node should provide Lewis acid sites and remarkable stability under reaction conditions. In addition, cyanohydrins have an asymmetric carbon atom and so the enantioselectivity in this process, which has hardly been studied for heterogeneous catalysts, can be assessed under different conditions.

Herein, we report the synthesis of zirconium coordination polymers with three different chiral organic linkers, i.e., tartaric acid, dibenzoyl tartaric acid and malic acid. After being characterized by different techniques, they have been tested as catalysts for the first time in cyanosilylation reactions. The activity and selectivity of these catalysts under different reaction conditions is reported. The influence of the ligand structure and the zirconium to ligand ratio has been described. Moreover, the stereoselectivity towards the chiral cyanohydrins has been determined.

5.1.1.2. Experimental

5.1.1.2.1. Reagents and materials

L-(+)-tartaric acid ($\geq 99.5\%$), L-(-)-malic acid ($\geq 99.5\%$), dibenzoyl-L-tartaric acid (98%), zirconium (IV) oxychloride octahydrate (99.5%) and N,N-dimethylformamide anhydrous (99.8%) were obtained from Sigma Aldrich. Formic acid pure (98%) was provided by PanReac AppliChem. For the catalytic activity tests, trimethylsilyl cyanide (98%) and benzaldehyde (99.5%) were supplied by Aldrich, whereas dodecane ($\geq 99.5\%$) was provided by Fischer Scientific. All reactants and solvents were used as received, without further purification.

5.1.1.2.2. Synthesis of the catalysts

The synthesis of all materials was carried out either in an autoclave under autogenous pressure (A) or in a batch reactor under atmospheric pressure. The molar ratios of the Zr salt (Z) and linker precursor (tartaric acid (T), malic acid (M) or dibenzoyl-tartaric acid (DBT)) were 1:1 and 1:3, respectively. A summary of the nomenclature and reaction conditions are given in **Table 1**. Thus, Z₁T₁-110A was prepared by solvothermal synthesis using an autoclave under autogenous pressure (A) according to the following procedure. A mixture of 1 mmol of ZrOCl₂ • 9H₂O (0.322 g) (Z₁) and 1 mmol of tartaric acid (0.150 g) (T₁) in 10 mL of N,N-dimethylformamide (DMF) was heated in a teflon vessel at 110 °C for 68 h. Later, the solid product was collected by membrane filtration and washed several times with DMF. To assure the complete removal of unreacted linker, the material was stirred in 25 mL of DMF for 24 h and then in ethanol for 24 h. Afterwards, the resulting material was dried under vacuum at 100 °C for 24 h.

Alternatively, Z₁T₁-120 was synthesized in a batch reactor. For that, a solution containing 1 mmol of ZrOCl₂ • 9H₂O (0.322 g) (Z₁), 1 mmol of tartaric acid (0.150 g) (T₁) and 20 mL of DMF was transferred to a batch reactor at 120 °C for 68 h. Then, the washing procedure was like the solvothermal synthesis. To increase the crystallinity of the materials synthesized in batch reactor, in some cases, formic acid (5 eq, 97.5 μL) was added to the reaction mixture as a modulating agent (m).

Two batches of some materials were prepared to confirm the reproducibility in their synthesis and catalytic properties (see **Scheme S1** in supplementary information).

Table 1. Nomenclature and reaction conditions for the synthesis of Zr-based coordination polymers.

Name	Ligand (L)	Zr:L ratio ^a	Solvent	T (°C)	Reactor
Z ₁ T ₁ -110A	Tartaric acid	1:1	DMF	110	autoclave
Z ₁ T ₁ -120	Tartaric acid	1:1	DMF	120	batch
Z ₁ T ₁ -120m	Tartaric acid	1:1	DMF	120	batch
Z ₁ T ₃ -120	Tartaric acid	1:3	DMF	120	batch
Z ₁ T ₃ -120m	Tartaric acid	1:3	DMF	120	batch
Z ₁ DBT ₁ -110A	Dibenzoyl tartaric acid	1:1	DMF	110	autoclave
Z ₁ DBT ₃ -120	Dibenzoyl tartaric acid	1:3	DMF	120	batch
Z ₁ DBT ₃ -120m	Dibenzoyl tartaric acid	1:3	DMF	120	batch
Z ₁ M ₁ -110A	Malic acid	1:1	H ₂ O	110	autoclave
Z ₁ M ₁ -150A	Malic acid	1:1	H ₂ O	150	autoclave
Z ₁ M ₁ -180A	Malic acid	1:1	H ₂ O	180	autoclave
Z ₁ M ₁ -120	Malic acid	1:1	H ₂ O	120	batch
Z ₁ M ₁ -120m	Malic acid	1:1	H ₂ O	120	batch
Z ₁ M ₃ -120	Malic acid	1:3	H ₂ O	120	batch
Z ₁ M ₃ -120m	Malic acid	1:3	H ₂ O	120	batch

5.1.1.2.3. Characterization of the catalysts

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 DISCOVER A25 with Cu-K α radiation of 0.15418 nm wavelength and a solid-state detector. The speed of the goniometer was 0.016 ° / min and the sweep between 2° <2 θ <70°. Nitrogen adsorption-desorption experiments were carried out using an Autosorb iQ/ASiQwin analyzer from Quantachrome Instruments at 77 K. Prior to measurements, the samples were outgassed at 90 °C for 24 h. The specific surface area of each material was determined using the Brunauer-Emmett-Teller (BET) method over a relative pressure (P/P₀) range of 0.025 - 0.996. The thermogravimetric analysis was carried out to establish the stability of the coordination polymers as a function of temperature. The TGA records were

obtained using a Mettler Toledo TGA/DSC instrument. The measurements were carried out in an O₂ atmosphere with a gas flow of 100 mL/min with a temperature range between 30 and 900 °C and a heating ramp of 10 °C/min. Raman spectra were acquired with a Renishaw Raman instrument (inVia Raman Microscope) by excitation with green laser light (532 nm) and a grating of 1800 lines/mm in a range 100-4000 cm⁻¹. A total of 15 scans per spectrum were performed to improve the signal-to-noise ratio. The ¹³C CP/MAS NMR spectra were recorded at 100.61 MHz on a Bruker AVANCE 400 WB spectrometer at room temperature. An overall of 1000 free induction decays were accumulated. The excitation pulse and recycle time were 6 ms and 2 s, respectively. Chemical shifts were measured relative to a tetramethylsilane standard.

5.1.1.2.4. Catalytic activity

5.1.1.2.4.1. General procedure

The catalytic activity of the materials was studied in the cyanosilylation reaction [22]. The catalyst (12 mg) was pretreated at 120 °C overnight under vacuum before the catalytic reaction and then added to a mixture of benzaldehyde (0.87 mmol), trimethylsilyl cyanide (2.6 mmol) and dodecane (0.39 mmol) as internal standard. The reaction was kept under nitrogen at different temperatures and reaction times. Samples collected at different times were analyzed by gas chromatography using a FID detector and VF-1MS capillary column (15 m x 0.25 mm ID). Benzaldehyde cyanohydrin was the only product identified. The enantioselectivity (% e.e.) was calculated by gas chromatography (VARIAN 450-GC) using a chiral capillary column (Restek Rtr-bDEXm).

For the cyanosilylation reaction of benzaldehyde and derivatives with TMSCN in presence of solvent, the molar ratios of reactants were kept, and 1 mL of solvent was added to the reaction mixture.

5.1.1.2.4.2. Hot filtration tests

The reactions were carried out as described previously, but alternatively after 1 or 3 h of reaction, the mixture was filtered off at room temperature using a syringe fitted with a 0.20 µm nylon membrane filter, to remove all catalyst particles. In each case, the clear solution obtained was transferred to a round-bottomed flask at room temperature under nitrogen atmosphere and stirred for further 17 h.

5.1.1.3. Results and discussion

5.1.1.3.1. Characterization of the catalysts

Different reaction conditions for the synthesis of Zr-coordination polymers based on chiral ligands were employed (see Experimental Section, **Table 1**). Zirconium malates were obtained in water at different temperatures. Unlike, zirconium tartrates could not be formed in water under the conditions studied and therefore DMF was used as solvent. This solvent was also chosen in the synthesis of zirconium dibenzoyltartrates due to the high insolubility of dibenzoyl tartaric acid in water. In some cases, the metal to ligand ratio was a determining parameter in the synthesis. For example, no precipitate was obtained in batch reactor with a Zr:DBT ratio of 1:1, being required a molar ratio of 1:3. In addition, in order to increase the crystallinity, a modulating agent (formic acid) was added in those synthesis performed in batch reactor.

After the synthesis, the stability of all coordination polymers was confirmed by solubility tests in different solvents such as water, ethanol, hexane and ethyl acetate.

The X-ray diffraction (XRD) patterns of some coordination polymers are depicted in **Fig. 1**. Under similar reaction conditions, only the material with malate as linkers exhibited crystallinity. All polymers based on tartaric acid, regardless of the metal to ligand ratio, showed a broad band at the interval $2\theta = 4 - 15^\circ$, which indicates poorly ordered materials (**Fig. S1**). Similar patterns were observed for those consisting of dibenzoyl tartaric acid (**Fig. S2**). Other Zr(IV) coordination polymers such as those based on 1,3,5-benzenetrisphosphonic acid and carboxylate-substituted derivatives have also been found to be poorly crystalline [23]. Unlike, malic acid led to amorphous materials when the metal:ligand ratio was 1:1 whereas crystalline materials were obtained with a metal:ligand ratio of 1:3 (**Fig. S3**). This difference of crystallinity for Zr-based coordination polymers could be related with the nature of the organic linkers. On one hand, the steric hindrance of the dibenzoyl groups could lead to an amorphous structure and, on the other hand, the presence of two hydroxyl groups in the tartaric linker provides additional coordination modes that could affect the metal coordination and, therefore, their crystalline arrangement.

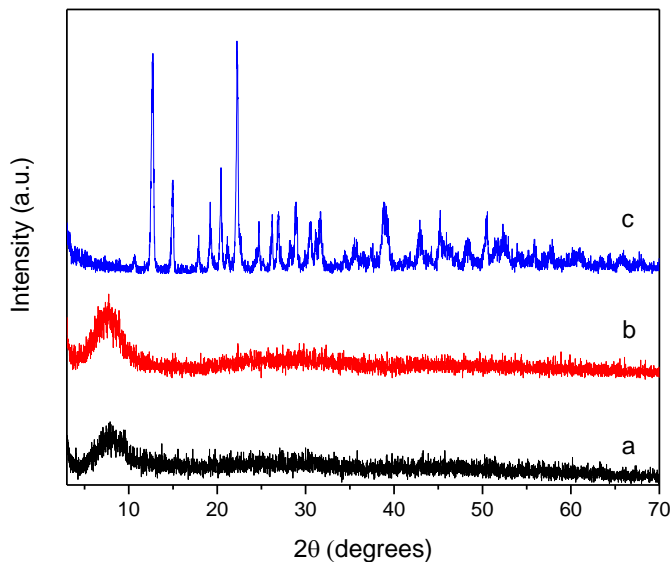


Fig. 1. X-ray diffraction patterns of Z_1T_3 -120m (a), Z_1DBT_3 -120m (b) and Z_1M_3 -120m (c).

The adsorption-desorption isotherms for all samples, regardless of the synthesis conditions, were essentially type-IV with wide pore size distributions particularly in the mesopore range. For instance, adsorption-desorption isotherms and pore size distribution of Z_1M_1 -110A, which has been used as catalyst (vide infra), are depicted in **Fig. S4**. Surface areas, pore volumes and pore radii are given for all coordination polymers in **Table 2**. All Zr-tartrate materials displayed a low specific surface area (below $20 \text{ m}^2 \text{ g}^{-1}$), which slightly increased for Zr-dibenzoyl tartrates. Nevertheless, Zr-malates showed remarkable areas with up to $192 \text{ m}^2 \text{ g}^{-1}$. For these coordination polymers, a slight decrease of the surface area was observed with the temperature of synthesis. However, the area dramatically decreased to ca. $30 \text{ m}^2 \text{ g}^{-1}$ when the zirconium to malic acid molar ratio in the synthesis medium was 1:3. In addition, pore radii increased because the contribution of small pores in a more cross-linked structure is reduced.

Thermogravimetric analysis was carried out to ascertain the stability and composition of the different materials (**Figs. 2, S5, S6 and S7**). Tartaric acid-based polymers displayed three weight losses. The first one up to $150 \text{ }^\circ\text{C}$ is attributed to the removal of solvent molecules. The second loss between 250 and $350 \text{ }^\circ\text{C}$ would correspond to the decomposition of the ligand molecules, i.e., tartaric acid. The decomposition of some fragments of the organic ligands in the form of carbonate ions bound to zirconium

cations could be responsible for the third weight loss at ca. 550-650 °C. Similar losses were observed for polymers with dibenzoyl tartaric acid, although the third loss occurred at somewhat lower temperature (ca. 450-500 °C). In the case of malic acid-based polymers, some differences were observed depending on the metal to ligand ratio. Those polymers synthesized with a metal to ligand molar ratio of 1:1 exhibited three weight losses: up to 150 °C, between 300 and 400 °C and between 550 and 650 °C. However, the second loss in these materials occurred in two stages. Nevertheless, more differences were observed for those solids obtained with a metal to ligand ratio of 1:3. The first loss was centered at ca. 200 °C, clearly revealing a stronger interaction with solvent molecules in these materials. In addition, following the second loss, which was very steep, the weight remained constant.

Table 2 Physico-chemical properties of Zr-based coordination polymers

Name	Zr:L ratio ^a	Zr/L ratio ^b	Weight loss (%)	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore radius (Å)
Z ₁ T ₁ -110A	1:1	0.8	64.7	7	0.016	43
Z ₁ T ₁ -120	1:1	1.1	57.4	19	0.033	38
Z ₁ T ₁ -120m	1:1	1.0	59.9	8	0.019	49
Z ₁ T ₃ -120	1:3	0.8	65.7	5	0.020	76
Z ₁ T ₃ -120m	1:3	1.0	61.9	8	0.016	41
Z ₁ DBT ₁ -110A	1:1	1.9	63.9	19	0.018	19
Z ₁ DBT ₃ -120	1:3	2.2	61.4	60	0.108	36
Z ₁ DBT ₃ -120m	1:3	2.0	63.2	26	0.049	38
Z ₁ M ₁ -110A	1:1	2.0	40.0	192	0.257	27
Z ₁ M ₁ -150A	1:1	2.4	41.9	121	0.207	32
Z ₁ M ₁ -180A	1:1	2.5	37.4	117	0.193	32
Z ₁ M ₁ -120	1:1	1.4	51.3	86	0.160	37
Z ₁ M ₁ -120m	1:1	1.4	50.8	190	0.146	15
Z ₁ M ₃ -120	1:3	0.8	59.9	28	0.120	87
Z ₁ M ₃ -120m	1:3	0.8	58.4	29	0.138	94

^a Zr:L ratio in the synthesis medium; ^b Experimental Zr/L ratio calculated from TGA.

A rough estimate of the metal to ligand ratio can be obtained analyzing the TG curves of these materials, i.e. losses of organic ligands in relation to the remaining metal oxides [24]. The calculated values are given in **Table 2**. As can be seen, the metal to ligand ratios depended on several factors. In the case of zirconium tartrates, those values are close to 1,

regardless of the relative amounts of Zr and tartaric acid present in the starting reaction mixture. This is the ratio for the most known zirconium metal organic framework, i.e. UiO-66 [24]. The metal to ligand ratio increased to ca. 2 for zirconium dibenzoyl tartrates. Interestingly, when malic acid was used as ligand, the metal to ligand ratio ranged from 0.8 to 2.5, depending on the relative amounts of the reactants, i.e. Zr and malic acid, and the reaction conditions. When the metal to ligand ratio is compared for the three types of ligands under the same reaction conditions, an increase of the ratio is observed with the decrease in the number of coordinating functional groups of the ligands (-COOH and -OH). Consequently, the structure of the coordination polymers is more connected in the following order: Zr-tartrate \geq Zr-malate \geq Zr-dibenzoyl tartrate.

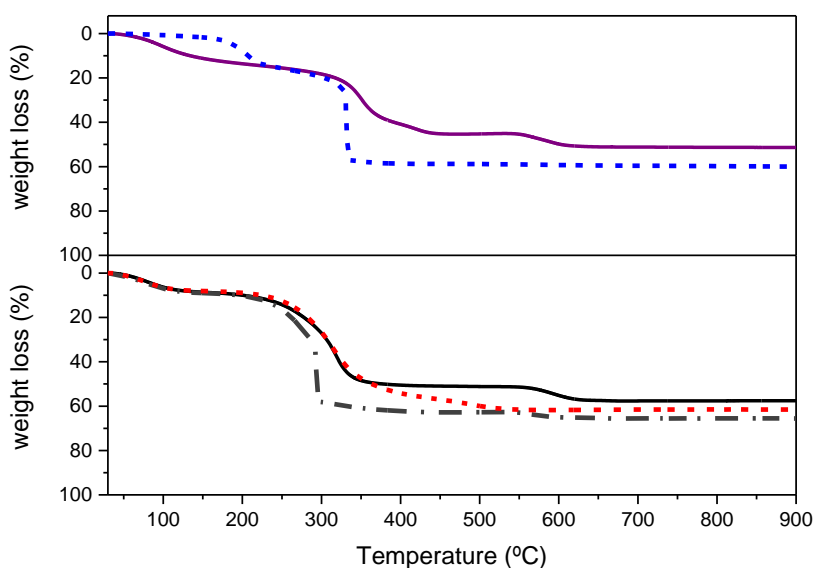


Fig. 2. Thermogravimetric curves for coordination polymers. Bottom: Z₁T₁-120 (solid line); Z₁T₃-120 (dotted-dashed line); Z₁DBT₃-120 (dashed line). Top: Z₁M₁-120 (solid line); Z₁M₃-120 (dashed line).

Raman spectra of the materials confirmed the presence of the corresponding linkers and so the formation of hybrid coordination polymers (**Figs. 3, S8, S9 and S10**). All materials showed several bands in the range 2800 – 2975 cm⁻¹ attributed to the C-H stretching of the chiral ligands. A signal centered at 1670 cm⁻¹ can be assigned to the C=O stretching vibrations. Aromatic C-H stretching bands at 3072 and 3015 cm⁻¹ were present in materials containing dibenzoyltartaric acid. Additionally, polymers based on tartaric acid showed a band at 3100 cm⁻¹ indicating

hydrogen bonding interaction between water molecules and carboxyl groups in the material [25]. Zr-O coordination was also confirmed in the polymers by the vibration modes at 663, 619 and 408 cm^{-1} ascribable to Zr-O stretching [26].

In some cases, the linkers in coordination polymers can undergo chemical transformations. For example, upon heating, lithium L-malate undergoes topotactic dehydration to form a phase containing the unsaturated fumarate ligand, in which the original 3-D framework remains intact [27]. To assure that the ligands stay intact during the synthesis, ^{13}C NMR experiments were accomplished. The ^{13}C CP/MAS NMR spectra of $\text{Z}_1\text{M}_1\text{-110A}$, $\text{Z}_1\text{T}_3\text{-120m}$ and $\text{Z}_1\text{DBT}_1\text{-110A}$ without previous activation are shown in **Fig. 4**. $\text{Z}_1\text{M}_1\text{-110A}$ and $\text{Z}_1\text{T}_3\text{-120m}$ showed similar spectra with two sets of resonance peaks. A first set located in the range of 160-200 ppm is attributed to the carboxyl carbon atoms of the chiral ligands, which can be in different chemical environments. The second set at high field (30-80 ppm) is assigned to the Csp^3 of the organic linkers, being more deshielded the carbon atoms bearing hydroxyl groups. For $\text{Z}_1\text{DBT}_1\text{-110A}$, the ^{13}C NMR spectrum showed additional signals in the 120-140 ppm range which correspond to the aromatic rings of the benzoyl groups. The presence of signals associated to DMF molecules was present in all materials. These signals were absent after activation of the catalysts at 120 $^\circ\text{C}$ overnight under vacuum (see experimental section and **Fig. S11** in supplementary information).

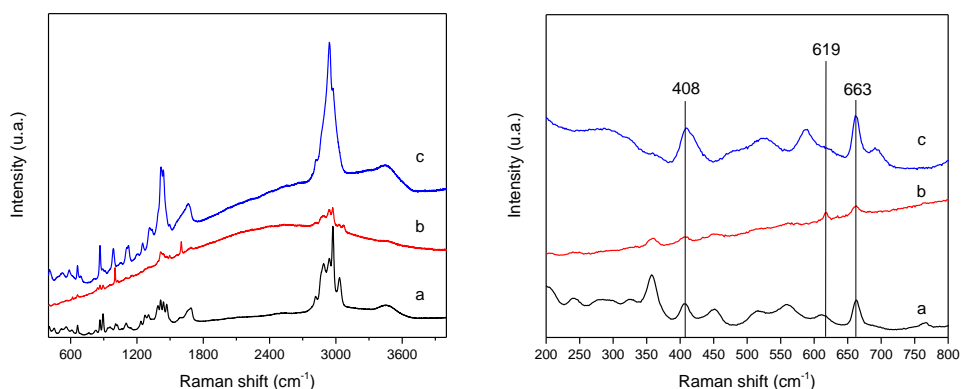


Fig. 3. Raman spectra of samples $\text{Z}_1\text{T}_1\text{-110A}$ (a), $\text{Z}_1\text{DBT}_1\text{-110A}$ (b) and $\text{Z}_1\text{M}_1\text{-110A}$ (c).

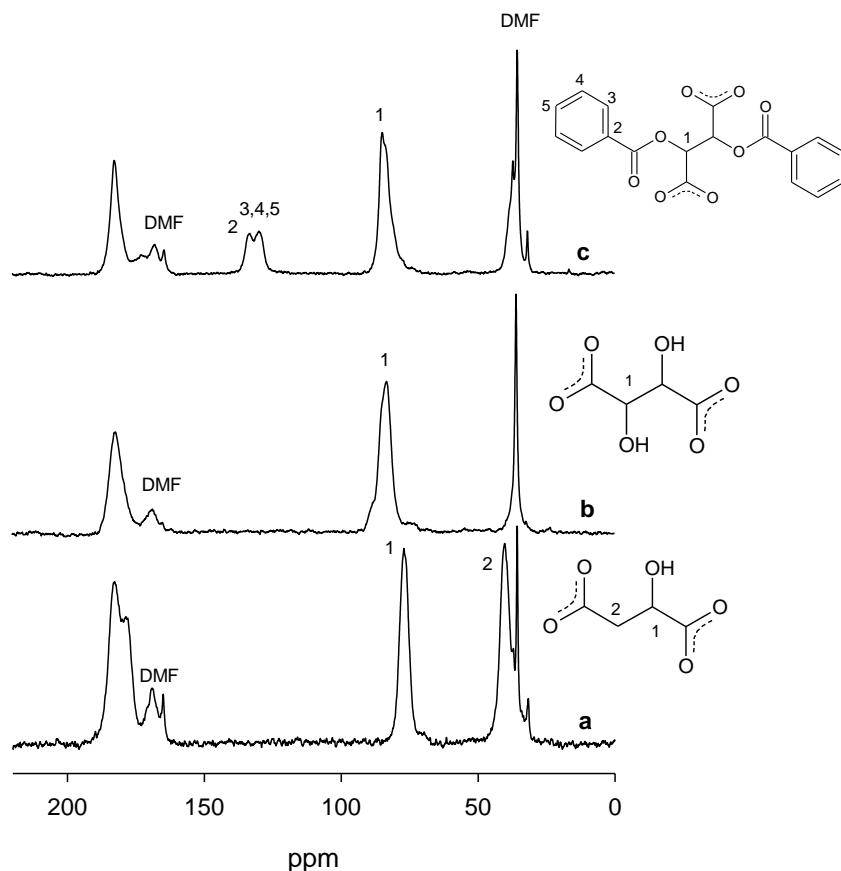


Fig. 4. Solid-state ^{13}C CP/MAS NMR spectra of $\text{Z}_1\text{M}_1\text{-110A}$ (a), $\text{Z}_1\text{T}_3\text{-120m}$ (b) and $\text{Z}_1\text{DBT}_1\text{-110A}$ (c).

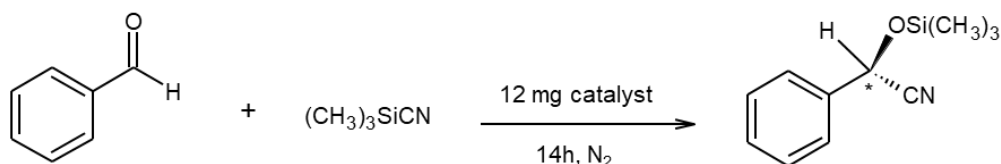
In order to prove that ligands do not undergo racemization under the synthesis conditions, vibrational circular dichroism measurements were undertaken. Unfortunately, they were not conclusive. Instead, degradation of the polymer followed by derivatization of the ligand and chiral GC analysis (**Fig. S12** in supplementary information) demonstrated that the optical purity of the ligands remained intact during the synthesis procedure.

5.1.1.3.2. Catalytic activity

5.1.1.3.2.1. Solvent-free cyanosilylation of benzaldehyde with trimethylsilyl cyanide (TMSCN)

All coordination polymers were tested as catalysts for the cyanosilylation reaction of benzaldehyde with trimethylsilyl cyanide

(TMSCN) (**Scheme 1**) under solvent-free conditions. In absence of any catalyst, the blank reaction gave a conversion of 18 % after 14h at room temperature (**Fig. S13**).



Scheme 1. Cyanosilylation of benzaldehyde with TMSCN.

Zr-tartrates exhibited relatively low activity as catalysts (**Fig. 5**). The maximum conversion obtained for such materials was 47%. Most of dibenzoyl tartrate polymers were inactive except for Z₁DBT₁-110A, which gave rise to a 67% conversion.

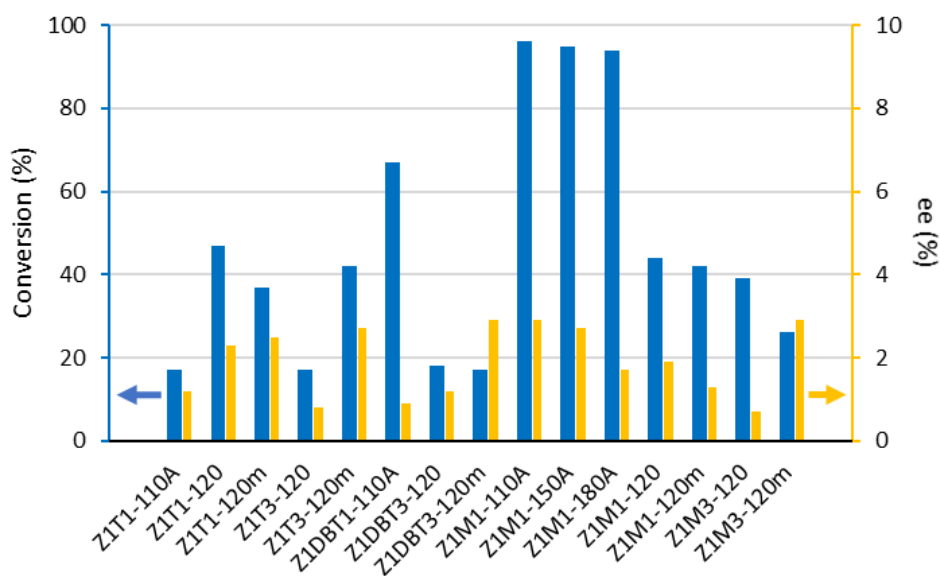


Fig. 5. Conversion (%) and ee (%) in the cyanosilylation of benzaldehyde with TMSCN at RT for 14 h.

However, the most active coordination polymers were those synthesized from malic acid. Some of them provided a conversion around 95%. For example, polymer Z₁M₁-110A gave a conversion and TON (turnover number) comparable to other heterogeneous catalysts (**Table 3**).

Table 3 Activity of some heterogeneous catalysts reported in the literature.

Entry	Catalyst	Solvent	Yield (%)	TON	Ref.
1	Z₁M₁-110A	None	96	16.5	This work
2	Cu(II)- Arylhydrazone Coordination Polymers	MeOH	79.9	16	[30]
3	Cu(II) Mixed- ligand Coordination Polymers	None	95.2	47.6	[12]
4	Bu ₂ SnCl ₂	None	97	9.7	[31]
5	primary amide- based cationic metal complexes	None	99	49.5	[32]
6	Cp-Zr- Binol@SBA-15	Toluene	100	66.7	[33]
7	Eu ³⁺ -MCM-41	None	90	137	[34]
8	Cu ₃ (BTC) ₂	Pentane	57	10.9	[29]
9	UiO-66-A	dichloromethane	96	9.6	[35]
10	UiO-68-V	1,2-dichloroethane	85	17	[36]
11	MIL-101 (Cr)	None	96	320	[37]

Under the same conditions, the metal-organic framework UiO-66 was essayed, resulting in a conversion of 95%. In the case of Zr-malates, the metal to ligand ratio plays an important role in the catalytic activity. In fact, those materials with the highest activities have ratios about 2. The rest of Zr-malates with metal to ligand ratios between 1.4 and 0.8 gave conversions below 45%. In addition, the conversion decreased as the Zr/L ratio decreased. To compensate the lower content of Zr in sample Z₁M₃-120m compared to polymer Z₁M₁-110A, the catalyst weight for the latter was increased by 2.5 times, while maintaining the rest of conditions, and its catalytic activity remained very low, ca. 23%. This fact revealed the importance of the connectivity of the coordination polymer. Indeed, increasing the number of ligand molecules around Zr decreases the catalytic activity, thus corroborating the role of Zr cations as Lewis acid sites. If they are buried by ligands, they are no longer accessible to the reactants. Similarly, it has been reported that the catalytic activity of UiO-66 in the Fischer esterification increased when defects consisting of coordinatively unsaturated Zr ions with Lewis acid properties were present in its structure [14]. In particular, the activation of TMSCN by adsorption on Lewis acid sites (Zr ions) has been suggested for the cyanosilylation of benzaldehyde in sulfated-zirconia catalysts [28]. The metal-organic framework compound Cu₃(BTC)₂(H₂O)₃·xH₂O (BTC= benzene 1,3,5-tricarboxylate) was tested as catalyst in the cyanosilylation of benzaldehyde [29]. Prior to its application it had to be dehydrated in high vacuum at 100 °C in order to remove physically and chemically bound water molecules and so give Lewis acid Cu(II) sites. However, maximum yield was not higher than 57% even after 72 h. In addition, it was very sensitive to the reaction conditions.

The three ligands used for the synthesis of the coordination polymers are chiral. Accordingly, the enantiomeric excess (e.e.) was determined in every reaction. These results are shown in **Fig. 5**. In general, all materials provided a clear enantioselectivity but with e.e. values below 3%. Even so, it should be noted that, in the catalyst free reaction, enantioselectivity was not achieved, just obtaining the racemic mixture of the corresponding cyanohydrin. Those polymers composed of malic acid synthesized in autoclaves at different temperatures gave the highest conversion and enantioselectivity. Concerning these materials, a decrease in the e.e. value was observed as the synthesis temperature increased, which also corresponded with an increase in the metal to ligand ratio. Recent studies on rare-earth metal complexed to chiral pyrrolyl-substituted 1,2-

diimino ligands in cyanosilylation reactions have reported similar yields but the products were racemic [38].

To further investigate this reaction, Z₁M₁-110A, the most active polymer with higher enantiomeric excess (e.e.) among catalysts tested, was selected to perform additional studies on cyanosilylation reactions.

5.1.1.3.2.2. Effect of reaction temperature

In order to ascertain the effect of reaction temperature, particularly on enantioselectivity, the cyanosilylation reaction was also carried out at 10 and -10 °C. As observed in **Table 4**, the temperature clearly affected the enantioselectivity. The lower the temperature, the higher the e.e. value. Thus, at -10 °C, the e.e. was ca. 6%, even though the yield was greatly reduced. Although this e.e. is low, it is significant because the active sites, i.e., Zr cations, are not directly attached to chiral centers but they are located in a chiral environment provided by chiral ligands.

Analogous results were reported by Lin et al. [39] with coordination polymers consisting of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ligands (BINAP) and different lanthanides, which gave rise to e.e. below 5% in the cyanosilylation of aldehydes. Obviously, higher enantiomeric excess have been reported on catalysts based on transition metal complexes with chiral privileged ligands, such as those metal-organic frameworks [22] and periodic mesoporous organosilicas [40] containing homochiral vanadium-salen complexes, which yielded e.e. around 70% and 30%, respectively.

Table 4 Conversion and enantiomeric excess in the cyanosilylation reaction at different temperatures using Z₁M₁-110A as catalyst.

Temperature (°C)	Time (h)	Conversion (%)	e.e. (%)
rt	14	96	2.9
10	20	95	5.1
-10	20	55	5.9

5.1.1.3.2.3. Solvent and promoter effects

Although previous studies have revealed that this type of reaction progresses very well under solvent-free conditions [41], additional experiments were performed in presence of different solvents to examine their role in the cyanosilylation reaction. As seen in **Table 5**, the presence of solvent in the reaction media produced a decrease in the conversion, from 96 % under solvent-free conditions to 18% when DMF was added. The polarity of the solvent clearly influenced on the cyanosilylation reaction. [42] Non-polar solvents, as hexane, did not affect the reaction rate. Unlike, the use of polar solvents such as DMF, CH₃CN and THF reduced the yield, which was lower than 25%. Unlike, the reactions in moderately polar solvents like CH₂Cl₂ and Et₂O gave higher conversions. This decrease in polar solvents can be probably due to the coordination ability of the solvent molecules to unsaturated Zr-sites.[37] Although the conversions in presence of solvents were greatly reduced, the ee values were higher in all cases, with 10.6 and 11.4 % ee in toluene and Et₂O, respectively. These results showed the important role of the solvent on the enantioselectivity of this type of reaction.

The enantioselective cyanohydrin formation has been a subject of study by numerous researchers. Not only the solvent has shown to have an important impact on asymmetric catalytic systems, but also the addition of “promoters”, such as CH₃P(O)Ph₂, Bu₃PO and Ph₃PO have been beneficial for the yields and enantioselectivities obtained [43]. Ph₃PO has been found to be a superior cocatalyst [44] and so, in order to evaluate this effect, additional catalytic experiments on the reaction of benzaldehyde with TMSCN under different solvents in the presence of Ph₃PO were carried out. The results obtained are listed in Table 4. In most cases, the reaction rates were enhanced by the addition of the promoter. In contrast, the enantioselectivities values did not show an increasing tendency in all solvents when the promotor was added. Only those reactions in CH₃CN and DMF increased twice the ee values.

In addition, those conditions providing higher conversions and enantiomeric excess were selected to perform the experiments at low temperature (-10 °C) The cyanosilylation reaction of benzaldehyde in the presence of toluene and Ph₃PO at -10°C gave a conversion of 15% and ee of 11.1%. Moreover, in Et₂O and without any added Ph₃PO, the reaction reached the highest ee, 12.6%. These results confirmed that the yield and

enantiomeric excess on asymmetric catalytic systems are very sensitive to small changes in the reaction conditions.

Table 5 Z₁M₁-110A catalyzed cyanosilylation reaction of benzaldehyde under different conditions (solvents and promoter).

Solvent	Promoter	Conv. (%)	ee (%)
CH ₂ Cl ₂	-	36	9.0
	Ph ₃ PO	84	7.1
THF	-	25	9.6
	Ph ₃ PO	71	6.3
CH ₃ CN	-	24	4.1
	Ph ₃ PO	74	9.2
Hexane	-	94	7.9
	Ph ₃ PO	89	8.4
DMF	-	18	3.9
	Ph ₃ PO	75	5.3
Toluene	-	44	10.6
	Ph ₃ PO	74	9.7
	Ph ₃ PO	15(*)	11.1(*)
Et ₂ O	-	78	11.4
	Ph ₃ PO	70	9.3
	-	19(*)	12.6(*)
Solvent free	-	96	2.9

*The reaction was performed at -10°C; Promoter, Ph₃PO, 0.2 equiv.

5.1.1.3.2.4. Scope of the reaction

In order to assess the scope of this catalytic system, tests were carried out using the catalyst Z₁M₁-110A to demonstrate its effectiveness in reactions with different p-substituted benzaldehydes. The experimental conditions were established considering the solubility of the different reactants. dichloromethane was selected because it dissolved all of the tested p-substituted benzaldehydes. In addition, the Ph₃PO promoter was added to the reaction mixture because it improved the catalytic results when using dichloromethane as solvent (vide supra).

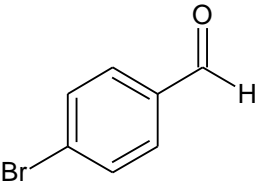
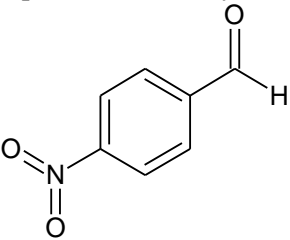
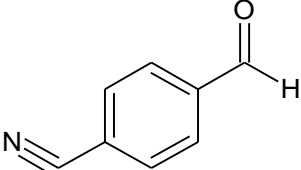
The conversion and enantioselectivity results for the different substrates are shown in **Table 6**. It can be observed that the p-substituted

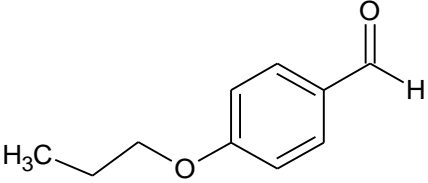
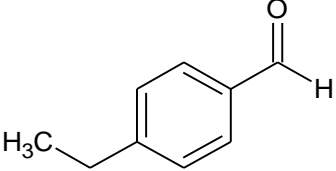
benzaldehydes bearing electron withdrawing substituents such as nitro, cyano or bromo give rise to high conversion and ee. On the other hand, the p-substituted benzaldehydes with electro donating groups produced poorer yields in the catalytic process [37].

5.1.1.3.2.5. Heterogeneity tests

In order to check the heterogeneity of the cyanosilylation reaction, two hot filtration tests were undertaken with Z₁M₁-110A catalyst at different conversions (**Fig. 6**). After the removal of the catalyst, the reaction did not progress, thus revealing that the reaction occurred under heterogeneous conditions [45]. That was also indicative of the stability of these coordination polymers under the reaction conditions.

Table 6 Catalytic cyanosilylation of p-substituted benzaldehydes after 14 h at room temperature in CH₂Cl₂ using 0.2 eq of Ph₃PO as promoter.

p-substituted benzaldehydes	Conversion (%)	ee (%)
p-bromobenzaldehyde 	88.7	8.4
p-nitrobenzaldehyde 	54.6	11.3
p-cyanobenzaldehyde 	>99	5.2

<p>p-propoxybenzaldehyde</p> 	31.1	n.a. ¹
<p>p-ethylbenzaldehyde</p> 	50.1	n.a. ¹

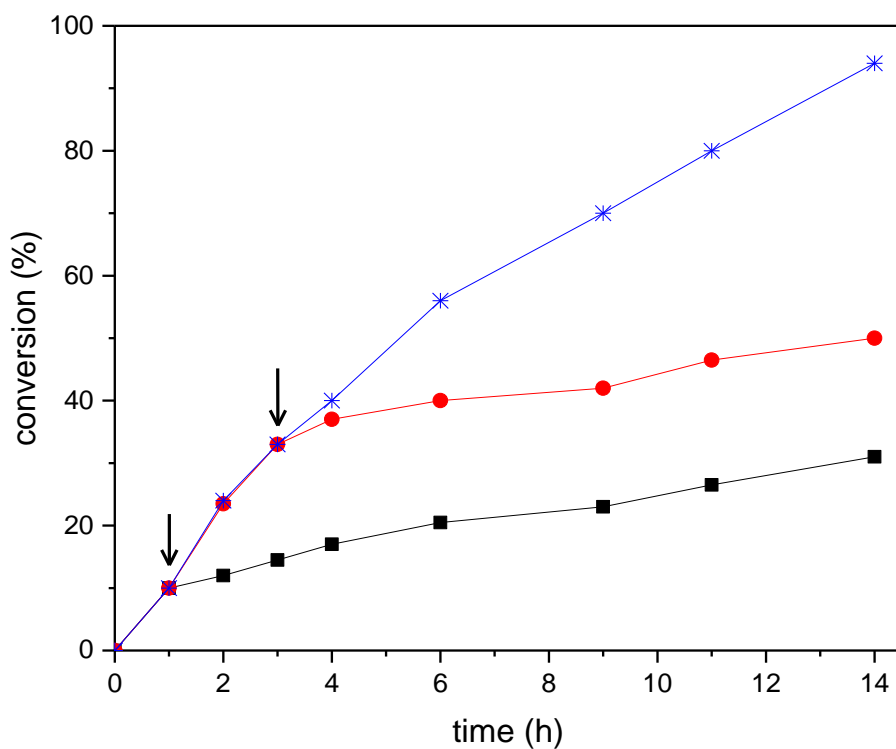


Fig. 6. Hot filtration test in the solvent-free cyanosilylation of benzaldehyde with TMSCN. Conversion vs time for the catalyzed reaction (*) and for the reaction after filtration of the catalyst at 1 h (■) and 3 h (●).

5.1.1.4. Conclusions

Zirconium-based coordination polymers with different chiral ligands (L-tartaric acid, dibenzoyl-L-tartaric acid and L-malic acid) were synthesized under solvothermal conditions in batch reactor or autoclave.

Textural and structural properties of the resultant polymers were directly related to the chiral ligand, the synthesis conditions and the metal:ligand ratio. Most of the resulting materials were amorphous except for some malic acid coordination polymers which showed high crystallinity. Zr-malates exhibited higher specific surface areas than Zr-tartrates and Zr-dibenzoyltartrates, although it strongly depended on the Zr to ligand ratio. Several characterization techniques showed that the organic linkers remained unaltered under the synthesis conditions.

Several materials were active in the cyanosilylation reaction of benzaldehyde with TMSCN, particularly some coordination polymers containing malic acid as ligand, giving rise to conversions comparable to UiO-66.

In general, a high Zr to malic acid ratio resulted in a higher catalytic activity. Furthermore, the use of Ph_3PO as promoter tended to increase the conversion whereas the activity in polar organic solvents decreased. Interestingly, enantiomeric excess of up to 12.6%, depending on the reaction conditions, has been observed.

Different p-substituted benzaldehydes have also been used as substrates exhibiting moderate to good conversion toward the corresponding cyanosilylated product and variable enantioselectivity. Thus, these materials can be considered as promising green catalysts for Lewis acid-catalyzed organic processes.

Acknowledgments

The authors wish to acknowledge the financial support from Ramon Areces Foundation (Spain), Andalusian Regional Government (FQM-346 group), Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981) and a project MAT2013-44463-R, Feder Funds, the technical staff from the Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN) and Servicio Central de Apoyo a la Investigación (SCAI).

5.1.1.5. References

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Appendix I: Supplementary Information

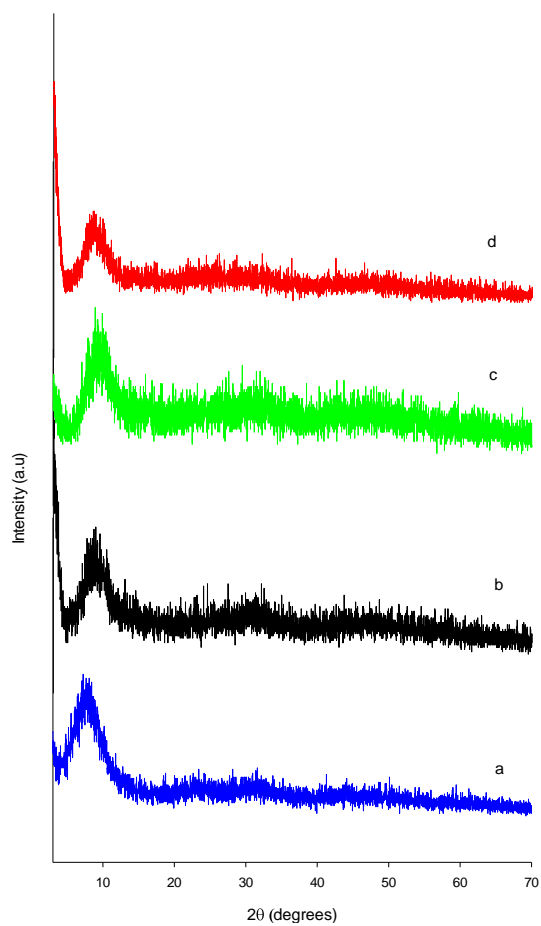


Fig. S1. X-ray diffraction patterns of Z_1T_1 -110A (a), Z_1T_1 -120 (b), Z_1T_1 -120m (c) and Z_1T_3 -120 (d).

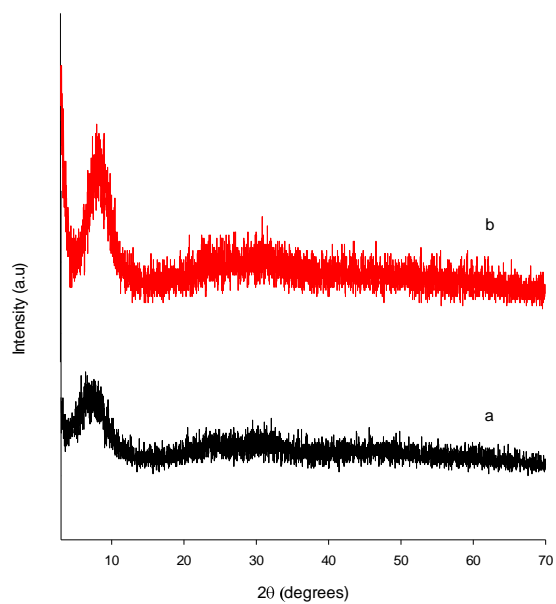


Fig. S2. X-ray diffraction patterns of Z_1DBT_1-110A (a) and Z_1DBT_3-120 (b).

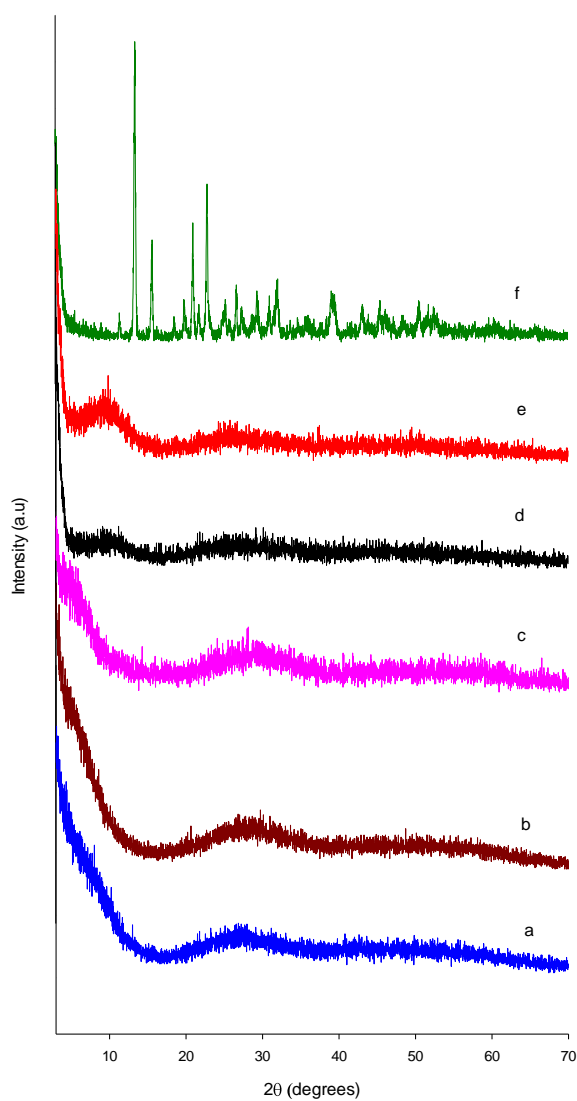


Fig. S3. X-ray diffraction patterns of Z_1M_1 -110A (a), Z_1M_1 -150A (b), Z_1M_1 -180A (c), Z_1M_1 -120 (d), Z_1M_1 -120m (e) and Z_1M_3 -120 (f).

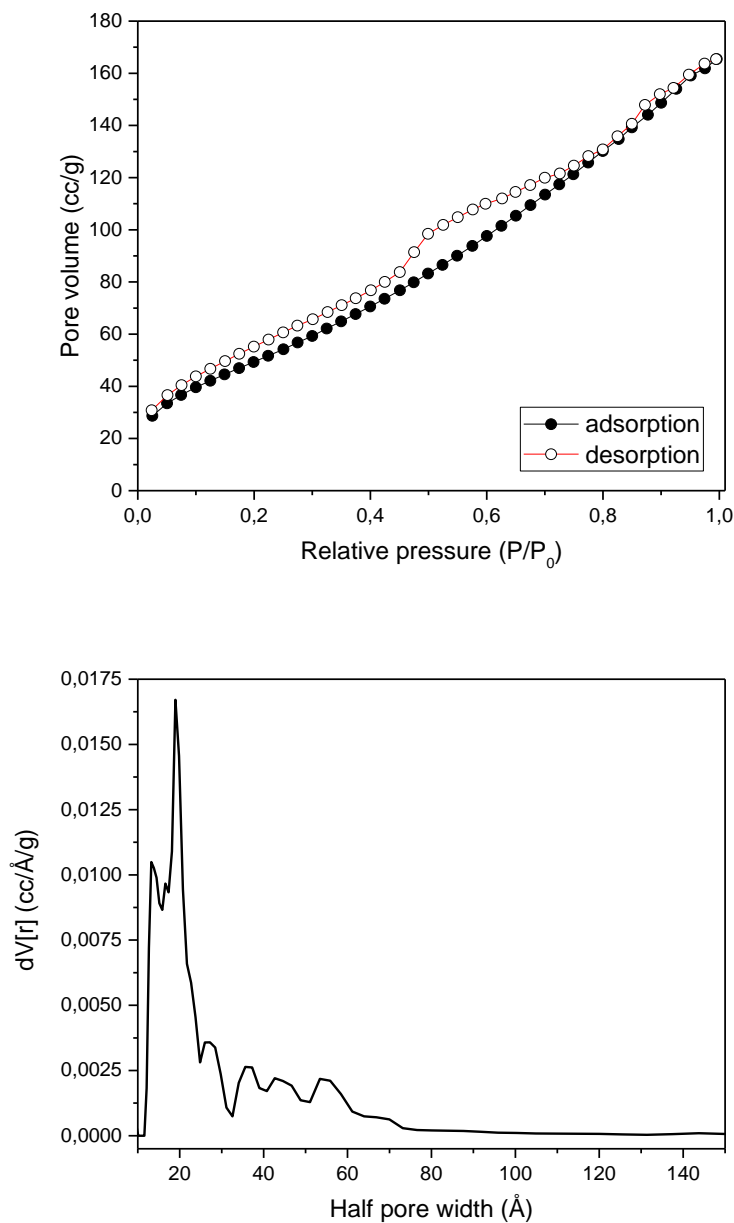


Fig. S4. Nitrogen adsorption-desorption isotherms (top) and pore size distribution (bottom) of Z₁M₁-110A

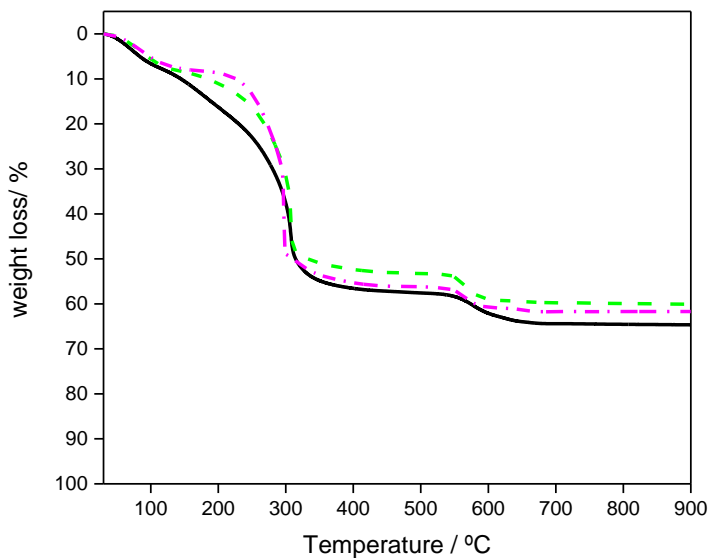


Fig. S5. Thermogravimetric curves for coordination polymers. Z₁T₁-110A (solid line); Z₁T₃-120m (dotted-dashed line); Z₁T₁-120m (dashed line).

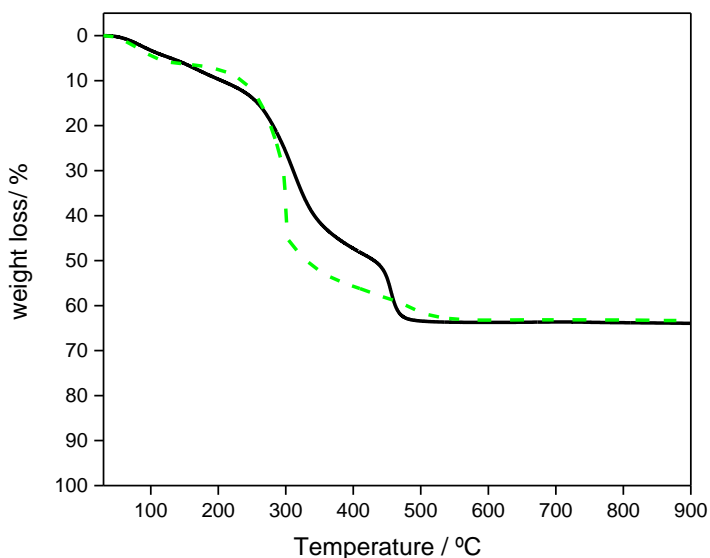


Fig. S6. Thermogravimetric curves for coordination polymers. Z₁DBT₁-110A (solid line); Z₁DBT₃-120m (dashed line).

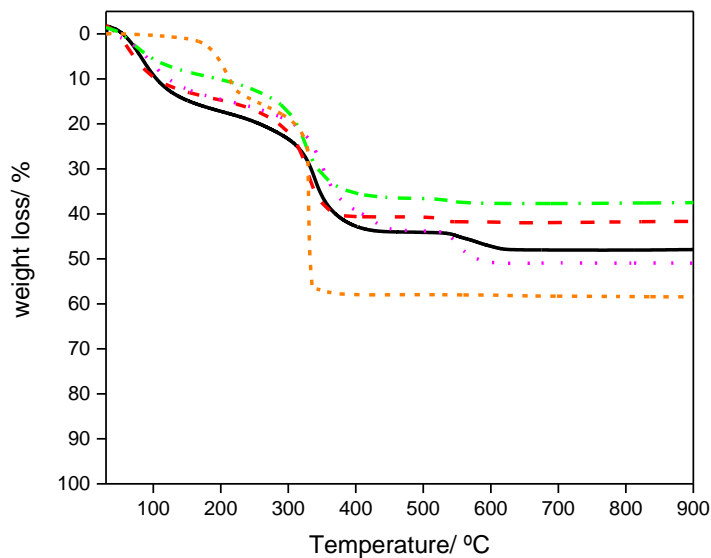


Fig. S7. Thermogravimetric curves for coordination polymers. Z_1M_1-110A (solid line); Z_1M_1-150A (dashed line); Z_1M_1-180A (dotted-dashed line); Z_1M_1-120m (dot line); Z_1M_3-120m (short dash line).

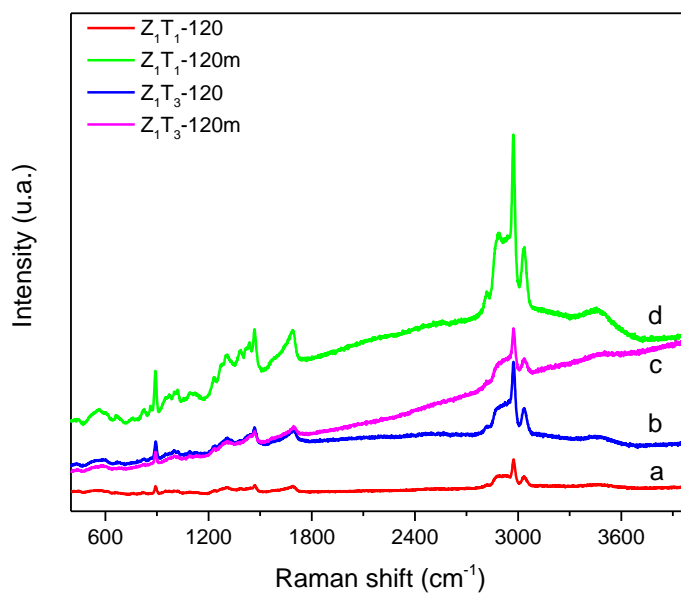


Fig. S8. Raman spectra of samples Z_1T_1-120 (a), Z_1T_3-120 (b), Z_1T_3-120m (c) and Z_1T_1-120m (d).

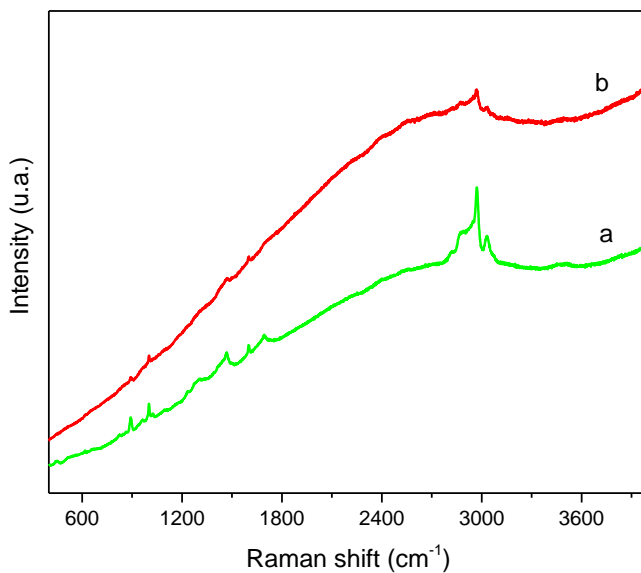


Fig. S9. Raman spectra of samples Z_1DBT_3-120m (a) and Z_1DBT_3-120a (b).

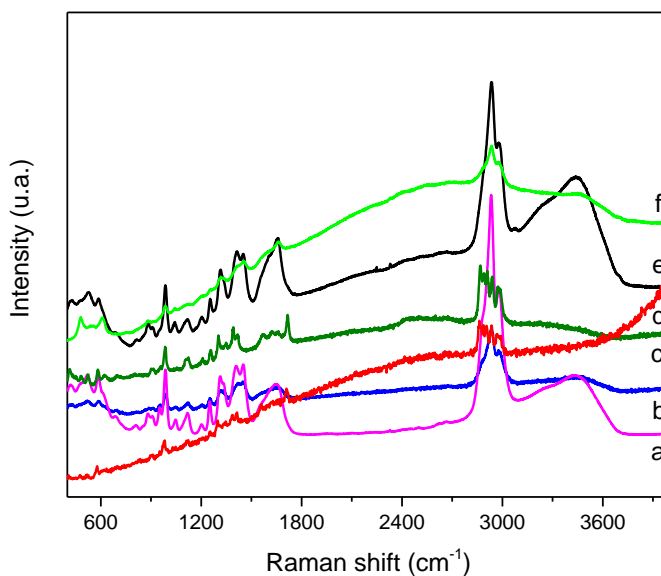


Fig. S10. Raman spectra of samples Z_1M_1-120m (a), Z_1M_1-120 (b), Z_1M_3-120 (c), Z_1M_3-120m (d), Z_1M_1-150A (e) and Z_1M_1-180A (f).

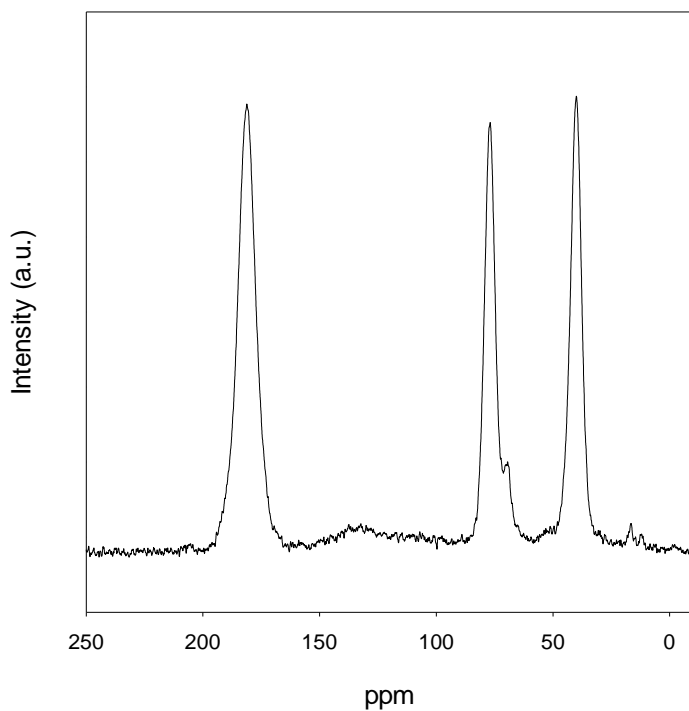


Fig. S11. Solid-state ^{13}C CP/MAS NMR spectra of $\text{Z}_1\text{M}_1\text{-150A}$ after activation at $120\text{ }^\circ\text{C}$ overnight under vacuum. See Fig. 4 for signal assignment.

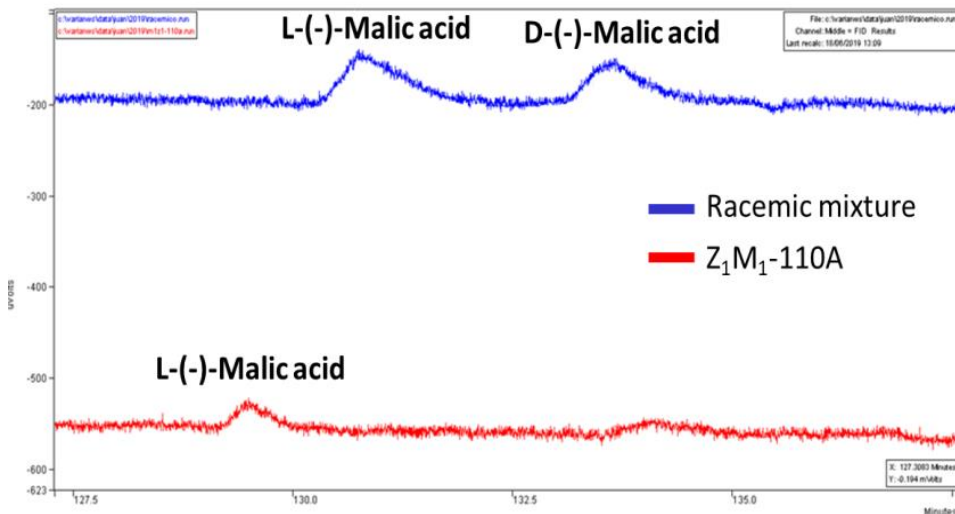


Fig. S12. Chiral GC analysis of the derivatized linkers coming from a racemic mixture of malic acid (blue line) and the degradation of the polymer (red line) according to the following treatment. 10 mg of L(-)-malic acid and 10 mg of D(-)-malic acid were reacted with $\text{BF}_3 \cdot \text{MeOH}$ (1:100) for 3 h at room temperature. Then, the resulting solution was extracted with 2 mL of hexane. The organic fraction was analysed in a gas chromatograph provided with a chiral cyclodextrin column. The coordination polymer $\text{Z}_1\text{M}_1\text{-110A}$ was subjected to the same experimental procedure

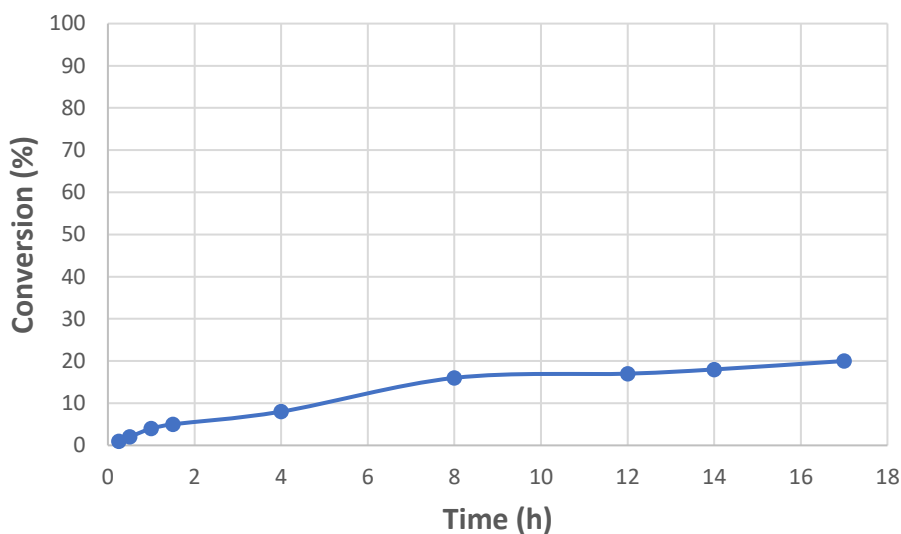
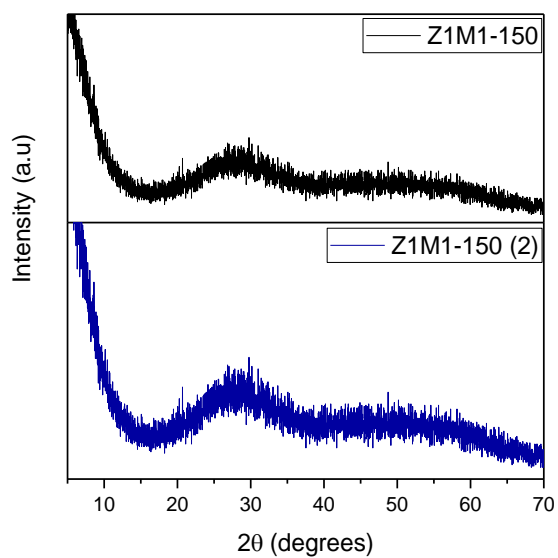


Fig. S13. Blank reaction kinetic in the cyanosilylation of benzaldehyde with TMSCN .



Coordination polymer	Conversion (%)	ee (%)
Z ₁ M ₁ -150A	95	2.7
Z ₁ M ₁ -150A (2)	97	2.4

Scheme S1. X-ray diffraction patterns and catalytic results of two different batches of amorphous catalysts Z₁M₁-150A.

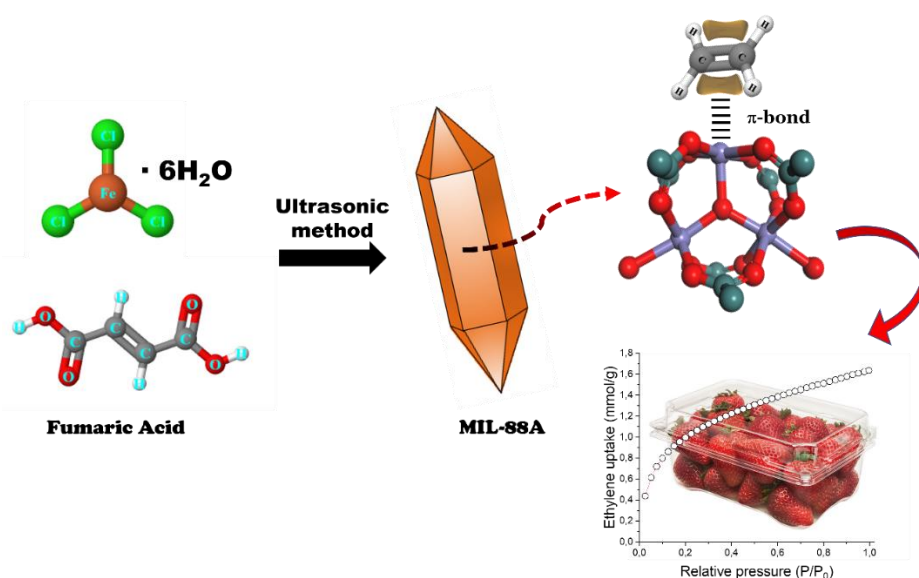
5.1.2. Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents

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Published in *Ultrasonics Sonochemistry*

Ultrasonics Sonochemistry, 2019, vol. 50, p. 59-66

DOI: <https://doi.org/10.1016/j.ultsonch.2018.08.027>

Abstract

Highly crystalline MIL-88A particles have been successfully synthesized via fast ultrasound-assisted processes. The influence of the sonication generator and synthesis time on the structure, crystallinity, morphology and surface area of the materials were studied in detail. Under this modified ultrasonic method, X-ray diffraction patterns of MIL-88A particles showed highly crystalline structures in contrast to those reported in literature. Significant differences on surface areas and microporosity were appreciated under ultrasound conditions employed. Specific surface areas in the range between 179 and 359 m² g⁻¹ were obtained. That material synthesized under ultrasound batch conditions during 1 h had the highest surface area and microporous character. Different particle sizes and morphologies were obtained depending on the synthesis procedure. In general, probe sonicators led to smaller particle sizes. Moreover, a comparative study of the ethylene adsorption of the MIL-88A particles and several common MOFs in the ethylene adsorption was investigated. The results suggest that the modified ultrasound-assisted procedure for the synthesis of MIL-88A is effective to obtain highly crystalline particles, which are very efficient to adsorb ethylene molecules.

Keywords: MOF, MIL-88A particles, Ultrasound irradiation, Ethylene adsorption

5.1.2.1. Introduction

Metal Organic Frameworks (MOFs) have been increasingly studied [1,2] due to their feasibility in applications such as gas storage [3] and separation [4], catalysis, and drug delivery [5], among others. These compounds consist in metal ions coordinated to organic ligands. The combination of these two components in a MOF provides limitless opportunities to tailor different materials with a chosen purpose. One of the most used synthetic routes for MOF particles involves the use of solvothermal conditions [6]. Even though this route exhibits a reasonably good performance in the quality of the obtained product, it requires relative long periods of heating and high temperatures. So, it is still challenging to precisely set the conditions -timing, temperature, solvent, modulating agent- during synthesis to keep the structural integrity of the framework.

Ultrasonic syntheses have been scarcely used for the preparation of MOFs [7,8]. This is an interesting method in which ultrasonic waves interact with the liquid solution generating small bubbles that provoke pressure and temperature alterations. This promotes effective collisions between particles and simplifies the reaction mechanism by helping the product crystallization. This route also enables the coordination reaction, improving surface morphology by facilitating the percolation of the reagents solution into the porous structure of the initial formed crystals, thus aiding a faster and more homogeneous crystal growth [9]. Different MOF materials such as UiO-66, HKUST-1, TMU-34 have been synthesized by ultrasound irradiation showing important effects on the morphology and growth process of their particles [10–13]. Recently, the ultrasound-assisted synthesis of DUT-32 and other Zn(II)-based MOFs have been carried out and their application as drug and pollutant adsorbents have been reported [14–17].

Also, structured coordination polymers have been successfully synthesized by sonochemical routes, validating it as a very attractive method for the preparation of particles with diverse shapes, sizes and morphologies [18]. In addition, the ultrasound-assisted synthesis of composites of MOFs, specifically HKUST-1, with activated carbon or molecularly imprinted polymers, useful as adsorbents, have been reported [19,20].

Iron (III) MOFs have been previously studied by different groups and they have shown their innocuous character in human health for drug

delivery [21]. Although Fe-MIL-88 serial MOFs have been produced by ultrasonic synthesis, only poorly crystalline and not well-defined morphology products were obtained in their studies [22]. One of these materials is MIL-88A which possesses a 3D flexible framework based on oxocentered trimers of iron (III) octahedra connected by fumarate dianions, creating interconnected pores and cages with open channels running along the *c* axis [23]. This arrangement provides a large specific surface area and a high porosity, making it attractive for many applications such as CO₂ separation and adsorption [24], photocatalysis for the degradation of organic pollutants under visible light irradiation, [25,26] or biomaterials encapsulation [27]. Its structure has also been studied as a precursor in other applications, for instance electrodes for energy storage. Its flexibility promotes the electrode/electrolyte contact, reduces the mechanical stress because of the volume change during cycling and boosts the electronic conductivity thanks to its derived composites [28,29].

MIL-88A framework exhibits a good concentration of coordinatively unsaturated metal cations, which are the primary interaction sites for guest olefin molecules through π -complexation, thus making it attractive for in the adsorption of gases such as ethylene [30]. In this application, many conditions should be considered for selecting a proper adsorbent. Tunable pores and open metal sites can notably enhance the C₂H₄ uptake capacity [31]. In addition, cheap ligands and metal salts for synthesis would make more attractive from the industrial point of view [32].

Furthermore, fruit ripening is a post-harvest problem due to inherent ethylene production. This gas generates irreversible changes that lead to rapid quality loss and decay if the fruit is not consumed within a short window of time. Lee and coworkers [33] have demonstrated that accelerated ageing and the initiation of ripening can occur following exposure to ethylene concentrations as low as 0.1 mL · L⁻¹, or its equivalent to 4.46 $\mu\text{mol} \cdot \text{L}^{-1}$. Consequently, ethylene capture and elimination in the packaging process are necessary to hold out “Best before” date. Therefore, technologies to slow down the ripening process after its onset are in high demand [34]. A compromise between good gas inhibition and harmless materials is also necessary [35].

In this work, a modified ultrasonic method demonstrated its feasibility to produce well-defined MIL-88A particles with high crystallinities and high surface areas. The reported methodology provides

a simple and fast procedure for the synthesis of MIL-88A materials with improved properties and variable morphologies. In addition, their enhanced surface area makes them attractive for their use as gas adsorbents. These materials showed a good performance in ethylene adsorption, which is comparable to other MOFs studied.

5.1.2.2. Experimental section

MIL-88A samples were prepared by an ultrasonic assisted procedure using an ethanolic solution of sodium hydroxide as modulating agent according to previous studies reported about this synthesis method [21,22]. This solution was prepared by dissolving the appropriated amount of sodium hydroxide (PanReac) in absolute ethanol (PanReac) to eventually obtain a 0.05 g NaOH/mL with the minimum amount of water. The presence of water leads to a fast nucleation, generating small-sized particles which interfere with proper crystal formation and growth. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (PanReac) and fumaric acid (PanReac) in equimolar amounts (1:1) were dissolved in a mixture of dimethylformamide (DMF, PanReac) and the ethanolic solution previously prepared with a proportion in volume 4.5:1 obtaining a 0.8:1 NaOH to Fe ratio in the reaction media. Considering the solvation effect, DMF slows the MOF crystallization rate by strongly solvating Fe(III) ions in the organic media.

A first synthesis was carried out by placing the reagents into an ultrasound bath (*B: Ultrasons, JP Selecta, 150 W*) for 2 h (*Fe-fum-B2*). Then, the final precipitate was recovered by centrifugation at 9000 rpm for 10 min, washed in DMF and in ethanol by redispersion twice. Finally, the sample was dried and activated in a vacuum oven at 85 °C overnight. In addition, a reduction in time to 1 h in the ultrasonic bath was tested (*Fe-fum-B1*).

Also, two ultrasonic probes (*PP: pulsed probe, Cole-Parmer 4710 Series; and CP: continuous probe, Branson Sonifier 150*) immersed in the solution for 10 (*Fe-fum-PP10*) and 5 min (*Fe-fum-PP5*) in the case of PP, and 10 min in the case of CP (*Fe-fum-CP10*) were used. The stirring conditions were set at 750 W 20 kHz and pulse duration of 10 s for probe PP, and 20 W 10 kHz in continuous wave mode for probe PC, respectively. Afterward, the precipitates were recovered by centrifugation, washed, and dried as previously described.

The crystalline phases were checked by Powder X-Ray Diffraction (XRD) on a BrukerD8 Discover A25 diffractometer using filtered Cu K α radiation within a 2θ angle range between 5° and 30° and a scan rate of a $0.01^\circ/\text{s}$ in continuous mode. The unit cell parameters were calculated with TOPAS software. The crystallite size was calculated using the Scherrer equation for which an average of the five maximum intensity peaks for each pattern, i.e. (010), (011), (110), (022) and (103) diffraction planes, were considered. The non-zero contributions to the reflection width were corrected by using an XRD pattern of pure LaB $_6$ from which the broadening at Full Width at Half Maximum (FWHM) was taken. This value was subtracted from the closest signals to its angle reflection in our patterns and the result was considered as the instrumental width. This instrumental width was used to correct each reflection broadening in order to be used in the Scherrer equation. Scanning Electron Micrographs (SEM) were acquired in a JEOL JSM 7800F microscope. Raman spectroscopy was implemented in a Renishaw Raman instrument (*InVia Raman Microscope*) furnished with a Leica microscope using a green laser light excitation source (532 nm). The specific surface areas were determined from the N $_2$ adsorption–desorption isotherms measured at liquid nitrogen temperature (-196°C) with an Autosorb iQ Station2 (*Quantachrome*). The samples were previously outgassed under vacuum at 120°C overnight. The isoelectric points of the materials were measured on a Zetasizer Nano ZSP coupled to a MPT-2 titrator using NaOH or HCl to adjust the pH.

The ethylene adsorption measurements were performed with a pure C $_2$ H $_4$ stream at 0°C with an Autosorb iQ Station2 (*Quantachrome*). All MIL-88A samples and other MOFs synthesized as previously reported in bibliography (A520-BASF [36], MOF-801[37], UiO-66 [10], and HKUST-1 [38]) were previously outgassed under vacuum at 120°C overnight.

5.1.2.3. Results and discussion

The X-ray diffraction patterns of the studied samples revealed a set of narrow well-defined reflections, thus clearly improving the previous patterns reported for this type of synthesis (**Figure 1**) [22]. This highly crystalline structure is as referenced by quite similar to those previously reported by solvothermal synthesis as well as to the simulated XRD pattern (**Figure S1**) and single-crystal X-ray diffraction [39]. This improved crystallinity for ultrasonic synthesis was observed in all samples, but with an important decrease in the reflection's intensity for Fe-fum-PP5. The

incidence of such diminution in crystallinity can be understood by the cavitation collapse uniqueness. Ultrasounds create bubbles as high energy microreactors, which leads to the rapid formation of small particles. This interaction is different depending on the sonication generator which affects the framework formation. If the particles do not get enough energy to keep the coordination bond, low crystallinity is induced by a simple array of the molecules around the metallic center. Shorter synthesis time in ultrasonic bath (0.5 h) and continuous probe (5 min) resulted in X-ray diffraction patterns ascribable to amorphous materials.

The obtained reflections could be indexed in the $P-62c$ space group of the hexagonal system as there was previously calculated for this family of dicarboxylic iron compounds [23,40]. Cell parameters for these materials are given in **Table 1**. The improvement in ultrasonic synthesis allowed to match the reflections with the refinement data obtained for single crystal XRD [23]. Highly crystalline patterns were obtained for all samples, except for Fe-fum-PP5. In addition, the appearance of reflections ascribable to impurities was not clearly observed evidencing the validity of the ultrasonic method to provide high purity crystalline samples.

It was expected that different sonication conditions led to the formation of regular crystal shapes according to the coordination system of the iron (III). **Figure 2** shows SEM images of the studied samples. These materials displayed particles with a prismatic central portion (body) and pyramidal end portions (tips). Fe-fum-B2 sample showed large micrometric particles (ca. 2.7-5.4 μm long x 1.6-3.2 μm wide) with defined elongated crystals and rough surfaces. A close inspection of that texture evidenced the presence of subnucleation structures over these large particles. A long sonication period seemed to be the main reason for the generation of smaller aggregates over the first formed crystals. Thus, Fe-fum-B1, which stayed a shorter time (1 h) in the ultrasonic bath, exhibited a smaller crystal size (ca. 1.3 μm long x 0.55 μm wide), still at micrometric level but with a higher definition in their shape. The sample Fe-fum-PP10, synthesized in the pulsed probe sonicator for 10 min, showed a similar crystal morphology. Nevertheless, these crystals were highly compacted in aggregates consisting of primary small particles (ca. 500 nm long x 180 nm wide). A shorter sonication time as in Fe-fum-PP5 (5 min) provoked a significant reduction in crystallinity as revealed by XRD and so this material exhibited irregular particles with different shapes and sizes. Fe-fum-CP10 sample also had very demarcated small crystals with a smooth

surface (ca. 900 nm long x 250 nm wide). As can be observed, the sonication time and conditions influence the nucleation rate and crystal growth, which crucially determine the particle size and shape [41]. In general, the ultrasound-assisted synthesis leads to smaller particle sizes than the conventional methods based on hydrothermal synthesis, where reported sizes are ca. 2.6 μm long x 0.5 μm wide [26].

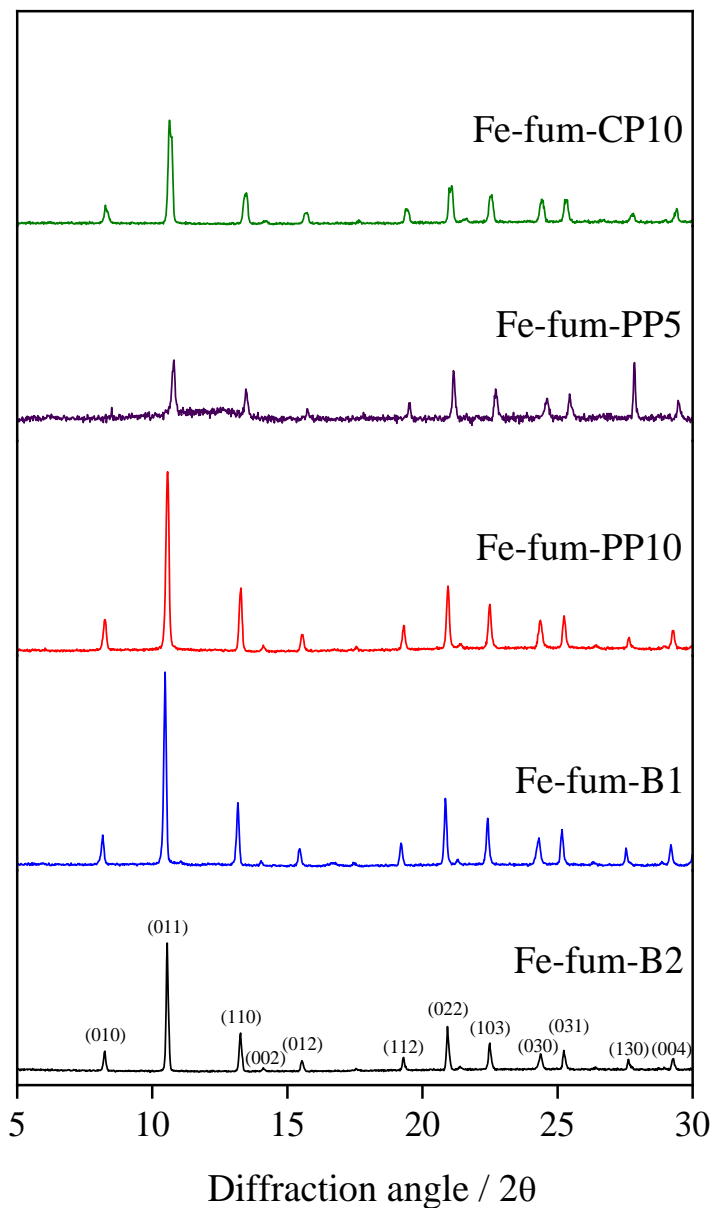


Figure 1. X Ray Diffraction patterns of MIL-88A samples.

Table 1. Unit cell parameters in the space group $P-62c$ of the hexagonal system for the synthesized MIL-88A samples.

	Fe-fum-B2	Fe-fum-B1	Fe-fum-PP10	Fe-fum-PP5	Fe-fum-CP10
$a / \text{Å}$	13.349 (2)	13.449 (1)	13.350 (1)	13.298 (1)	13.159 (2)
$c / \text{Å}$	12.515 (6)	12.553 (3)	12.506 (5)	12.420 (1)	12.300 (4)
Volume / Å^3	1931.3 (2)	1966.2 (6)	1930.2 (4)	1899.7 (8)	1844.5 (1)
Crystallite size (nm)	88.7	77.2	72.2	55.2	67.2

Not only the particle size of these materials was different, but also their aspect ratios. Thus, the ratio of the length between opposite tips to the body width was 1.7, 2.4, 2.8 and 4.0 for samples Fe-fum-B2, Fe-fum-B1, Fe-fum-PP10 and Fe-fum-CP10, respectively. In addition, the tip-body-tip length ratio was ca. 1:1:1 for Fe-fum-B2 and Fe-fum-B1, whereas it was 1:2:1 for Fe-fum-PP10 and Fe-fum-CP10. The use of ultrasonic probes with short sonication times (10 min) instead of the bath sonicator with long sonication times (1-2 h) gave rise to particles with higher aspect ratios and smaller sizes.

Nitrogen adsorption-desorption isotherms recorded at -196 °C are shown in **Figure 3**. The curves for Fe-fum-B2, Fe-fum-B1 and Fe-fum-PP10 samples are characteristic of microporous materials. Fe-fum-B2 and Fe-fum-B1, synthesized under US batch conditions, showed S_{BET} values of 317 and 359 $\text{m}^2\cdot\text{g}^{-1}$, respectively (**Table 2**). Unlike, Fe-fum-PP10 synthesized with the pulsed probe PP presented a lower surface area (179 $\text{m}^2\cdot\text{g}^{-1}$). In these materials, the presence of a slight hysteresis loop between adsorption and desorption branches at relative pressures $P/P_0=0.8-1.0$ revealed the presence of some mesopores. However, the main contribution in the surface area was microporous type with percentages of 72%, 82% and 72% for Fe-fum-B2, Fe-fum-B1 and Fe-fum-PP10, respectively. For Fe-fum-CP10, the curves of adsorption-desorption were a combination of type-I and -IV isotherms, being the contribution of the mesoporosity higher than in the other samples. The N_2 adsorption-desorption isotherm for Fe-fum-CP10 showed a smooth increase of volume with the relative pressure which suggests a wide pore size distribution spanning from microporous to mesoporous. Sample Fe-fum-PP5 also gave a wide distribution of pores but mainly in the upper mesopore range with total lack of micropores.

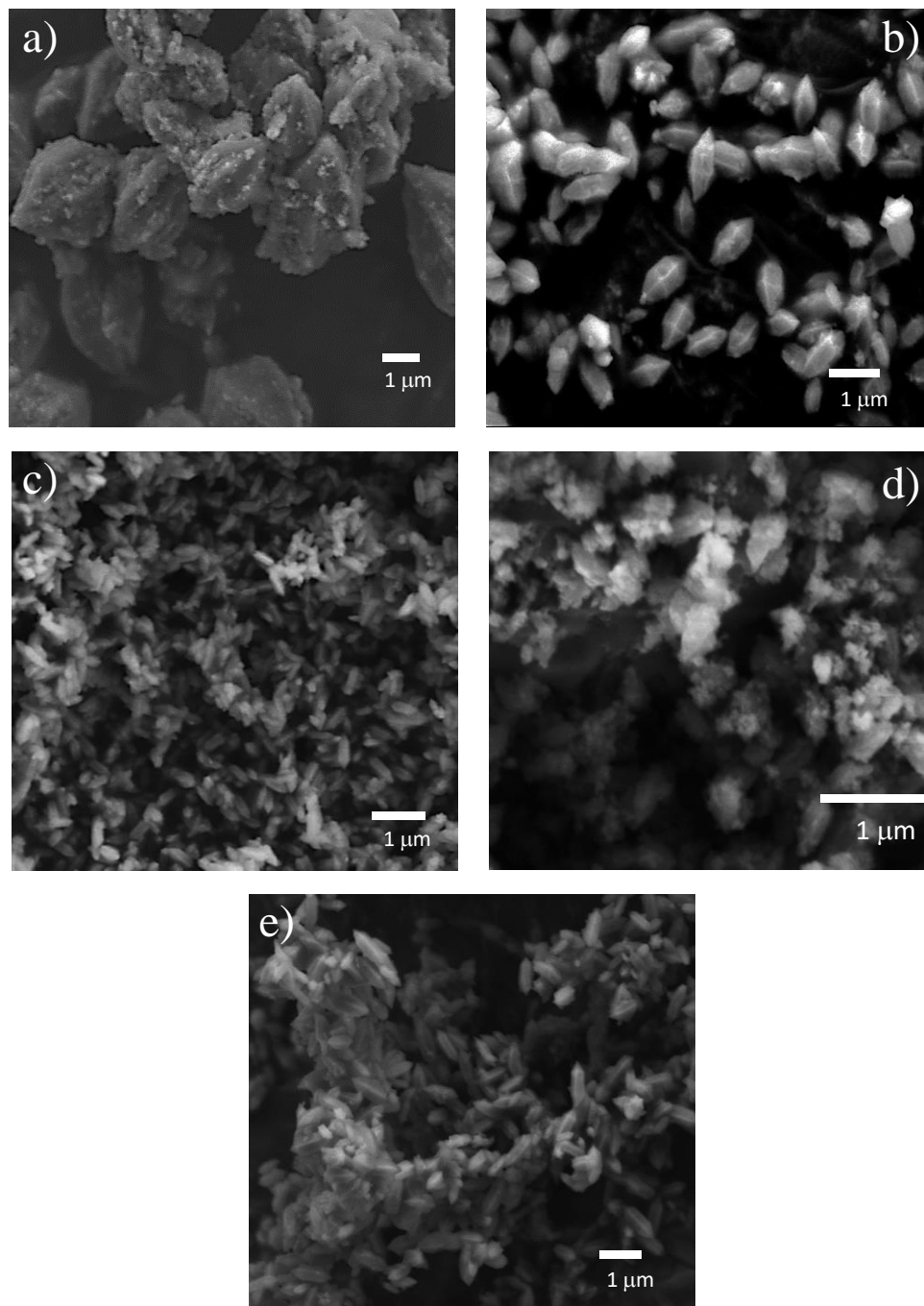


Figure 2. Scanning Electron Micrographs of MIL-88A samples (a: *Fe-fum-B2*, b: *Fe-fum-B1*, c: *Fe-fum-PP10*, d: *Fe-fum-PP5*, e: *Fe-fum-CP10*).

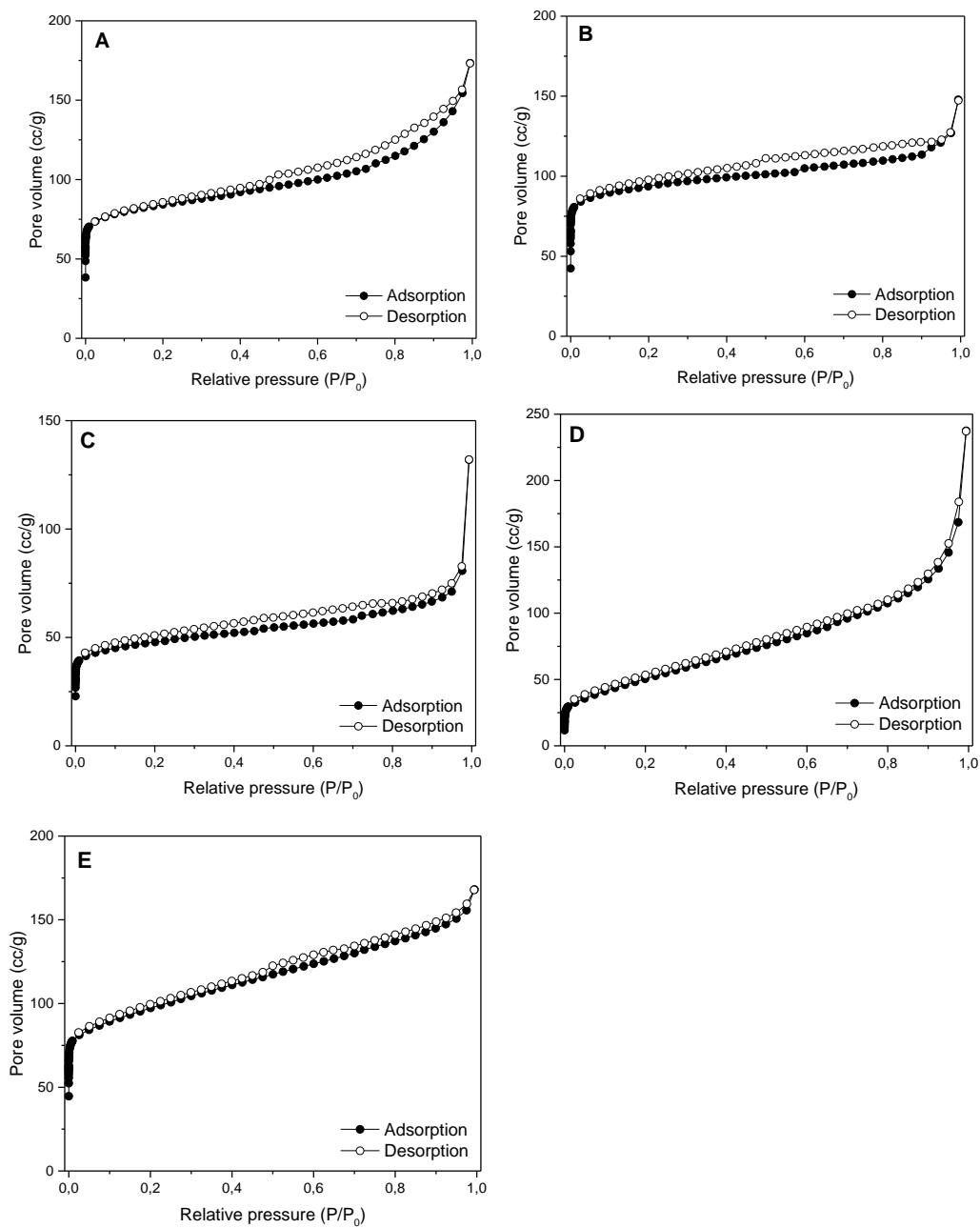


Figure 3. N_2 isotherms adsorption curves for MIL-88A samples (a: *Fe-fum-B2*, b: *Fe-fum-B1*, c: *Fe-fum-PP10*, d: *Fe-fum-PP5*, e: *Fe-fum-CP10*).

Table 2. BET Surface, External area, Micropore area, Micropore volume, Pore volume and width (DFT) calculated from the N₂ adsorption isotherms for the MIL88A samples.

Sample	S _{BET} (m ² ·g ⁻¹)	External area (m ² ·g ⁻¹)	Micropore area V-t method (m ² ·g ⁻¹)	Micropore volume V-t method (cm ³ ·g ⁻¹)	Pore volume DFT (cm ³ ·g ⁻¹)
Fe-fum-B2	317	88	229	0.092	0.256
Fe-fum-B1	359	63	296	0.118	0.179
Fe-fum-PP10	179	50	129	0.052	0.162
Fe-fum-PP5	189	189	-	-	0.306
Fe-fum-CP10	352	162	189	0.080	0.253

Raman spectra of the samples (**Figure 4**) evidenced the presence of the fumarate ligands in the framework. The band at 1650 cm⁻¹ was attributed to the symmetric vibration modes of the C=C, meanwhile the band at 3070 cm⁻¹ corresponds to the vibration =C-H, both present in fumaric acid [42]. The band at 1575 cm⁻¹ is attributed to the amide group, which can be associated to DMF coordination in the structure [43]. Even though the samples were dried under vacuum at 85 °C to remove the synthesis and washing solvents (DMF and anhydrous ethanol, respectively), the Raman spectra for all the samples still showed a remarkable band below 3000 cm⁻¹ which can be attributed to alkyl groups present in the organic solvents employed. These molecules are strongly attached by surface coordination and their presence was also revealed by the thermogravimetric analysis in **Figure 5**.

The thermogravimetric profile in all samples evidenced three losses. The first weight loss (below 100 °C) was attributed to the ethanol used in washing. The second loss starting at c.a. 150 °C was associated to the volatilization of DMF molecules. Slight degradation of the fumaric ligand started decomposing at 170 °C. The final loss at 275 °C corresponded to the complete decomposition of the ligand. Above 300 °C, the weight of MIL-88A was practically constant up to 800 °C.

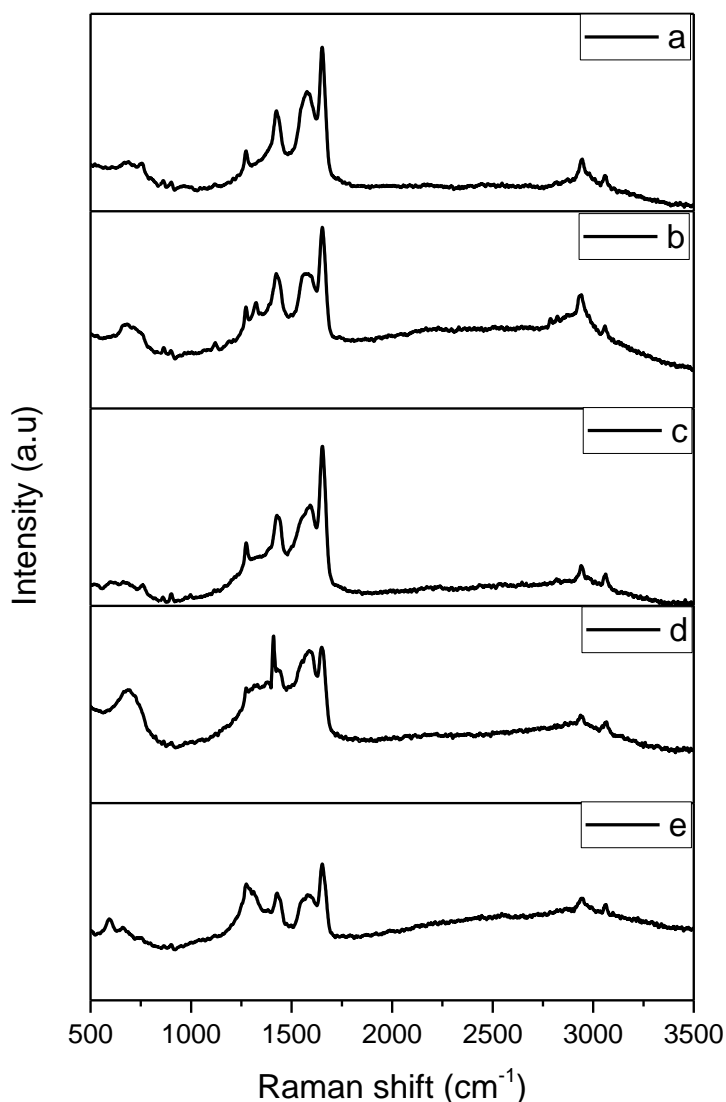


Figure 4. Raman spectra of MIL-88A samples recorded with a green light laser ($\lambda = 532$ nm). (a: *Fe-fum-B2*, b: *Fe-fum-B1*, c: *Fe-fum-PP10*, d: *Fe-fum-PP5*, e: *Fe-fum-CP10*).

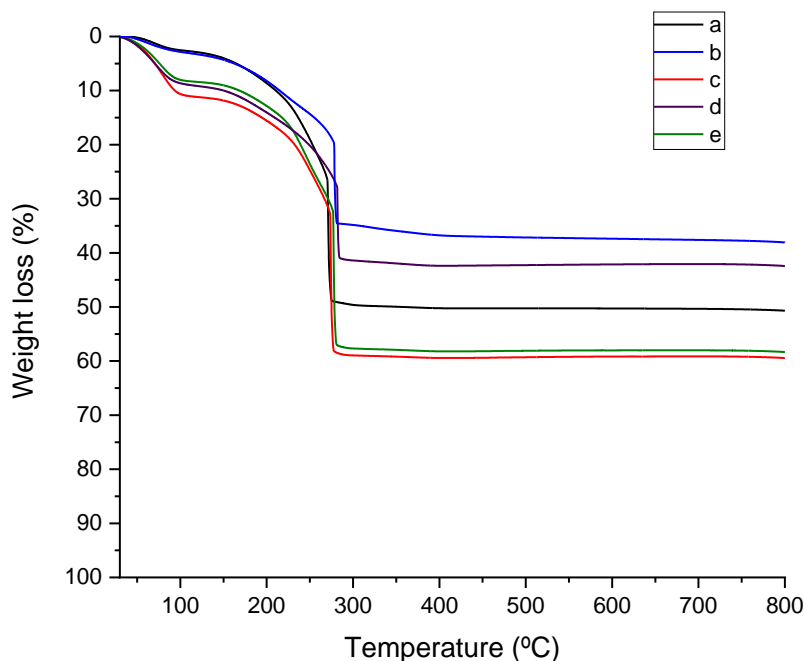


Figure 5. Thermogravimetric Analysis curves for MIL-88A samples. (a: *Fe-fum-B2*, b: *Fe-fum-B1*, c: *Fe-fum-PP10*, d: *Fe-fum-PP5*, e: *Fe-fum-CP10*).

The easy, fast and inexpensive synthesis of MIL-88A materials makes them promising candidates for gas adsorption. The performance of the MIL-88A samples and other MOFs as ethylene adsorbents was studied (Table 3). Figure 6 depicts the adsorption isotherms of C_2H_4 for all samples. As can be observed, each material exhibited a similar profile with a moderate increase in ethylene adsorption along the whole pressure range. The higher ethylene adsorption was obtained for *Fe-fum-B1* sample reaching $1.64 \text{ mmol} \cdot \text{g}^{-1}$ at atmospheric pressure and 273 K. This uptake capacity can be ascribed to its high crystallinity, optimal morphology and high micropore area. *Fe-fum-CP10* and *Fe-fum-B2* showed a lower ethylene uptake with 1.16 and $0.90 \text{ mmol } C_2H_4 \cdot \text{g}^{-1}$, respectively. Even though both samples had similar crystallinity, their textural properties and morphology are quite different and seem to be determinant factors in the adsorption process (see Figure 2 and Table 2). *Fe-fum-PP10* showed an adsorption value $0.68 \text{ mmol } C_2H_4 \cdot \text{g}^{-1}$ due to its low surface area (ca. $179 \text{ m}^2 \cdot \text{g}^{-1}$). The lowest value for ethylene adsorption was obtained by *Fe-fum-PP5* ($0.60 \text{ mmol } C_2H_4 \cdot \text{g}^{-1}$). Although this material possesses a surface area comparable to *Fe-fum-PP10*, the absence of microporous leads to a less interaction with ethylene molecules.

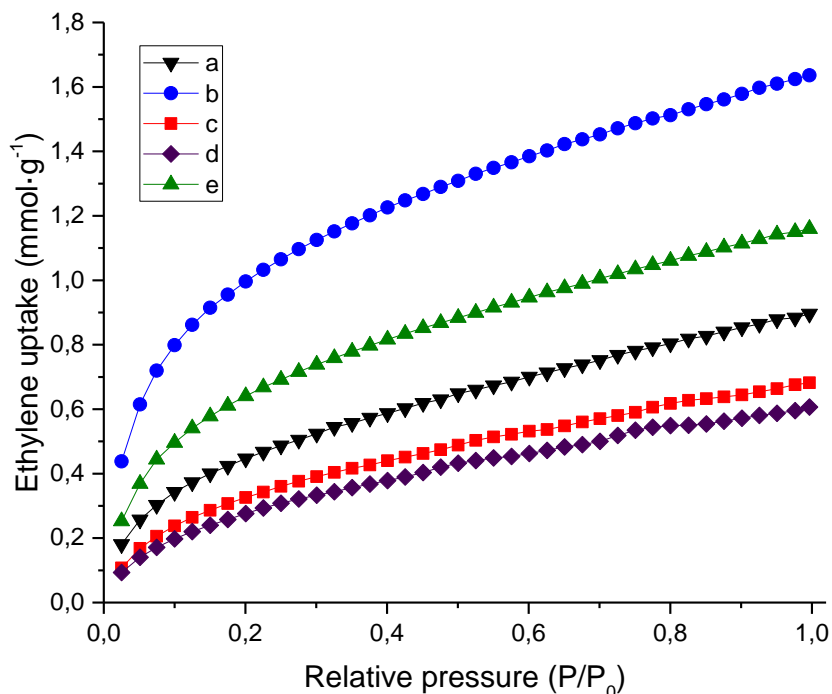


Figure 6. Ethylene adsorption curves for different MIL88-A (a: *Fe-fum-B2*, b: *Fe-fum-B1*, c: *Fe-fum-PP10*, d: *Fe-fum-PP5*, e: *Fe-fum-CP10*).

Finally, in order to compare the performance of MIL-88A samples in ethylene adsorption with other materials, several well-known MOFs (A520-BASF, MOF-801, UiO-66, and HKUST-1) were chosen for this study. Their textural properties and ethylene uptake are given in **Table 3**. Most of them have not previously been used as ethylene adsorbents. All the materials analyzed have an adequate pore size to encapsulate the ethylene molecule (4.163 Å [44]). All of them have much higher specific surface areas than MIL-88A. As it can be observed, the adsorption capacity was strongly dependent on the structure and properties of each MOF. Thus, HKUST-1 exhibited the highest ethylene uptake, followed by A520-BASF. If the adsorption isotherms were normalized by square meter (**Figure 7**), MIL-88A, specifically *Fe-fum-B1*, would have the highest specific uptake, with similar values to HKUST-1 and A520-BASF. However, materials MOF-801 and UiO-66 provided much lower values, both materials with Zr as the metal node. The differences in adsorption capacity for ethylene among the different MOFs materials cannot be attributed to surface charge divergences determined from measurements of the point of zero charge in solution (**Table 3** and **Figure S2**). It is assumed that metal- π interactions

are mainly responsible for the adsorption of ethylene in these materials (**Figure 8**). Accordingly, those MOFs that are more effective for ethylene adsorption must have a higher population of open metal sites, i.e. Lewis acid sites.

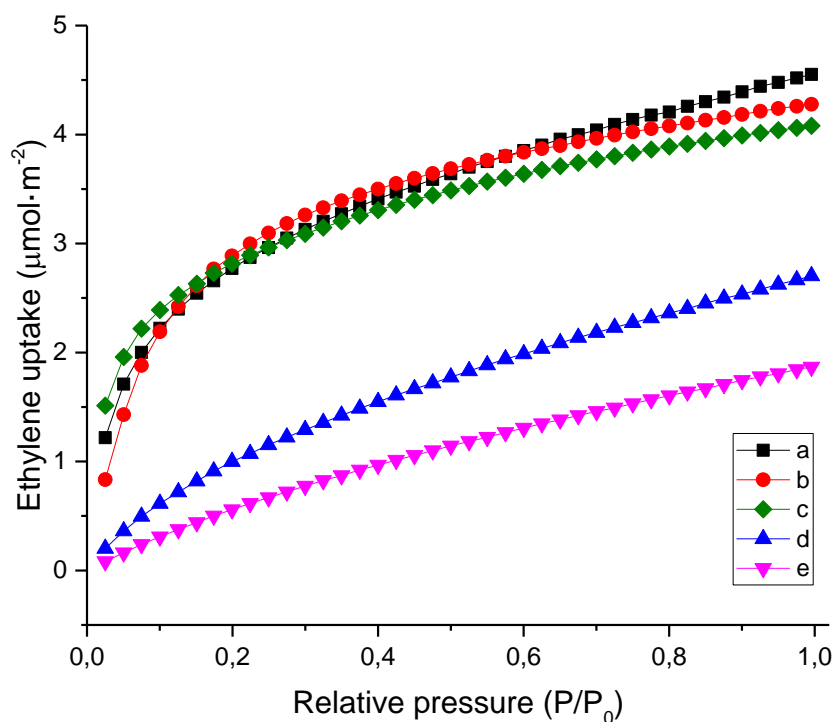


Figure 7. Ethylene adsorption curves for different MOF materials (a: *Fe-fum-B1*, b: *A520-BASF*, c: *HKUST-1*, d: *MOF-801*, e: *UiO-66*).

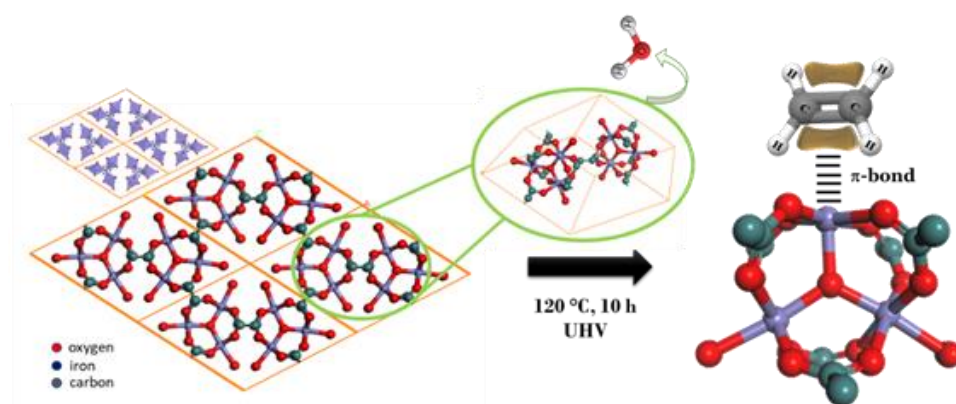


Figure 8. Mechanism of adsorption of ethylene on MIL-88A by Fe- π interactions.

Table 3. S_{BET} of studied MOF materials and their ethylene adsorption performance.

Material	Metallic center	Organic linker	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore size (\AA) (<i>reported in literature</i>)	Point of zero charge values	Ethylene adsorption ($\text{mmol}\cdot\text{g}^{-1}$)
Fe-fum-B1	Fe	Fumaric acid	359	6.0 [21]	6.6	1.63
A520-BASF	Al	Fumaric acid	911	5.8 [45]	6.9	3.90
MOF-801	Zr	Fumaric acid	856	4.8, 5.6, 7.4 [37]	4.3	2.31
UiO-66	Zr	1,4-benzenedicarboxylic acid	1400	7.5, 12 [46]	6.0	2.61
HKUST-1	Cu	1,3,5-benzenetricarboxylic acid	2042	9 [38]	3.3	8.33

The stability of these materials as adsorbents of ethylene was checked by carrying out three consecutive adsorption-desorption cycles with samples Fe-fum-B1 and A520-BASF (**Figures S3** and **S4**). Both materials provided practically identical isotherms in every cycle. The adsorption capacities of Fe fumarate were 1.62, 1.79 and 1.80, whereas those for Al fumarate were 3.92, 3.92 and 3.95. Furthermore, XRD analysis of the samples revealed that they remained intact after three ethylene adsorption-desorption cycles (**Figure S5**). Consequently, these materials can be reused for the adsorption of ethylene.

According to our results, fumarate-based MOFs, such as MIL-88A, are interesting materials for the adsorption of ethylene. In virtue of their biocompatibility and low cost, they can be considered as materials of choice for their application in the packaging of fruits. Nevertheless, further studies would be required to test these materials under real conditions.

5.1.2.4. Conclusions

A modified ultrasound method to synthesize MIL-88A crystals with high crystallinity and high surface area has been accomplished. X-ray

diffraction of MIL-88A particles showed more crystalline structures than those obtained in previous studies. Depending on the ultrasound conditions and reaction times, particles with different morphology, surface area and porosity were obtained. Those materials obtained using ultrasound probes exhibited smaller particles with a higher aspect ratio than those synthesized in an ultrasound bath. Also, those materials synthesized under ultrasound bath conditions, Fe-fum-B2 and Fe-fum-B1, exhibited higher surface areas and higher proportion of micropores. The incorporation of the fumarate linkers in the structure was confirmed by Raman and thermogravimetric analysis. Furthermore, MIL-88A particles showed a good response for ethylene adsorption. More concretely, Fe-fum-B1 possesses a specific ethylene adsorption comparable to other MOFs, even though its ethylene uptake is lower due to its moderate specific surface area. These materials can be reused several times without appreciable loss of adsorption capacity. The good performance in ethylene adsorption makes them promising materials for ethylene capture and elimination in the packaging of fruits.

Acknowledgements

The authors gratefully acknowledge the financial support from Ramon Areces Foundation, Spanish Ministry of Economy and Competitiveness (Project MAT2013-44463-R), Andalusian Regional Government (FQM-346 group) and Feder Funds. Also, the authors thank the scientific support from the Nanochemistry and Fine Chemistry Research Institute (IUIQFN) at the Córdoba University.

5.1.2.5. References

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Appendix II: Supplementary Information

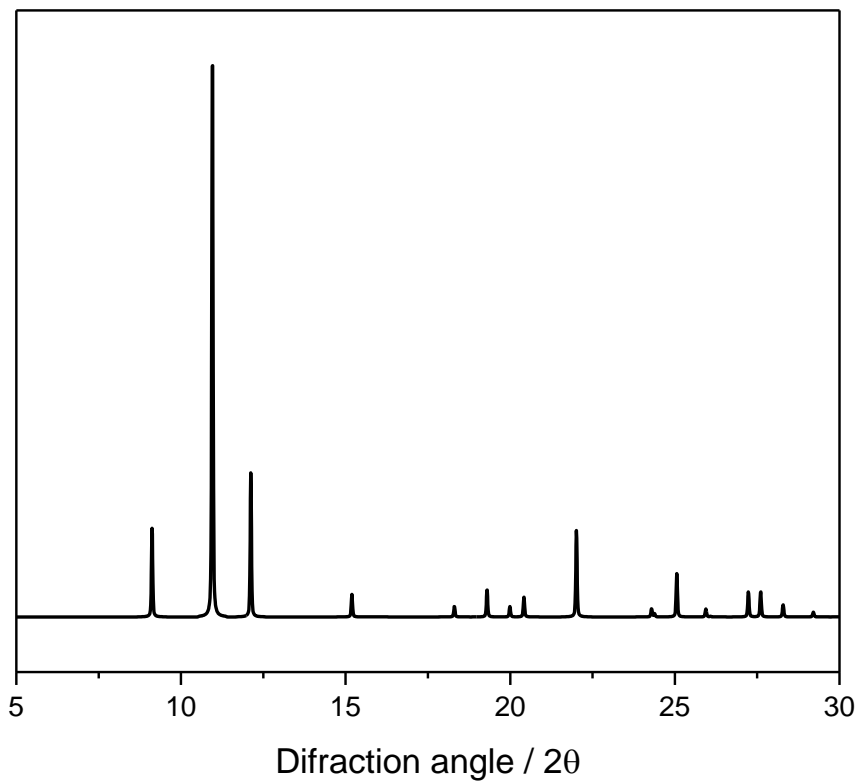


Figure S1. Simulated XRD pattern of MIL-88A

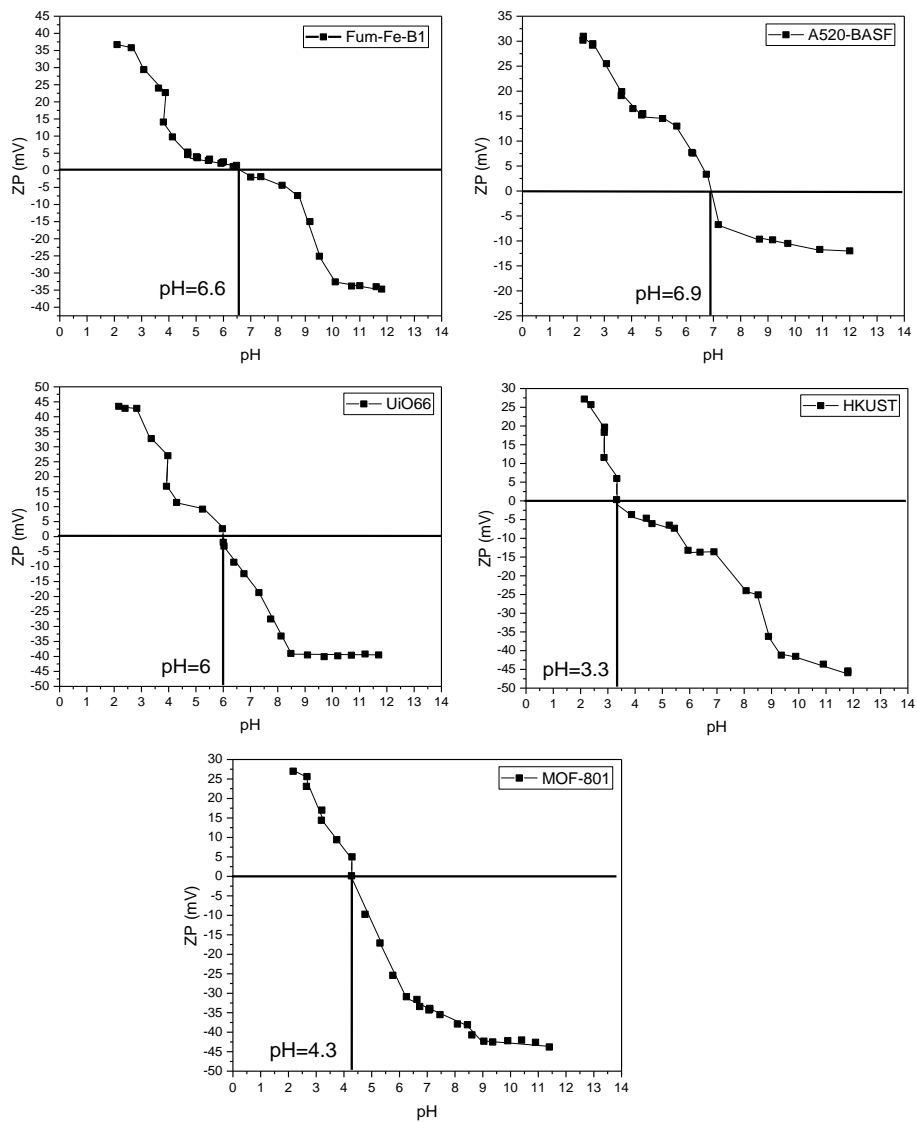


Figure S2. Variation of zeta potential as a function of pH for studied MOF materials.

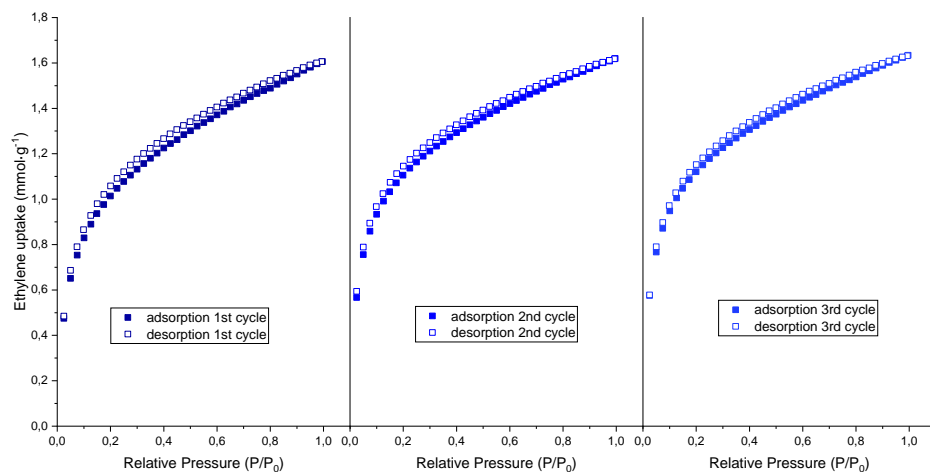


Figure S3. Consecutive ethylene adsorption-desorption cycles for Fe-fum-B1.

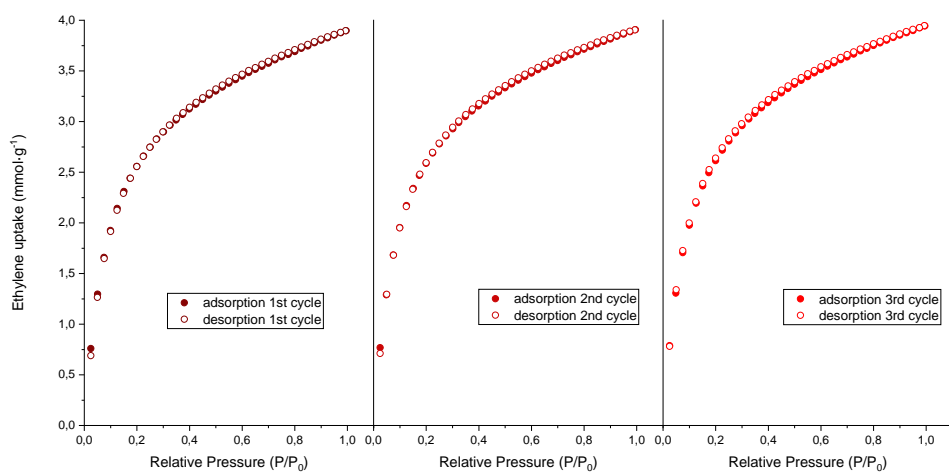


Figure S4. Consecutive ethylene adsorption-desorption cycles for A520-BASF.

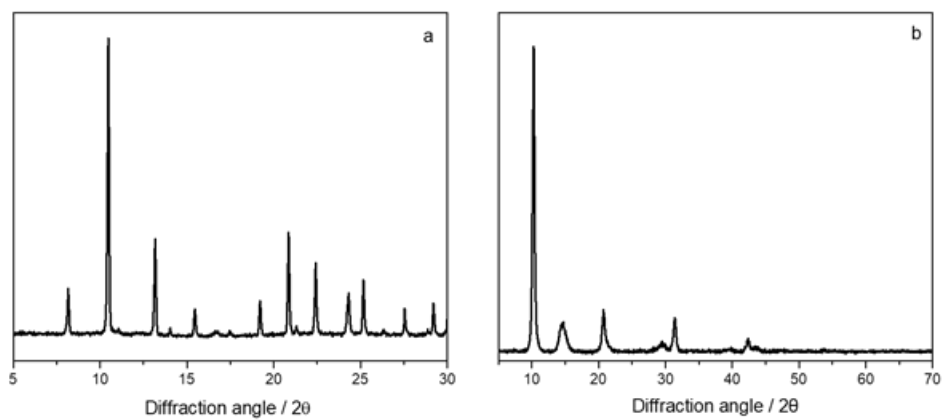


Figure S5. XRD analysis after three consecutive ethylene adsorption-desorption cycles for a) Fum-Fe-B1 and b) A520-BASF.

5.1.3. MIL-88A Metal-organic Framework as a Stable Sulfur-host Cathode for Long-cycle Li-S Batteries

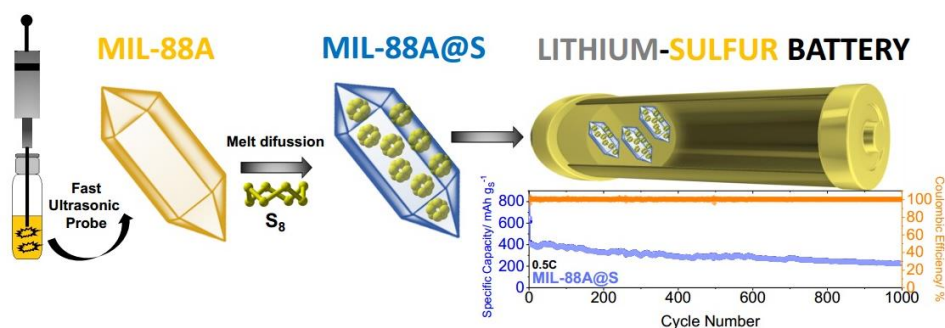
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Published in *Nanomaterials*

Nanomaterials, 2020, vol. 10, no 3, p. 424.

DOI: <https://doi.org/10.3390/nano10030424>

Abstract

Lithium-sulfur (Li-S) batteries have received enormous interest as a promising energy storage system to compete against limited, non-renewable, energy sources due to their high energy density, sustainability, and low cost. Among the main challenges of this technology, researchers are concentrating on reducing the well-known “shuttle effect” that generates the loss and corrosion of the active material during cycling. To tackle this issue, metal-organic frameworks (MOF) are considered excellent sulfur host materials to be part of the cathode in Li-S batteries, showing efficient confinement of undesirable polysulfides. In this study, MIL-88A, based on iron fumarate, was synthesised by a simple and fast ultrasonic-assisted probe method. Techniques such as X-ray diffraction (XRD), Raman spectroscopy, Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and N₂ adsorption/desorption isotherms were used to characterise structural, morphological, and textural properties. The synthesis process led to MIL-88A particles with a central prismatic portion and pyramidal terminal portions, which exhibited a dual micro-mesoporous MOF system. The composite MIL-88A@S was prepared, by a typical melt-diffusion method at 155°C, as a cathodic material for Li-S cells. MIL-88A@S electrodes were tested under several rates, exhibiting stable specific capacity values above 400 mAh g⁻¹ at 0.1 C. This polyhedral and porous MIL-88A was found to be an effective cathode material for long cycling in Li-S cells, retaining a reversible capacity above 300 mAh g⁻¹ at 0.5 C for more than 1000 cycles, and exhibiting excellent coulombic efficiency.

Keywords: Li-S battery; Metal-Organic Framework; Sulfur composite; Polysulfides confinement

5.1.3.1. Introduction

The current energy economy based on the demand for non-renewable sources, such as fossil fuels and oil, continues to be a high-risk social problem. The increase in CO₂ emissions, global warming, and dramatic climate change, are some of the main problems that are taking place and seriously worrying the future of world society [1–3]. Therefore, it is vitally important to replace these energy generation systems with others based on cleaner and more environmentally sustainable sources of renewable energy [4,5]. In this area, batteries are currently considered a fundamental energy storage system due to their high efficiency and lifetime, and are being postulated as the key to future development of power system applications [6–8].

Lithium-sulfur (Li-S) and lithium-oxygen (Li-O₂) batteries were proposed as promising high-energy rechargeable systems for emerging applications. Despite the various problems that still present, these two attractive systems exceed the initial expectations of them evolving rapidly, improving the efficiency and achieving high performances, which could lead to these devices to their possible implantation in the development of renewable energy sources, electric vehicles and modern electronics [9–11].

Specifically, Li-S batteries are at the forefront in the development of efficient and sustainable high energy systems receiving great interest in recent years [12]. These types of batteries consist of a sulfur cathode, a lithium metal anode, and a polymeric or liquid electrolyte, and are based on the following electrochemical reaction: $16 \text{Li} + \text{S}_8 \rightleftharpoons 8 \text{Li}_2\text{S}$ [13,14]. The most relevant feature of this type of energy storage system is the high theoretical specific capacity of 1675 mAh g^{-1} , and a high theoretical specific energy of 2600 Wh kg^{-1} , considering a total conversion which exceeds 5 times the theoretical energy supplied by Li-ion based systems [15–17]. Apart from these outstanding characteristics, elemental sulfur is a very abundant element in nature, low cost, and environmentally sustainable, while lithium provides advantages such as its low standard potential and light weight [18,19].

The current challenge in these type of systems is mainly focussed on reaching the theoretical values of specific capacity, which is rather complicated because there are several problems derived from practical applications [20]. The dissolution of the lithium sulfur polysulfides (Li₂S_x) inside the electrolyte generates the main problem of this type of battery,

which is called the “shuttle” effect [21]. The soluble polysulfides formed in the cathode are directed towards the anode, reacting with the Li surface forming insoluble species Li_2S and Li_2S_2 , that are continuously deposited at the anode during the charge/discharge cycles [22]. This sequence of unwanted reactions leads to a short life cycle in Li-S batteries, poor efficiency, corrosion of the lithium anode, and a fading of the specific capacity of these systems. Based on this, most research is focussed on the search for various solutions by developing functional materials that make it possible to mitigate this negative effect [23].

In view of novel materials that are attracting enormous attention in recent years, metal-organic frameworks (MOFs) have become one of the most researched areas by the scientific community due to their excellent properties [24]. These types of ordered materials are mainly constructed by metallic ions (clusters) interconnected through multidentate organic ligands (linkers) in networks of one, two, or three dimensions. The high surface area, crystallinity, controllable pore size, flexibility, and functionalisation of the porous surface are some of the main characteristics which determine the versatility of MOFs [25]. Due to their exceptional properties, great interest has been shown in these materials in numerous research areas such as adsorption, catalysis, photocatalysis, luminescence, and electrochemistry [26–29]. Of fundamental interest in applying porous materials based on MOFs in Li-S batteries is their excellent performance as sulfur hosts, and the confining capacity of the polysulfides generated in the charge/discharge processes, so reducing the undesirable “shuttle” effect [30,31].

Various factors affect the performance of Li-S batteries using a certain MOF as a cathodic host material, such as pore structure, adequate particle size, functional organic linkers, and open metal sites in the metal-organic structure [32]. There have been several works reported where MOF materials are included as components that constitute Li-S batteries as a cathode [33,34], or as a separator [35–37]. In most cases, MOF derivatives are used, or the incorporation of additives into the pristine MOF is carried out to improve the conductivity of these energy systems. For example, ZIF-8 is a widely studied material in this technology, showing a different specific capacity depending on the preparation of the composite used as a positive electrode in a range between 400–900 mAh g^{-1} [38–41].

The application of pristine MOFs as a cathode in Li-S systems is a field of research currently under development since most studies in recent years have been focussed on the preparation of composites by modifying

the initial metal-organic framework with the objective of improving its properties. The main advantage of the use of pristine MOFs in energy storage systems is their high porosity and crystallinity, so that they can be excellent sulfur hosts and confiners of the polysulfides generated in electrochemical cycling without the need for any additional experimental treatment to modify the original characteristics of the network. Some widely known pristine MOFs, such as NH₂-MIL-53 (Al), MIL-53 (Al), HKUST-1, or even ZIF-8, have been evaluated by Zhou et al., showing remarkable discharge capacities of 332, 347, 286, and 553 mA h g⁻¹ after 300 cycles, respectively [42]. However, in most studies on MOF-based sulfur cathodes, less than 100 cycles are normally reported, as is the case with MIL-100/1(Cr) [43,44], MIL-100(V) [45], Ni-MOF-867 [46], and [(CH₃)₂NH₂]₂[Cd(L)]·5DMF [47].

Herein, MOF MIL-88A as a host material in Li-S batteries is reported for the first time. MIL-88A is a metal-organic framework based on Fe (III) trimers, octahedrally interconnected through the dicarboxylates of fumaric acid [48]. MIL-88A has been considered as an electronic semiconductor material showing this ability for electronic conduction in photocatalytic [49] or in microbial reduction processes [50]. Some investigations of this material have already been reported in the field of Li-ion batteries, showing highly promising performances and improvements in electrochemical activity due to its high porosity which allows greater contact surface between electrode-electrolyte and an increase in the number of active reaction sites [51–54].

Therefore, in this work, the synthesis of MOF MIL-88A has been carried out by means of a simple, sustainable, and short-time method, assisted by ultrasound. Taking advantage of its textural and morphological properties, this pristine MOF has been used effectively to confine sulfur by the melt-diffusion method. Based on this, the resulting composite is considered a promising candidate as a cathode in Li-S batteries, showing remarkable electrochemical performances, especially during long-cycle testing.

5.1.3.2. Materials and Methods

5.1.3.2.1. Materials

Sodium hydroxide, iron (III) chloride hexahydrate, fumaric acid, absolute ethanol (99.8%), and *N,N*-dimethylformamide (DMF, 99.8%)

were obtained from PanReac AppliChem and used as-received. Sublimed sulfur powder (S, VWR Scientific, Hudson, NH, USA) was dried at 45°C under vacuum overnight. Carbon black Super P (CB, Timcal, Thermo Fisher, Kandel, Germany) and polyvinylidene fluoride (PVDF, Sigma-Aldrich, Merck, Madrid, Spain) were stored at 60°C. *N*-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) was supplied by Sigma-Aldrich. Lithium metal (Li, Gelon Lib, Qingdao, China, 15.6 mm diameter and 0.25 mm thick), 1,3-dioxolane (DOL, anhydrous, 99.8%, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, anhydrous, 99.5%, Sigma-Aldrich) were also used as-received but stored under an Ar-atmosphere. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich) and lithium nitrate (LiNO₃, Sigma-Aldrich) were dried at 120°C under vacuum for three days. Polyethylene membrane (PE, 25 µm thick, Celgard, Charlotte, NC, USA) was used as a separator and dried at 80°C under vacuum for 3 h. Carbon cloth Gas Diffusion Layer (GDL, ELAT LT1400W, FuelCellStore, College Station, Texas, USA, 454 µm thick) was used as a substrate.

5.1.3.2.2. Synthesis of MIL-88A and MIL-88A@S Composite

The ultrasonic method is a facile and rapid process widely used for the synthesis of MOFs [55,56]. In this case, MIL-88A was prepared using a continuous ultrasonic probe (Branson Sonifier, Danbury, CT, USA, 150) since it has been verified in a previous study that a smaller particle size, and a greater aspect ratio, were obtained with this method compared to an ultrasonic bath [57].

The detailed process consisted in the preparation of a 1.25 M ethanolic solution of sodium hydroxide, which was used to dissolve FeCl₃·6H₂O (1 mmol) in approximately 10 mL of the DMF:ethanolic solution with a volume ratio of 4.5:1, while maintaining a constant molar ratio (NaOH/Fe = 0.8). In parallel, an equimolar ratio of fumaric acid (1 mmol) was dissolved in 5 mL of DMF. Afterwards, both solutions were mixed and sonicated with a probe for 10 min, using 20 W and 10 kHz in continuous wave mode. Then, the obtained precipitate was centrifuged at 9000 rpm for 10 min and washed in DMF and in ethanol several times. Finally, the sample was recovered and dried under vacuum at 85°C, overnight, to obtain a porous iron fumarate MOF MIL-88A.

Sulfur can be effectively embedded into the MIL-88A structure by a classical melt diffusion method [58,59]. The as-prepared MIL-88A and elemental sulfur were dried under vacuum and then thoroughly mixed inside

an argon-filled glovebox using a mass ratio of 1:1. Then, the mixture was thermally treated in an Ar atmosphere at 155°C for 20 h. After cooling down, the sulfur solidifies and contracts forming sulfur crystals that bind closely to the host material, finally producing the MIL-88A@S composite.

5.1.3.2.3. Characterisation techniques

X-ray diffraction patterns (XRD) were obtained in a Bruker D8 Discover X-ray diffractometer equipped with a monochromatic Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The patterns were recorded within the 5–80° (2θ) range, using a step size of 0.04° and 1.05 s per step. Raman spectroscopy was applied with a Renishaw Raman instrument (InVia Raman Microscope) furnished with a Leica microscope using a green laser light excitation source (532 nm). The N₂ adsorption–desorption measurements were performed with an Autosorb iQ/ASiQwin (Quantachrome Instruments) and the samples were previously degassed. Sample morphology was investigated with a JEOL JSM-7800F scanning electron microscope (SEM). Also, to verify the sulfur content in the MIL-88A@S composite, thermogravimetric analysis (TGA) measurements were carried out using a Mettler Toledo-TGA/DSC under nitrogen atmosphere by heating the samples from 25 to 600°C at 5°C min⁻¹.

5.1.3.2.4. Cathode Preparation and Electrochemical Characterisation

The positive electrodes were prepared by doctor blade casting of a slurry formed by the MIL-88A@S composite (70 wt.%), carbon black (20 wt.%) as a conducting agent, and PVDF (10 wt.%) as a binder in 0.8 mL of *N*-methyl-2-pyrrolidone on a GDL foil. GDL carbon cloth has proven to be an effective current collector in cathodes of Li-S cells [60,61]. The electrode was dried at 80°C on a heating plate for 3 h and cut into discs of 13-mm diameter with a sulfur loading between 1.0–1.5 mg cm⁻². Then, the working electrodes were dried under vacuum at 45°C overnight.

CR2032-type coin cells were assembled inside a glove box (Ar-filled, M-Braun 150) with discs of Li as negative electrodes. The electrolyte was 1.0 M LiTFSI 1.0 M and 0.4 M LiNO₃ 0.4 M in DOL:DME (1:1 v/v) soaked in a porous polyethylene separator, cut into 16-mm diameter discs and dried at 80°C under vacuum, overnight, prior to use. The addition of LiNO₃ in the electrolyte causes the oxidation of the polysulfides which

become favourable components for the solid electrolyte interphase (SEI), resulting in a decrease in the shuttle effect and preventing parasitic redox reactions between Li and the polysulfides [62].

The electrochemical measurements were carried out using an Arbin BT2143 potentiostat–galvanostat system. The working electrodes were galvanostatically cycled between 2.6–1.85 V vs. Li⁺/Li. Specific capacity values are referred to the mass of elemental sulfur in the electrodes. Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) were recorded on an Autolab equipment. CV was performed at a scan rate of 0.1 mV s⁻¹ within the 1.7–2.6 V range. Impedance spectra were recorded at the open circuit voltage (OCV) condition and after the 3rd CV cycle, by applying an alternative voltage signal of 10 mV amplitude within the 500 kHz to 0.1 Hz frequency range.

5.1.3.3. Results and Discussion

5.1.3.3.1. Textural, morphological, and structural properties

The continuous probe ultrasound-assisted synthesis of the MOF MIL-88A was successfully performed in a short time. The N₂ adsorption-desorption isotherm and pore size distribution (obtained by the Density Functional Theory, DFT method) are shown in **Figure 1**. The textural properties obtained are characteristic for this type of material, showing a high specific surface area (S_{BET}) of 313 m² g⁻¹, pore volume of 0.22 cm³ g⁻¹, and an average pore width of 9.8 Å, sufficient to serve as a host of the sulfur and polysulfides generated in the charging and discharging in the Li-S systems. These surface area and pore volume values are higher than those reported for the MIL-88A MOF obtained by hydrothermal synthesis [63]. The adsorption-desorption curves for the MIL-88A were a combination of type IV isotherm, with a slight hysteresis loop at relative pressures P/P_0 between 0.5–0.8, revealing the presence of mesopores, and type I isotherms, with adsorption values in the filling range of micropores at low relative pressures. The analysis by the DFT model showed a wide distribution of pore sizes, comprising a similar proportion of micropores and mesopores. The micropore volume calculated by the t-method (0.08 cm³ g⁻¹) represents 36% of the total pore volume, confirming the dual meso-microporous character for this material. This interconnected micro-/mesopore system is an ideal candidate to host sulfur, be used as a cathode, and favour the entrapment of lithium polysulfides in Li-S batteries [64].

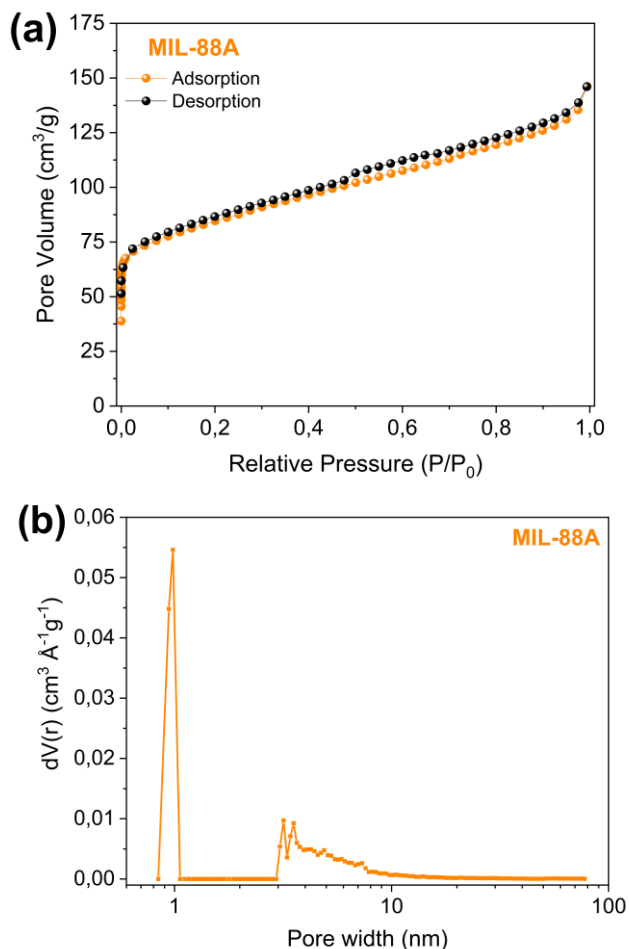


Figure 1. (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of MIL-88A.

SEM images of MIL-88A MOF are shown in **Figure 2**. Its morphology consisted of particles with a well-defined central prismatic portion and pyramidal terminations. It has been reported that ultrasonic assisted synthesis allows for smaller particle size growth of MIL-88A than in conventional solvothermal methods [57]. In this case, the crystal sizes of this MOF were approximately between 900–950 nm long and 200–250 nm wide. This particle shape and size is very suitable and promising to facilitate dispersion and optimal sulfur hosting. The morphology of the sub-micrometric elongated rod-like crystals presented in this MOF obtained by ultrasonic synthesis, is similar to that reported for MIL-88A prepared by different solvo/hydrothermal synthetic methods [56].

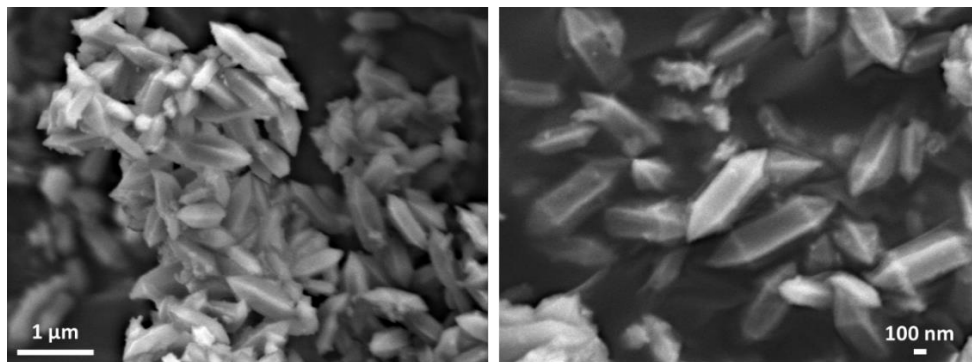


Figure 2. SEM images at different magnifications for MIL-88A MOF.

Raman spectra shown in **Figure 3** confirm the presence of the organic fumarate ligand in MIL-88A and sulfur in the MIL-88A@S composite. In **Figure 3a**, the double bond of the fumaric acid molecule in MIL-88A and MIL-88A@S was evidenced by the appearance of a band at 3071 cm^{-1} , corresponding to the stretching sp^2 C-H vibrations, and a strong peak at 1687 cm^{-1} associated to the symmetric vibration modes C=C [65]. The bands located at 1580 and 1430 cm^{-1} , in the case of fumaric acid, MIL-88A, and MIL-88A@S materials are attributed to the anti-symmetric and symmetric vibrations, respectively, of the carboxylate groups [66–68]. The C-O bond was observed as an intense peak centered at 1297 cm^{-1} . Additionally, the bending vibrations outside the plane of the bond =C-H were placed at Raman shifts of 970 , 953 , and 910 cm^{-1} . The Raman spectra of MIL-88A and MIL-88A@S show a peak below 3000 cm^{-1} that is attributed to sp^3 C-H bond vibrations of solvent molecules remaining coordinated to these materials, despite the drying treatment after the synthesis. As shown in **Figure 3b**, the sulfur contribution in the MIL-88A@S composite was corroborated by the presence of the characteristic S-S peaks in the orthorhombic octahedron $\alpha\text{-S}_8$ at 471 , 217 , and 151 cm^{-1} [69–71].

In **Figure 4a**, the crystallinity of MIL-88A and MIL-88A@S composite is studied by X-ray diffraction (XRD). The inserted image shows the main peaks of the pristine MIL-88A sample, and it can be verified that the position of all of them is in accordance with the structure of this MOF as observed in previous studies [63,72]. On the other hand, the MIL-88A@S composite exhibits well-defined peaks corresponding to the orthorhombic sulfur (PDF # 85-0799), and also the characteristic peaks of the lattice structure of this iron MOF.

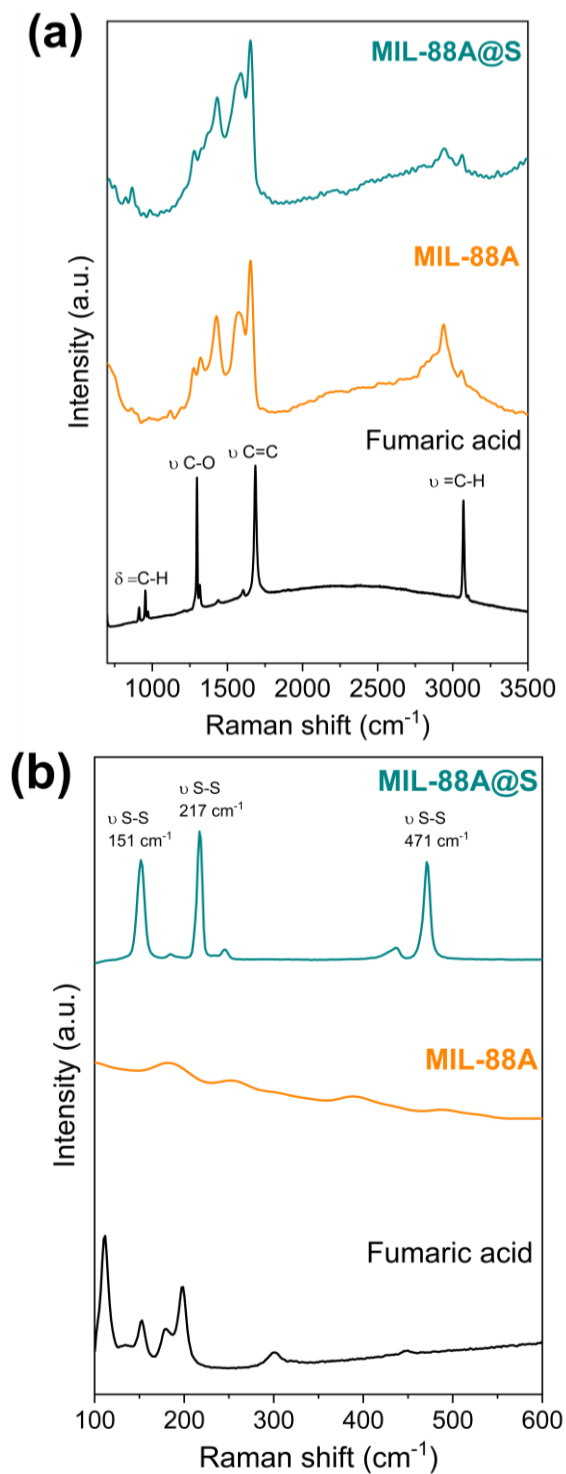


Figure 3. Raman spectra for commercial fumaric acid, MIL-88A and MIL-88A@S registered in shift ranges of 700–3500 (a) and 100–600 cm⁻¹ (b).

These results are attributed to the fact that the incorporation of sulfur does not alter the structural properties of the host material. It should be noted that the presence of the signals due to *S* would be justified when a slight excess of sulfur in the composite is demonstrated. This fact indicates that not all sulfur is confined in the porosity of the matrix but that part of this sulfur is deposited on the surface [73]. Moreover, **Figure 4b** depicts the thermogravimetric stability of the prepared MOF tested at a temperature range of 30–600°C using an N₂ flow. There are mainly three regions in the decomposition pattern. In the first step, the weight loss around 100°C was due to the loss of adsorbed water and the remaining solvent molecules. In addition, the organic ligand was progressively decomposed in a couple of stages, leading to the entire collapse of the organic structure at 420°C. Hence, the TGA curve of MIL-88A reinforces that the removal of residual solvent molecules from the pores results in a high surface and large pore volume [74]. Furthermore, the amount of sulfur fixed to the MOF structure could be quantified using the TGA curve of the sample MIL-88A@S in an inert atmosphere. In particular, the evaporation of sulfur occurs between 160–400°C, and finally, the percentage of sulfur assimilated by the host material was 40% by weight.

5.1.3.3.2. Electrochemical Properties

The study of the electrochemical performance of the Li-S battery using the MIL-88A@S composite was carried out by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic measurements (GCD), and was conducted to investigate the redox process of the active material. The cyclic voltammograms of the Li/LiTFSI-LiNO₃-DOL:DME/MIL-88A@S cell containing lithium metal anodes, liquid electrolyte, and composites cathodes of MOF and sulfur, are shown in **Figure 5a**. During the first scan, two cathodic peaks are observed at 2.32 V and 1.95 V respectively, and an anodic peak at 2.49 V. In this first discharge, the broad reduction peak could be due to the fact that the electrochemical reaction needs to overcome the absorbing energy between S and the conductive matrix, as well as the low dissolution capacity of the polysulfide in the liquid electrolyte [75]. During successive scans, the peaks appear displaced; in the discharge process at 2.33 V and 1.99 V, and during the oxidation process at lower values, around 2.44 V.

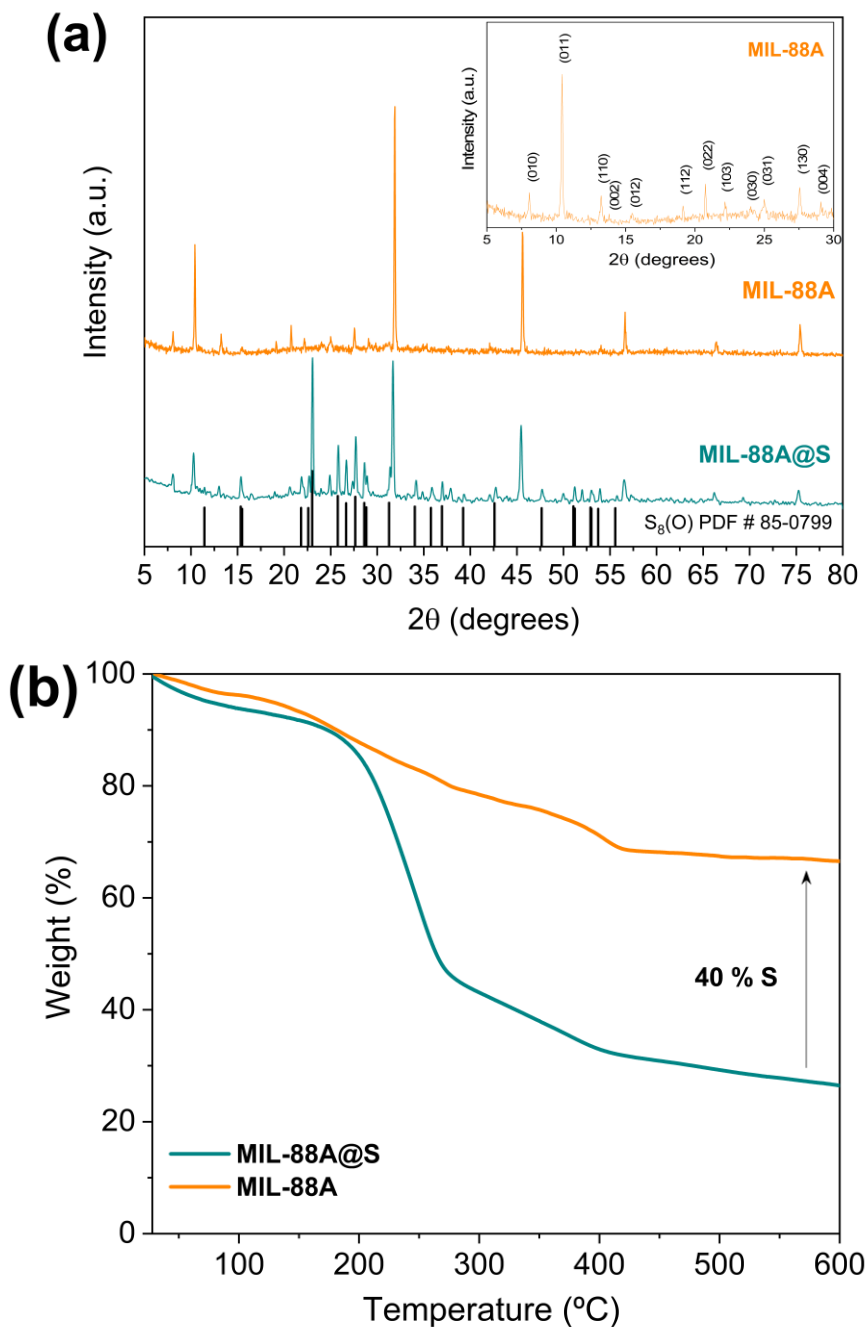


Figure 4. (a) XRD patterns of MIL-88A (orange), MIL-88A@S composite (green), and reference data for S_8 (PDF# 85-0799, black). Inset: XRD patterns of MIL-88A recorded from 5° to 30° (2θ); and (b) TGA curves of both synthesised samples.

After the shift of the potentials between the first CV curve and the remaining ones, a smaller potential gap between the anodic and cathodic peak takes place, resulting in a lower polarisation and resistance within the cell. This fact is corroborated with the EIS measurements of the positive electrode, consisting of a mixture of sulfur and an MOF based material. **Figure 5b** shows the Nyquist plots of the impedance spectroscopy test performed before and after the CV cycles. In both cases, the equivalent circuit of the cell would be $R_e(R_1Q_1)(R_2Q_2)Q_3$, where the electrolyte resistance (R_e) is similar in OCV and after the CV cycles, with values of 7.28 Ω and 7.22 Ω , respectively; the medium-high frequency semicircles (R_iQ_i) are related to the electrode/electrolyte interface, and consequently, to the formation of the SEI; and the low-frequency pseudo-capacitance (Q_3) represents the semi-infinite Li^+ diffusion or capacitive behaviour of the cell [76]. In addition, a marked decrease in global resistance values can be observed from 57.23 Ω , at the OCV, to values of 23.15 Ω after the cyclic voltammetry tests. This process, that entails a decrease in the resistance of the cell, indicates that electrode activation cycles would be necessary, and even, in some cases, the voltage window used for galvanostatic cycling at high rates should be modified [77].

The galvanostatic measurements of the Li/LiTFSI-LiNO₃-DOL:DME/MIL-88A@S cells were carried out by cycling at various currents as well as at a constant C-rate of 0.5 C. The rate capability test (**Figures 6a** and **b**) for the MIL-88A@S composite provided an initial capacity of 600 mAh g⁻¹ that was stabilized over the first five cycles, displaying an average discharge capacity of 482 mAh g⁻¹ at 0.1 C. This maximum capacity value gradually decreased to about 395, 374, 333, 274, 152, and 55 mAh g⁻¹, at 0.125 C, 0.2 C, 0.33 C, 0.5 C, 1 C, and 2 C, respectively, as demonstrated by the cycling trends of **Figure 6a**. When the current rate was restored to 0.1 C, the electrode recovered a capacity value of about 375 mAh g⁻¹. In addition, the coulombic efficiency of the cell is represented on the right axis and at low current densities (0.1 and 0.125 C), values thereof close to 95% can be observed, while for the remaining cycling rates, these values are close to 100%. This phenomenon is seen more clearly in **Figure 6b**, where the charge and discharge profiles during the first cycles are not well defined. Additionally, charge profiles of the 1st and 2nd cycles showed a high polarisation at the beginning of cycling as previously indicated in the first cycle of the CV, which could be caused by the greater resistance that the cell presents until the SEI is formed, as previously observed for MOFs as sulfur hosts in Li-S batteries [78].

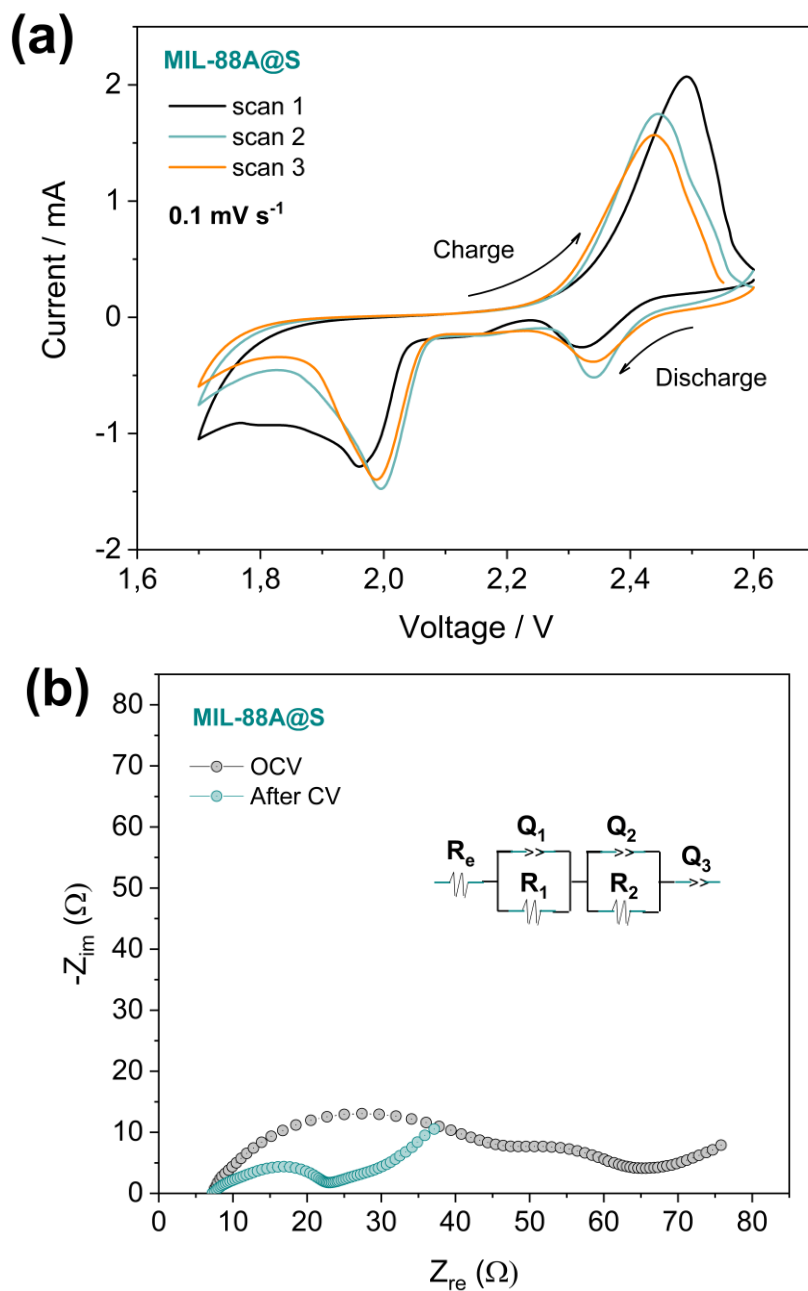


Figure 5. (a) CV profiles of Li/LiTFSI-LiNO₃-DOL:DME/MIL-88A@S battery at room temperature. Scan rate: 0.1 mV s^{-1} , voltage range: 1.7–2.6 V; and its corresponding (b) EIS measurements in open circuit voltage (OCV) and after the third CV cycle.

In order to avoid these harmful effects, the Li/LiTFSI-LiNO₃-DOL:DME/MIL-88A@S cell has been studied by a long-term cycling at a moderate constant current of 0.5 C (**Figure 7**), after two activation cycles performed at 0.1 C. As can be seen, two plateaus at 2.35 V and 2.0 V are clearly observed during the discharge process at 0.5 C, which correspond to the formation of long chain lithium polysulfides (Li₂S_x, 4 ≤ x ≤ 8), and short-chain lithium polysulfides (such as Li₂S₂ and Li₂S), respectively, and which correspond to the potential values of the cathode peaks obtained in the cyclic voltammetry measurements (**Figure 5a**). Such a discharge profile is typical for sulfur cathodes [79].

From the third cycle, the cell delivers an initial discharge capacity of about 400 mAh g⁻¹, and 200 mAh g⁻¹ after 1000 cycles, revealing a slow decay of 0.05% per cycle, possibly attributed to the progressive loss of active material caused by the irreversible formation of short-chain lithium polysulfides [80]. More strikingly, after more than 1000 cycles at 0.5 C, the Li/LiTFSI-LiNO₃-DOL:DME/MIL-88A@S cell is still working, providing 100% coulombic efficiency after activation cycles and exhibiting remarkable cycling stability.

Few previous studies have reported the long-term cyclability for simple MOF@S cathodes in Li-S batteries. Zhou et al. [42] demonstrated that Li-S cells, based on MOFs such as ZIF-8, MIL-53 (Al), NH₂-MIL-53 (Al), and HKUST-1, reach capacities of 550, 345, 330, and 285 mAh g⁻¹ respectively, after 300 cycles at 0.5 C rate. However, although the composites contained 50 wt.% sulfur, the electrodes had to be prepared with 30 wt.% conductive agent (CB), reducing the active composite content in the cathode.

To the best of our knowledge, only Bai et al. [33] have reported MOF-based cathodes with ultra-high cyclability. Sulfur composites based on ZIF-8, ZIF-67, and HKUST-1, have delivered specific capacities of 170, 150, and 250 mAh g⁻¹ respectively, after 1000 cycles at 0.2 C rate. Two disadvantages are found compared to the MIL-88A@S presented in our work: the need to previously synthesise sulfur nanoparticles, and the lower active sulfur content in composites (below 30 wt.% S).

Therefore, the MIL-88A MOF is presented for the first time as an effective sulfur host for Li-S cells, with an appropriate sulfur content in the cathode and remarkable stability in long-term cyclability.

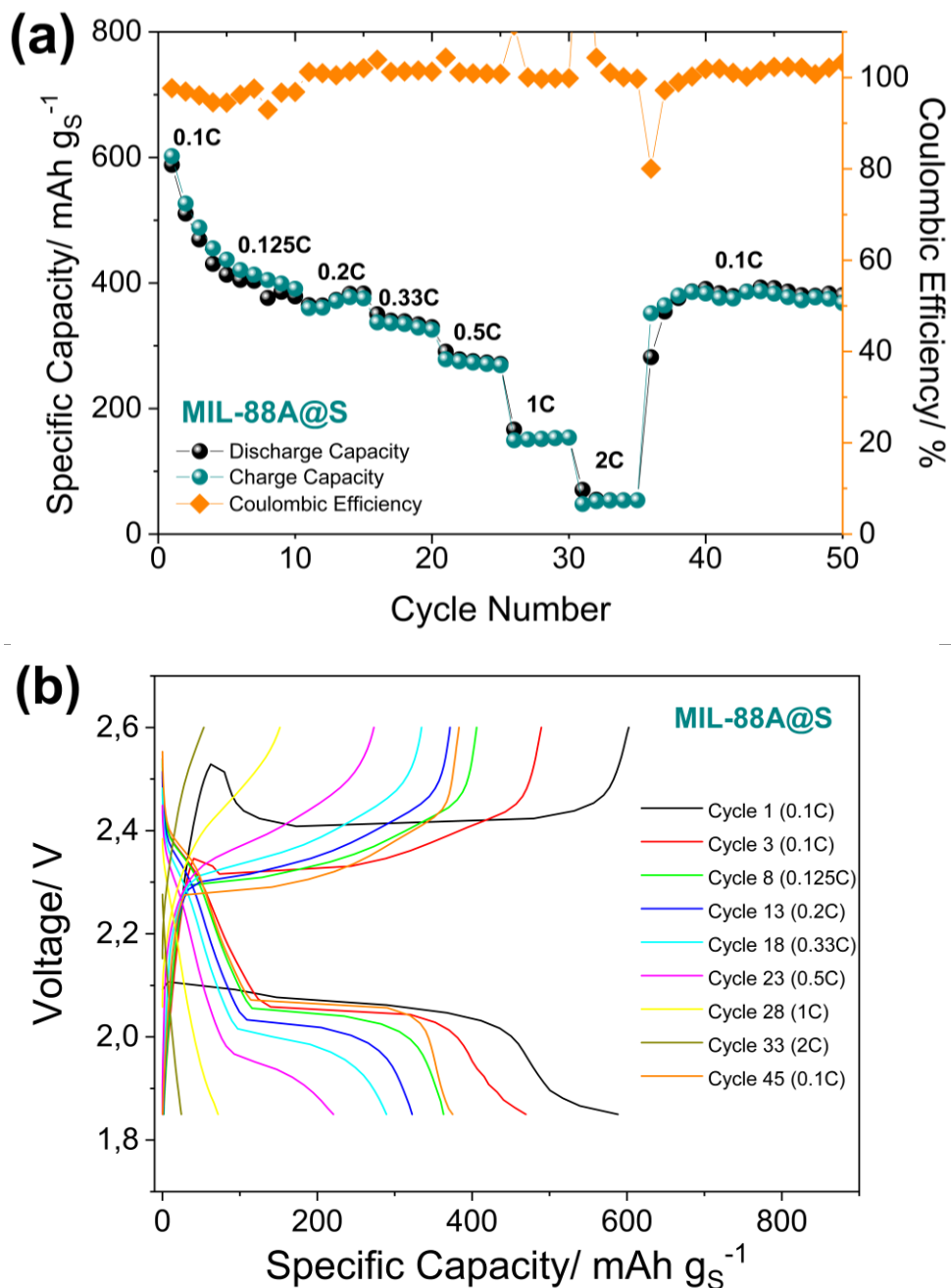


Figure 6. (a) Rate capability cycling behaviour performed at $C/10$, $C/8$, $C/5$, $C/3$, $C/2$, 1 C, and 2 C ($1\text{C} = 1675 \text{ mA g}^{-1}$) at room temperature, and (b) corresponding voltage profiles of a Li/S cell using the LiTFSI-LiNO₃-DOL:DME electrolyte and MIL-88A@S electrode. Voltage limits 1.85 V–2.6 V.

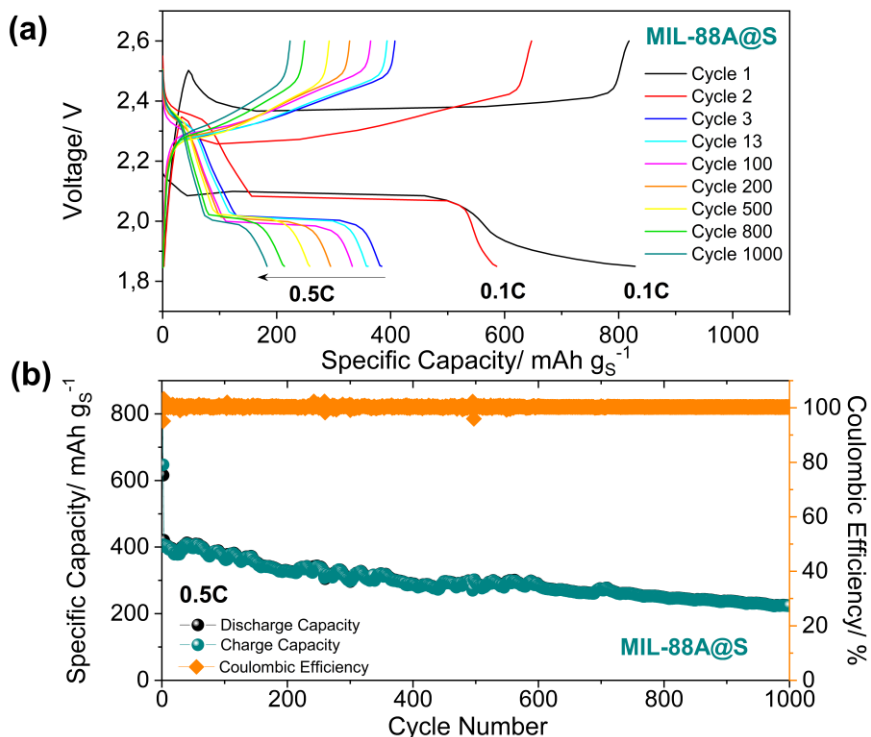


Figure 7. (a) The discharge and charge profiles of a Li-S cell using a constant rate of 0.5 C ($1\text{ C} = 1675\text{ mA g}^{-1}$) within a potential range of 1.85–2.6 V vs. Li^+/Li , and (b) the delivered capacity from the discharge and charge and coulombic efficiency vs. the cycle number.

5.1.3.4. Conclusions

In summary, an iron metal organic framework (MIL-88A) has been prepared by fast ultrasound-assisted synthesis. XRD and textural analyses have confirmed that the MIL-88A material exhibited a high crystallinity, specific area and pore volume, suitable to be used as a matrix to host sulfur in Li-S batteries. Sulfur was incorporated by the melt-diffusion method at 155°C because the conventional composites preparation methods for carbonaceous matrices were unsuccessful. In fact, the main problems initially observed in the synthesis of composites were the loss of the morphology by the use of ball milling, or the deterioration of the MOF due to the use of certain solvents. Next, the positive electrode was directly prepared using the primitive MOF, without calcining and without adding any additional additives to those commonly used for the manufacture of electrodes (CB and PVDF). MIL-88A@S composite demonstrated good storage capacity at high current densities and a brilliant electrochemical

response during prolonged cycling to 1000 cycles, supplying an average specific capacity of 300 mAh g^{-1} at a sizeable rate of 0.5 C. The results thus suggest that this composite material could be a promising component for lithium-sulfur batteries. Besides, the appealing property of these cathodes is the excellent long-term cycling stability, considering that it works directly with the primitive MOF.

Author Contributions: Conceptualisation, A.C. and F.J.R.-S.; investigation, A.B. and J.A.-G.; writing—original draft preparation, A.B. and J.A.-G.; writing—review and editing, A.C., D.E. and F.J.R.-S.; supervision, J.M..

Funding: The research was supported by Ramon Areces Foundation, Spanish Ministry of Economy and Competitiveness (RTI2018-101611-B-I00, MAT2017-87541-R), Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981), Andalusian Regional Government (FQM-346 and FQM-175 groups) and Feder Funds.

Acknowledgments: The authors wish to acknowledge the technical staff from the Instituto Universitario de Nanoquímica (IUNAN) and Servicio Central de Apoyo a la Investigación (SCAI) of the Cordoba University.

Conflicts of Interest: The authors declare no conflict of interest.

5.1.3.5. References

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**5.2. Section 2: Silica-based
organic-inorganic hybrid
materials - Periodic
Mesoporous Organosilicas
(PMOs)**

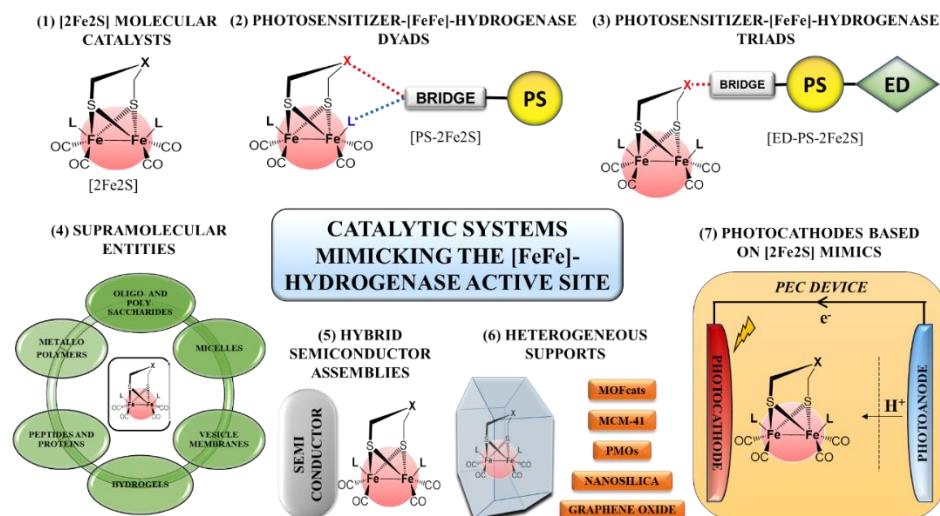
5.2.1. Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production

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Published in *Coordination Chemistry Reviews*

Coordination Chemistry Reviews, 2021, vol. 448, p. 214172

DOI: <https://doi.org/10.1016/j.ccr.2021.214172>

Abstract

A global hydrogen economy could ensure environmentally sustainable, safe and cost-efficient renewable energy for the 21st century. Solar hydrogen production through artificial photosynthesis is a key strategy, and the activity of natural hydrogenase metalloenzymes an inspiration for the design of synthetic catalyst systems.

[FeFe]-hydrogenase enzymes, present in anaerobic bacteria and green algae, are the most efficient class of biological catalysts for hydrogen evolution. The enzymes operate in an aqueous environment, utilizing electrons that ultimately stem from photosynthesis as the only energy source. Functional synthetic models of the [FeFe]-hydrogenase enzyme active site have garnered intense interest as potential catalysts for the reduction of protons to molecular hydrogen.

Herein, we take an extensive journey through the field of biomimetic hydrogenase chemistry for light-driven hydrogen production. We open with a brief presentation of the structure and redox mechanism of the natural enzyme. Synthetic methodologies, structural characteristics, and hydrogen generation metrics relevant to the synthetic diiron catalysts ([2Fe2S]) are discussed. We first discuss multi-component photocatalysis systems with the [2Fe2S] cluster, followed by photosensitizer-[2Fe2S] dyads and molecular triads. Finally, strategies for the incorporation of [2Fe2S] complexes into supramolecular assemblies, semiconductor supports, and hybrid heterogeneous platforms are laid out. We analyze the individual properties, scope, and limitations of the components present in the photocatalytic reactions. This review illuminates the most useful aspects to rationally design a wide variety of biomimetic catalysts inspired by the diiron subsite of [FeFe]-hydrogenases and establishes design features shared by the most stable and efficient hydrogen producing photosystems.

Keywords: Photochemistry, Biomimetic Chemistry, Artificial Photosynthesis, Light-Driven Hydrogen Evolution, Bioinorganic Chemistry

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Declaration of Competing Interest

Acknowledgments

5.2.1.10. References

5.2.1.1. Introduction

The depletion of non-renewable energy sources has prompted the scientific community to search for inexhaustible, economically viable and environmentally friendly alternative energy supplies [1,2]. The conversion and storage of energy from sunlight in fuels is a promising alternative to satisfy the future energy demand of our society on a large scale [3]. Solar energy applied to the chemical decomposition of water is a key strategy for obtaining hydrogen [4–6]. Many future sustainable energy systems are based on hydrogen as an energy carrier due to its high gravimetric energy storage density (142 MJ kg^{-1}), zero emissions, non-toxicity and potential to be sourced from water, an abundant resource [7,8]. Hydrogen can be utilized in the presence of oxygen by combustion or in fuel cells that generate electricity. Hydrogen gas is also essential to carry out many industrial processes, but it is currently obtained largely from steam reforming of fossil fuels [9].

Nature uses sunlight to generate chemical energy through photosynthesis, which consists of sequential chain reactions carried out in thylakoid membranes of algae, bacteria and higher plants. The processes of light capture by antenna pigments (mainly chlorophyll and carotenoid), water splitting, NADP^+ reduction, and ATP formation take place in several protein complexes of oxygenic organisms [10–13]. The process is driven by absorption of photons from sunlight by the light-harvesting complexes of photosystem (PS) I and PSII. Light-driven water oxidation in PSII generates electrons that pass along an electron-transport chain via plastoquinone (PQ), cytochrome b_6/f (cyt b_6/f), plastocyanin (PC), PSI and ferredoxin (Fd). The photoexcitation of the antenna complex in PSI activates the electron transfer from the ferredoxin- ADP^+ oxidoreductase enzyme to NADP^+ with the subsequent formation of NADPH. The protons released in the oxygen evolution reaction (OER) are taken up by ATP synthase to produce ATP molecules from ADP. The ATP and NADPH that are generated in the process provide the energy needed for the fixation of CO_2 in the Calvin Benson cycle to produce sugars- plant fuel- such as glucose and starch.

Under anaerobic conditions, [FeFe]-hydrogenase enzymes in the chloroplasts of unicellular green algae catalyze the hydrogen evolution reaction (HER) [14]. A simplified scheme of the natural photosynthesis carried out by these systems is presented in **Figure 1**. The reaction cycle begins with the initial absorption of light by the PSI primary electron donor

(P700), ultimately leading to reduced ferredoxin (Fd). The catalytically active [FeFe] hydrogenases accept electrons from reduced Fd which are then used for the HER [15–17]. [FeFe] hydrogenase metalloenzymes catalyze the reversible interconversion of protons and electrons into molecular hydrogen ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) at the remarkable rate of up to 9000 hydrogen molecules per second per enzyme [18,19].

The structure of the [FeFe] hydrogenase active site (H-cluster) was determined by X-ray crystallography to consist of an organometallic diiron subcluster [2Fe]. The proximal iron (Fe_p) is linked to a cubane subcluster [4Fe-4S] by the sulfur of a cysteine residue (**Figure 1**) [20,21]. While Fe_p has a saturated coordination sphere, the distal iron (Fe_d) provides an available coordination site for proton or hydrogen binding [22]. The [2Fe2S] cluster contains a bridging azadithiolate ligand (aza-propane-1,3-dithiolate, adt), two terminal cyanide and carbon monoxide strong-field ligands at the low-valent iron sites, as well as a carbon monoxide ligand bridging both metal centers. The H-cluster is deeply buried within the protein scaffold in a hydrophobic pocket where catalysis takes place. This arrangement aids proton and electron transport to and from the active site and confers a certain degree of O_2 tolerance [23,24].

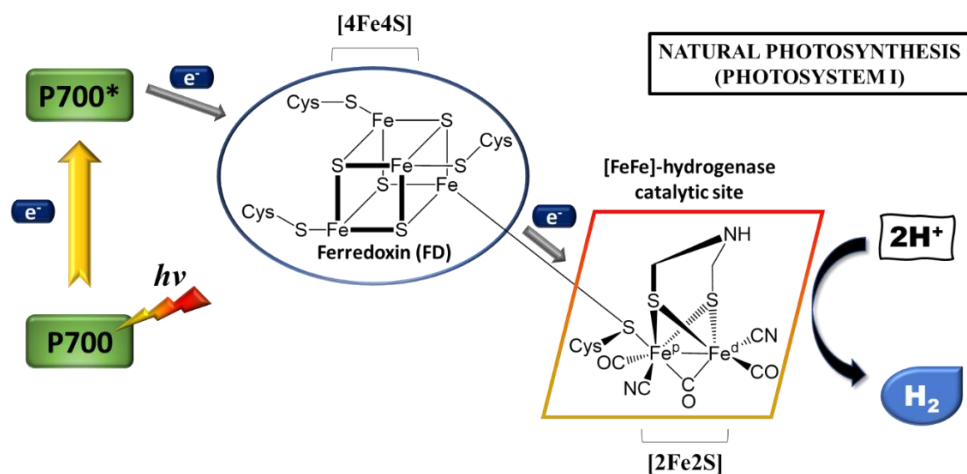


Figure 1. Schematic representation of electron flow from Photosystem I to an [FeFe]-hydrogenase via a ferredoxin redox mediator (Photosystem I).

The enzymatic hydrogen formation mechanism as proposed by Lubitz and co-workers [25,26] is shown in **Figure 2**. In the enzyme's most oxidized resting system (H_{ox}), the [4Fe4S] cubane is in a 2+ oxidation state

while the catalytic subcluster $[2\text{Fe}]$ is a mixed valence $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ state. The first one-electron reduction results in the formation of the H_{red} state where the $[\text{4Fe4S}]$ subcluster is reduced to a $1+$ oxidation state. Protonation of the *adt-N* triggers an intramolecular charge shift to form $\text{H}_{\text{red}}\text{H}^+$ in which the $[\text{4Fe4S}]$ cubane is in the $2+$ state and the $[2\text{Fe}]$ subsite reduced to a homovalent $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ state. Subsequent one-electron reduction of the subcluster $[\text{4Fe4S}]$ gives rise to the “super-reduced” state $\text{H}_{\text{sred}}\text{H}^+$, well-characterized by EPR and FTIR spectroscopy [27]. In the next step of the catalytic cycle, an intermediate hydride state $[\text{H}_{\text{hyd}}]$ is formed by an intramolecular proton shift from the *adt-N* to the distal iron F_d , a process that is coupled to an electron rearrangement in the $[2\text{Fe}]$ subsite, leading to a formal $\text{Fe}^{\text{II}}\text{Fe}^{\text{II}}$ oxidation state. Recently, this terminal hydride intermediate has been detected directly by ^1H NMR spectroscopy at room temperature [28]. Addition of a second proton coupled to another charge shift from the reduced $[\text{4Fe4S}]$ to the $[2\text{Fe}]$ subsite either in one or two discrete steps gives rise to $[\text{H}_{\text{hyd}}\text{H}^+]$ that is characterized by a formal $\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ oxidation state. At this point, there is an equilibrium between the $\text{H}_{\text{hyd}}\text{H}^+$ and $\text{H}_{\text{ox}}[\text{H}_2]$ in which the hydride and the proton are combined to a hydrogen molecule at the distal iron of the system. The catalytic cycle is closed by H_2 release, returning to the initial H_{ox} configuration.

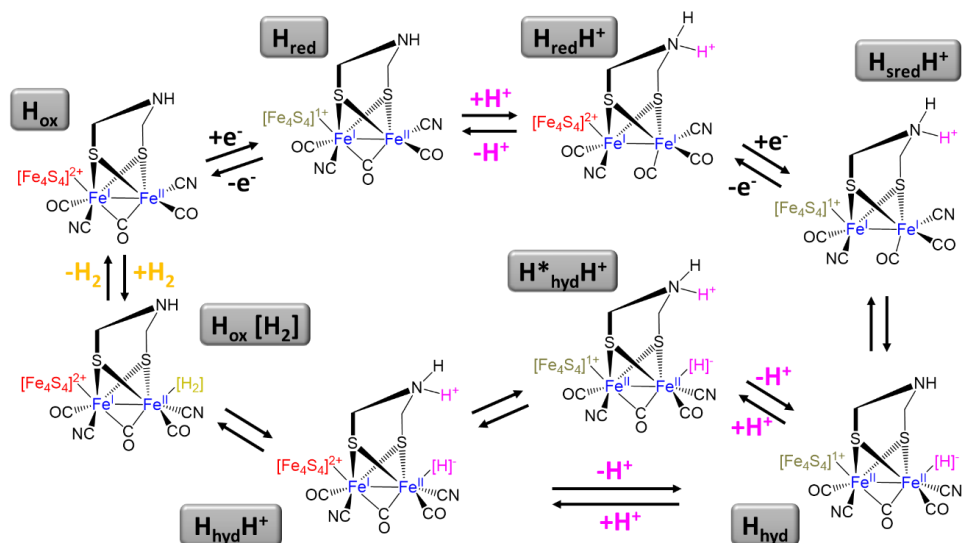


Figure 2. Proposed mechanistic cycle for hydrogen evolution by $[\text{FeFe}]$ -hydrogenase adapted from Lubitz et al. [25] with permission from Elsevier.

For more details on the species involved in each step of this reaction mechanism as deduced from X-ray crystallography, spectroelectrochemical studies, EPR and DFT theoretical calculations, the reader is referred to excellent literature contributions [29–34].

Hydrogenase metalloenzymes show high turnover rates for hydrogen production at mild reduction potential in neutral aqueous solution [24,35,36], making them competitive with commonly used platinum-based metal catalysts [37]. However, they exhibit irreversible deactivation in the presence of oxygen. Detailed studies on the mechanism of enzymatic inactivation of the dinuclear subsite by oxygen have been carried out to understand and improve the resistance against irreversible oxidative degradation and/or inhibition of the catalytic cycle [38–40]. Similarly, intermediate reaction species of [FeFe]-hydrogenases have been characterized using spectroscopic techniques and theoretical calculations [24,41,42]. Progress on O₂ tolerance in the artificial maturation of [FeFe]-hydrogenases has been reported to overcome this obstacle [43,44]. Thus, understanding the chemistry of [FeFe]-hydrogenases is key to deducing principles essential for the design of artificial biomimetic systems based on these enzymes.

Due to the low availability of natural hydrogenases, numerous studies have focused on the development of biomimetic catalysts that exhibit similar activity as the enzymes, with the aim of designing an artificial photocatalytic system for light-driven proton reduction [45,46]. **Figure 3** shows a bibliometric analysis that highlights how the interest in hydrogenase enzymes in general (columns) and, [FeFe]-hydrogenases in particular (line), as a research topic has grown in recent years.

In an artificial light-driven system for solar fuel generation, light absorption is followed by the separation of electrons and holes. Electrons are used in the catalytic fuel formation reaction, and the holes are replenished by electrons from water oxidation. However, photon absorption leads to the separation of single electron-hole pairs, while both water oxidation and fuel production involve multiproton and multielectron reactions. Therefore, the accumulation of electrons and holes (accumulative charge separation) by successive absorption of photons is necessary to complete all the catalytic reactions [47]. Engineering a molecular system that combines both the fuel production and water oxidation half reactions and that is powered by light-induced charge separation is still a challenge for the scientific community. Among others, the following difficulties can

be identified: i) charge recombination before catalyst turnover, ii) balancing the rates of the two half reactions and iii) undesirable secondary reactions, such as, for example, peroxide instead of oxygen formation.

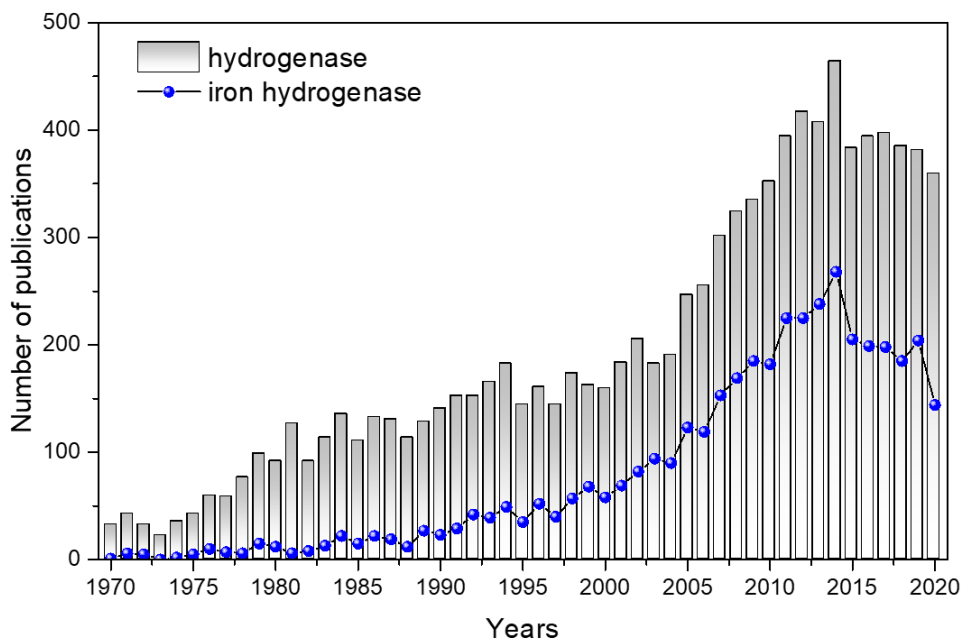


Figure 3. Number of publications per year in the period (1970-2020) following Web of Science (WOS) database. Column and line correspond to searches with words in title, abstract or keywords as reported in the inset.

To address this, the separate half-reactions - water oxidation or fuel production - have been optimized separately, in particular, by achieving long-lived high-energy charge-separated states, that can then be coupled via a redox compartmentalization [47–50]. The independent half-reactions are powered either electrochemically or by the use of sacrificial oxidants or reductants [51]. Photochemical catalysis employs a photosensitizer and a sacrificial electron acceptor or donor to supply the redox equivalents for water oxidation and hydrogen production, respectively. For the light-induced hydrogen generation catalyzed by [FeFe]-hydrogenase active site mimics, a schematic representation is shown in **Figure 4**. Excitation of the photosensitizer initiates the photocatalytic process. Photo-induced charge separation from the excited photosensitizer (PS) provides electrons in a diffusional process to the [2Fe2S] catalyst that is responsible for driving proton reduction. The sacrificial electron donor (ED) must be easily oxidizable to make the overall electron transfer process (ET)

thermodynamically feasible and to ensure rapid recovery of the PS before charge recombination can occur. This process has to be repeated twice to accumulate two electrons in the $[2\text{Fe}2\text{S}]$ catalyst, which can then reduce two protons to produce a H_2 molecule [52].

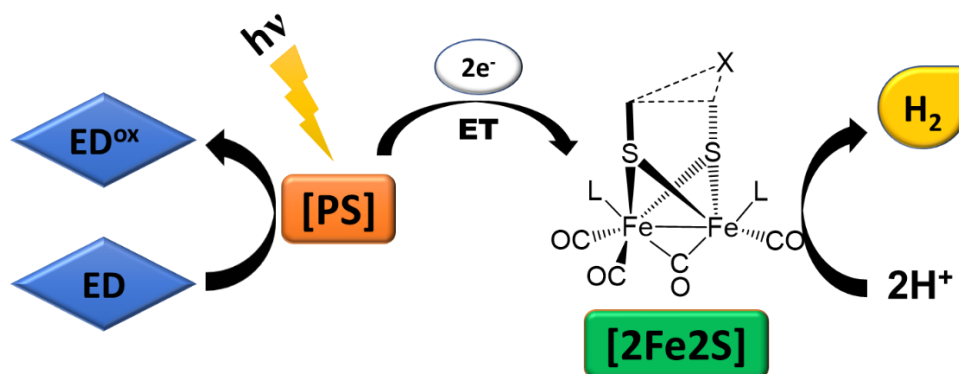


Figure 4. Schematic representation of light-driven hydrogen production mechanism. ED: electron donor, PS: photosensitizer and $[2\text{Fe}2\text{S}]$: diiron active site (L: CN^- , CO or PR_3 , X: CH_2 , CH_2R , NH, NHR, O or OR, dashed lines: different linking possibilities in the dithiolate subcluster).

The concept of artificial photosynthesis in sacrificial half-reactions was first reported in 1977 by Lehn and co-workers. In this seminal paper, light-driven proton reduction was achieved in a photochemical system consisting of $\text{Ru}(\text{bpy})_3^{2+}$ as the visible-light-absorbing PS, $\text{Rh}(\text{bpy})_3^{2+}$ as the electron mediator, triethanolamine (TEOA) as the sacrificial agent and colloidal platinum as the catalyst [53,54]. Similar systems were reported a year later by Grätzel's research group, using the same $\text{Ru}(\text{bpy})_3^{2+}$ photosensitizer, methyl viologen as the electron mediator and EDTA electron donors [55–57]. These early reports have influenced the development of model complexes mimicking the structure and function of natural $[\text{FeFe}]$ -hydrogenase enzymes and the optimization of other components that participate in the photosystem (PS and ED), as well as other influencing parameters (solvent, pH, excitation wavelength and power), with the aim of maximum efficiency for light-driven hydrogen evolution.

The electron donor is a sacrificial agent such as triethylamine (TEA), triethanolamine (TEOA), ethylenediaminetetraacetic acid (EDTA) or ascorbic acid (AscOH) that can be easily oxidized. This property ensures

the thermodynamic viability of the catalytic reactions and prevents unproductive back-electron transfer [58]. In this context, the pH of the reaction medium of the ED is very important as it determines the acid-base equilibria. In the case of ascorbic acid, for example, the anionic ascorbate (AscO^-) is a stronger reducing agent than its protonated form, AscOH , and therefore requires a pH above 4 ($\text{p}K_{\text{a}1} = 4.17$) [59,60]. EDTA contains two amino groups and four carboxylic acid groups that can act as electron donors at a more neutral pH between 5-7 [61]. If TEA ($\text{p}K_{\text{a}} = 7.9$) or TEOA (10.7) is used as a sacrificial agent, it is essential to work at a pH close to their $\text{p}K_{\text{a}}$ values to avoid the excessive protonation of the free amine that would inhibit its function as ED [61]. The selection of the most suitable ED is mainly empirical and depends on the functional units present in the photocatalytic system. Considerations must be given to the relative redox potentials, solubility, and the pH of the reaction medium that, in turn, is set to optimize hydrogen production.

Visible light harvesting by the PS is essential for efficient electron transfer reactions and to obtain a maximum quantum yield (QY) in the photocatalytic hydrogen evolution. A wide absorption range, a redox potential suitable for electron transfer from the ED to the excited PS, long excited state lifetimes, high photostability and appropriate solubility in the reaction solution are all important aspects [62]. Organic dyes such as rose Bengal [63] and Eosin Y [64], among others [65], and metal complexes such as $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ir}(\text{bpy})(\text{ppy})_2]\text{PF}_6$ have been extensively studied for several decades. Metal-free organic dyes are cheap, easily engineered, environmentally friendly and readily accessible. They feature high molar extinction coefficients compared to metal complexes but also suffer from some drawbacks such narrow absorption bands in the visible region, quenching of the photoluminescence promoted by multichromophoric interactions, photochemical instability and sometimes short excited state lifetimes [65–69]. $[\text{Ru}(\text{bpy})_3]^{2+}$ is the most widely employed PS in photocatalysis for hydrogen production, presenting a broad absorption band in the visible light range ($\lambda_{\text{max}}=450$ nm) and a relatively long lifetime of its excited state. A usual problem with this PS is its frequent instability under experimental photocatalytic conditions [70,71]. In contrast, PSs based on Ir (III) are considered highly effective because they exhibit good stability and excellent excited-state properties [72]. However, their large-scale application is limited by Ir scarcity and high cost. These challenges have been addressed through the investigation of alternative light harvesters, such as semiconductor nanoparticles (ZnS or TiO_2) or quantum dots (CdSe

or CdTe), which exhibit long-term stability and broad absorption bands in the visible part of the spectrum.

The concentration of both the PS and ED has a crucial influence on the rate of hydrogen production. Frequently, an excess of ED is used in a photocatalytic reaction for hydrogen evolution to ensure the kinetic control and high charge separation yield, while a higher concentration of PS usually results in faster hydrogen productivity. In tethered systems, also the distance between the PS and the catalyst or ED must be controlled to avoid competing reaction pathways. More details about the use of ED and PS in photosystems for light-induced hydrogen evolution are discussed in the next sections of this review.

Concerning the diiron catalyst, the reduction of the active subsite [2Fe2S] can be carried out in two different ways, *i.e.* by following an oxidative or reductive quenching pathway of the excited PS (**Figure 5**) [14]. In the first case, oxidation of the excited *PS occurs by transferring an electron to [2Fe2S]. The oxidized PS is regenerated by the ED. On the other hand, the ED can perform a reductive quenching of the excited species *PS. The thereby produced, photo-reduced PS can successively reduce the catalytic [2Fe2S] cluster by transfer of an electron, recovering the original state of the PS. The exact mechanism will depend on the excited-state oxidation and reduction potentials of the PS, the reduction potential of the catalyst for the reduction of protons and the oxidation potential of the ED to re-establish the original state of the PS. In the event that both pathways are thermodynamically feasible, the predominant mechanism will be the one with the highest quenching rate [73].

In recent decades, great efforts have been directed towards the design diiron complexes that mimic the structure and function of natural [FeFe]-hydrogenases, and to include them in schemes for light-induced hydrogen formation. Biologically inspired functional models of hydrogenases contain first, second, and outer coordination spheres, each contributing to the photocatalytic process [74,75]. The first coordination sphere describes the ligands directly bound to the diiron core [2Fe] influencing the properties of the metal center: vacant coordination sites for substrate binding, modification of redox potentials, electron density, and steric hindrance for the accessibility of reactants. Strong-field ligands such as cyanide (CN⁻) or carbon monoxide (CO) are present in the enzyme active site to ensure low-spin complexes. The second coordination sphere includes functional groups of the ligands that react with the substrate. They play a

fundamental role in moving electrons through the [4Fe-4S] cubane and shuttling protons via amino acids and the amine bridgehead of the active site. The outer coordination sphere of metalloproteins has dimensions normally greater than 4 Å from the metal and encompasses the entire remaining scaffold of [FeFe]-hydrogenase [76].

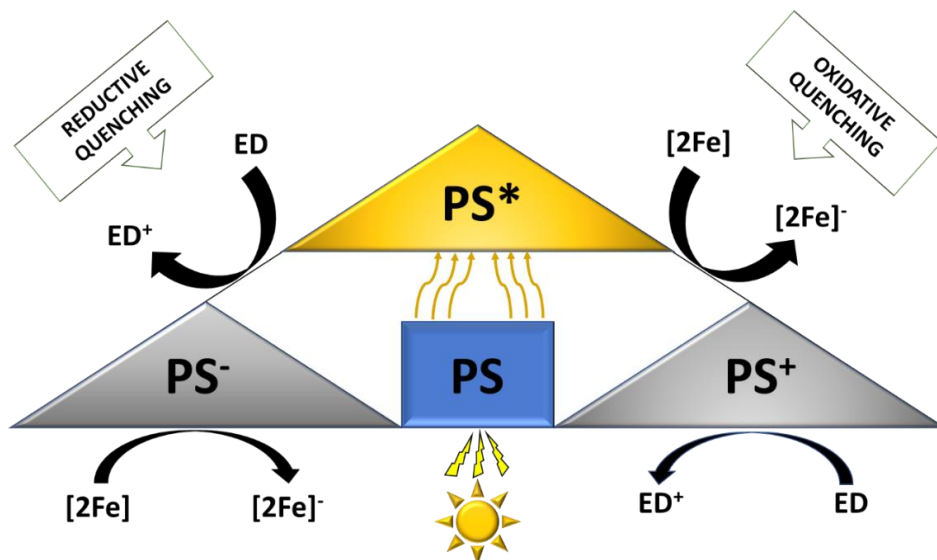


Figure 5. Oxidative and reductive quenching pathways for reduction of [2Fe] active subsite.

Artificial bioinspired diiron complexes can be fine-tuned by engineering each of these coordination spheres in the following ways:

a) First coordination sphere: ligand substitutions of the archetypical dithiolate-bridged hexacarbonyl diiron complexes are essential for the formation of the mixed-valence state $\text{Fe}^{\text{II}}\text{Fe}^{\text{I}}$, to reproduce the “rotated conformation” of the enzyme, and the formation of terminal hydride species [75,77–80]. In general, two strategies have been taken: i) the replacement of CO with CN^- to stabilize a specific orientation of the diiron subcluster in the active site and promote the formation of the hydride intermediates; or ii) the substitution of CO with electron-rich phosphine ligands, among others, to provide photostability, higher electron density, and proton relays.

b) Second coordination sphere: The exhaustive control in the design of the second coordination sphere is crucial for the protonation mechanism of the complex [81], the creation and stabilization of hydride species [24], assistance in the heterolytic H_2 cleavage/formation, [82] and proton-

coupled electron transfer reactions (PCET) [83]. In addition, problems intrinsic to most diiron hydrogenase mimics such as the large overpotentials required for the catalytic proton reduction process can be addressed. The following modifications can be beneficial: i) the incorporation of ligands in the dithiolate bridging group bearing novel features such as pendant amine groups or substituted aromatic dithiolate bridgehead; ii) the addition of functional groups or reactive structures at the ligands on the [2Fe] core in the first coordination sphere. Modification of the secondary coordination sphere can allow the integration of functionalized amino groups similar to those existing in the natural enzyme, or the addition of novel functionalities in the bridging dithiolate, for example, a photosensitizer to allow for *intramolecular* photo-induced charge separations.

c) Outer coordination sphere: most [FeFe] hydrogenase active site models are only soluble in an organic phase. Supramolecular control via outer coordination sphere interactions is of vital importance to create and modulate an analogous protein environment around diiron catalysts that enables operation in aqueous solvents [23,36]. Protein scaffolds, supramolecular cage assemblies or heterogeneous supports can be used to control the hydrophilic/hydrophobic catalytic environment of the functionalized [2Fe2S] subunit (isolated or dye-linked).

Considering the primary and extended coordination spheres in the synthesis of [2Fe2S] complexes provides opportunities to enhance the performance of light-driven hydrogen production by promoting electron and proton transfer [84,85], catalyst stability and reactivity [86], and catalyst solubility in aqueous solutions [87,88].

Herein, we present a comprehensive review of [FeFe]-hydrogenase inspired catalysts for light driven hydrogen production, highlighting the most recent trends in this topic. The different systems will be presented in groups by increasing complexity and their chronological development (**Figure 6**). In **Section 2**, catalysts inspired by the [FeFe]-hydrogenase ([2Fe2S]) active site will be described in the presence of PS and ED. The incorporation of PS in the catalytic system gives rise to photosensitizer-[FeFe]-hydrogenase active site model dyads [PS-2Fe2S], which will be reviewed in **Section 3**. Further, linking ED to the dyads results in triads [ED-PS-2Fe2S], reported in **Section 4**. In **Section 5**, we explore covalent or non-covalent interaction of [2Fe2S] with different supramolecular entities. Direct assembly of the catalyst on inorganic materials will be subject of **Section 6** and **7**. In **Section 6**, the inorganic component is a

semiconductor, which acts as photosensitizer, whereas in **Section 7**, the inorganic component is simply a support. In **Section 8**, photoelectrochemical (PEC) hydrogen evolution catalyzed by photocathodes bearing [2Fe2S] catalysts is addressed.

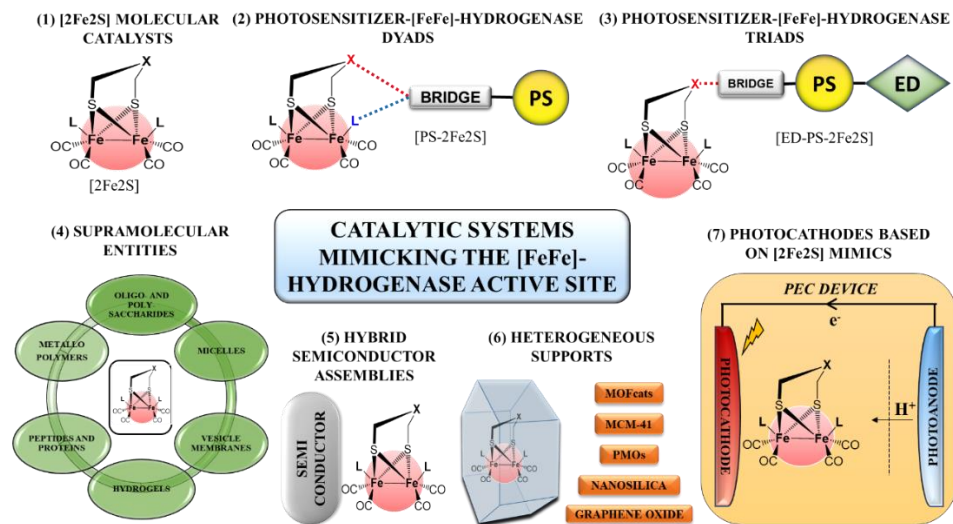


Figure 6. Overview of catalytic systems mimicking the [FeFe]-hydrogenase active site: (1) [2Fe2S] molecular catalysts (Section 2), (2) Photosensitizer-[FeFe]-hydrogenase dyads (Section 3), (3) Electron donor-photosensitizer-[FeFe]-hydrogenase triads (Section 4), (4) Supramolecular entities (Section 5), (5) Hybrid semiconductor assemblies (Section 6), (6) Heterogeneous supports (Section 7) and (7) Photocathodes based on [2Fe2S] for PEC devices (Section 8). The nomenclature used for catalytic systems 1, 2 and 3 is indicated while for catalytic systems 4, 5, 6, and 7, the molecular catalyst and supramolecular entity, semiconductor, support or photocathode will be included following the nomenclature reported by the authors in the corresponding articles.

5.2.1.2. Bioinspired [2Fe2S] catalysts: Bimolecular reactions

In this section, we focus on catalytic systems composed of a photosensitizer and a molecular catalyst with the [2Fe2S] unit, abbreviated as PS/[2Fe2S]. Diffusional PS/[2Fe2S] reactions are considered as bimolecular reactions where electron transfer takes place between the excited or reduced state of a suitable PS (depending on the quenching mechanism, see above) and an [2Fe2S] catalytic center. These catalytic systems offer the opportunity to screen a wide variety of [2Fe2S] catalysts

using conventional PSs. The [PS:2Fe2S] ratio can be tuned to modulate the generation of reducing equivalents for optimal photocatalytic hydrogen production [14]. Additionally, [2Fe2S]-containing molecular catalysts have the following advantages: i) the synthesis of the biomimetic model is often relatively simple, following well-established strategies; ii) the redox properties and stability can be adjusted by replacing ligands in the first coordination sphere or by incorporating functionalities in the second coordination sphere via the dithiolate bridging group [82,86,89]; iii) electrochemical/spectroscopic characterization and computational elucidation of reaction mechanisms can be applied to well-defined molecular catalysts [24].

Inspired by these features, herein we review bioinspired [2Fe2S] catalysts that have been used in molecular photocatalysis systems, the structures of which are shown in **Figure 7**. Their performance in light-driven hydrogen production reactions, as measured in turnover number (TON), along with the applied PS and selected reaction conditions are detailed in **Table 1**.

In 2007, electron transfer between a PS and a [2Fe2S] active site was demonstrated by Sun and co-workers. They identified reduced $\text{Ru}(\text{bpy})_3^+$ species photogenerated by reductive quenching using a diethyldithiocarbamate sacrificial agent with a strong driving force for electron transfer from $\text{Ru}(\text{bpy})_3^+$ to the [2Fe2S] active site $\{(\mu\text{-SCH}_2)_2\text{X}\}[\text{Fe}(\text{CO})_3]_2$ (X: CH_2 or $\text{NCH}_2\text{C}_6\text{H}_5$). Time-resolved optical spectroscopy showed a decrease in the lifetime of this strong reductant $\text{Ru}(\text{bpy})_3^+$ in the presence of the [2Fe2S] complex, confirming the visible light-driven intermolecular electron transfer and serving as proof-of-concept for future photochemical hydrogen production experiments catalyzed by [2Fe2S] complexes [90]. Sun et al. later reported the first bimolecular system for light-induced hydrogen production using AscOH as both a proton source and reductive quencher [91].

Since most diiron hexacarbonyl complexes are gradually degraded under light irradiation, resulting in CO-release from the complexes to the reaction media [92], replacement of CO by common phosphine ligands improves the photostability and raises electron density of the [2Fe2S] core. However, functional analogues of [2Fe2S] active sites with strong electron-donating phosphines ligands are characterized by cathodically shifted reduction potentials that make electron transfer from the PS to the [2Fe2S] complex thermodynamically challenging [93–95].

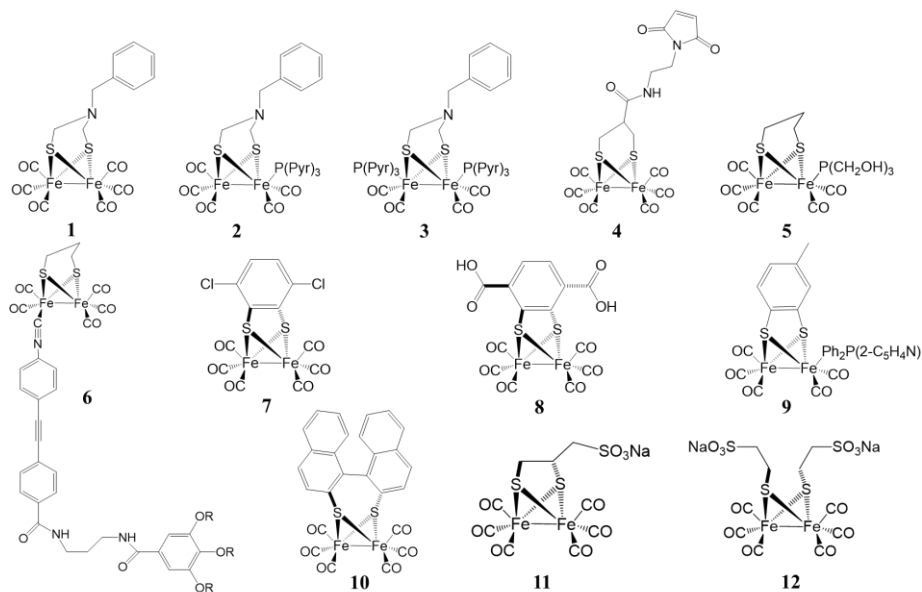


Figure 7. Structures of biomimetic [2Fe₂S]-hydrogenase catalysts that operate in conjunction with a PS reported in literature.

Accordingly, [2Fe₂S] complexes with weaker electron donor N-pyrrolyl phosphines (P(Pyrr)₃) ligands [96,97] were evaluated for photochemical hydrogen production (**Figure 7: 1, 2** and **3**). In water/acetonitrile solution (1:1), the monosubstituted P(Pyrr)₃ diiron complex **2** showed the highest photostability and catalytic activity achieving a TON of 4.3 per catalyst (**Table 1**, entry 2). This result was justified by the increased feasibility of electron transfer from Ru(bpy)₃⁺ to **2** due to the small cathodic shift in reduction potential ($\Delta E = 30$ mV) compared to the all-CO diiron complex **1**, thus resulting in the highest rate of hydrogen production (6.7×10^{-7} mol/min) because of the photostability provided by the P(Pyrr)₃ ligand [91]. However, the diiron catalyst still decomposed by CO ligand release under light irradiation, as detected by FTIR spectroscopy, limiting TONs. Nevertheless, this work established and demonstrated the fundamentals of photochemical hydrogen production using bioinspired [2Fe₂S]. Under optimized conditions, catalyst **2**, a cyclometalated iridium (III) PS and triethylamine (TEA) as a sacrificial ED working at basic pH in acetone/water provided a TON of 466 after irradiation for 8 h [98]. Additionally, it was reported that the performance of this system is limited by the decomposition of the iridium PS [99], since the re-addition of cyclometalated iridium complex after 8 hours of reaction re-established activity at the initial rate.

Table 1. Photocatalytic performance of artificial biomimetic [FeFe]-hydrogenase molecular photocatalysts [2Fe2S] in light-induced hydrogen formation and the conditions selected.

Entry	[2Fe2S] MC	PS	Selected conditions ¹	Light	Time	TON ²	Ref.
1	1	Ru(bpy) ₃ ²⁺	H ₂ O/MeCN (1:1), 1 mM 1 , 0.1 mM PS, 100 mM AscOH, pH= 3.7	Xe lamp (500 W), λ>400 nm	3	0.78	[91]
2	2	Ru(bpy) ₃ ²⁺	H ₂ O/MeCN (1:1), 1 mM 2 , 0.1 mM PS, 100 mM AscOH, pH= 3.7	Xe lamp (500 W), λ>400 nm	3	4.3	[91]
3	2	[Ir(ppy) ₂ (bpy)] ⁺	Acetone/H ₂ O (9:1), 0.05 mM 2 , 0.05 mM PS, 140 mM TEA, pH= 11.0	Xe lamp (500 W), λ>400 nm	8	466	[98]
4	3	Ru(bpy) ₃ ²⁺	H ₂ O/MeCN (1:1), 1 mM 3 , 0.1 mM PS, 100 mM AscOH, pH= 3.7	Xe lamp (500 W), λ>400 nm	3	1.7	[91]
5	4	Ru(bpy) ₃ ²⁺	H ₂ O/THF (1:0.04), 2.1 μM 4 , 140 μM PS, 200 mM, AscO ⁻ , pH=4.5	Hg lamp (power not specified), λ>400 nm	2	180	[100]
6	5	Eosin Y	EtOH/H ₂ O (1:1, v/v) solution, 0.1 mM 5 , 1.0 mM PS, 10% TEA, pH=10	LED (3W), λ>450 nm	15	226	[101]
7	6	MPA-CdTe	Water, 156 μM 6 , 50 μM PS, 85.2 mM AscOH, pH=4.03	Hg lamp (500W), λ>400 nm	10	505	[103]
8	7	Ru(bpy) ₃ ²⁺	DMF/H ₂ O (1:1), 14 μM 8 , 140 μM PS, 100 mM AscOH, pH=5.5	Lamp not specified, λ=455-850 nm	2.5	200	[110]
9	8	Ru(bpy) ₃ ²⁺	Water, 59 μM 9 , 0.5 mM PS, 100 mM AscOH, 1 M acetate buffer, pH=5.0	LED (power not specified), λ>470 nm	2.5	1.7	[111]
10	9	TPP-GO	EtOH/H ₂ O (1:24), 4.8 μM 10 , 44 μM PS, 1.8 mM cysteine, pH=1.5	Hg lamp, (450W), λ>380 nm	5	2.82	[112]
11	10	Eosin Y	MeCN/H ₂ O (1:1), 0.2 μM 11 , 0.2 μM PS, 10 % TEA, pH=10.0	Xe lamp, (300W), λ>420 nm	2	224	[114]
12	11	Ru(bpy) ₃ ²⁺	Water, 0.1 mM 13 , 0.4 mM PS, 100 mM AscOH, pH=4.0	Hg lamp, (500W), λ>400 nm	4	88	[115]
13	11	CdSe QD	Water, 1 μM 13 , 5.2 μM PS, 200 mM AscOH, pH=4.0	LED (power not specified), λ>450 nm	12	18800	[116]
14	12	Ru(bpy) ₃ ²⁺	Water, 1 μM 14 , 0.1 mM PS, 200 mM AscOH, pH=4.0	LED (power not specified), λ>450 nm	6	178	[116]
15	12	CdSe QD	Water, 1 μM 14 , 5.2 μM PS, 200 mM AscOH, pH=4.0	LED (power not specified), λ>450 nm	12	26500	[116]

¹Solvents and reagents abbreviations: MeCN: acetonitrile, THF: tetrahydrofuran, EtOH: ethanol, DMF: N,N-Dimethylformamide, H₂O: water, AscOH: ascorbic acid, AscO⁻: ascorbate, TEA: triethylamine.

² TON based on [2Fe2S] catalyst

Following the structural skeletons of **1**, **2**, **3** but replacing the amine in the adt bridge with a methylene resulted in [2Fe2S] complexes **4**, **5** and **6** (**Figure 7**) with a propyldithiolate (pdt) bridge. Inagaki et al. carried out the synthesis of the [2Fe2S] complex **4** tethered with a maleimide group and all-CO ligands and grafted it onto a heterogeneous support (see **Section 7**) [100]. Working in a homogeneous system using the photosensitizer Ru(bpy)₃²⁺ and AscOH as a sacrificial agent in 4% THF aqueous solution under optimized conditions (**Table 1**, entry 5), a remarkable TON of 180 was obtained. However, decomposition of the catalyst was observed after 20 min under irradiation. The bioinspired diiron complex **5** (**Figure 7**) reported by Sun and co-workers was designed with a simple structure containing a pdt bridge and a CO ligand replaced by a water-soluble phosphine (P(CH₂OH)₃) [101]. In this case, they used an inexpensive xanthene PS, Eosin Y, and TEA as ED in water-ethanol solution under alkaline conditions (**Table 1**, entry 6). This system displayed a great efficiency for hydrogen production with a TON of 226 after 15 h of reaction under visible light irradiation. A unique mechanism for photocatalytic hydrogen formation was proposed in this photosystem because the high reduction potential of **5** precludes the electron transfer (ET) from the xanthene dye. EPR, fluorescence transient absorption, time-resolved UV-Vis and thermodynamic studies elucidated an alternative pathway based on the formation of neutral alkyl radicals Et₂NĊHCH₃ [102] by reductive quenching of the triplet excited state of the PS. This directs ET from these photogenerated TEA radicals towards **5**, enabling the hydrogen formation. Using the same diiron dithiolate catalytic structure as **5**, Wu et al. reported the [2Fe2S] complex **6** (**Figure 7**) by exchanging a terminal CO at the proximal iron by an isonitrile ligand that contains multiple ether groups [103]. This functionality resulted in a water-soluble molecular photocatalyst that was employed along with a CdTe quantum dot PS stabilized with 3-mercaptopropionic acid (MPA-CdTe) and AscOH as a sacrificial ED and proton source. Under optimized conditions (**Table 1**, entry 7), this three-component system showed high efficiency for light-induced hydrogen formation achieving a TON of up to 505 and a turnover frequency (TOF) of 50 h⁻¹, the highest photocatalytic activity reported using [2Fe2S] thus far (**Figure 7, 1-5**).

An appropriately substituted aromatic dithiolate bridgehead is a promising design strategy for a bioinspired [2Fe2S] to overcome the limitations inflicted by the relatively irreversible reductions at negative potentials that are typical for aliphatic dithiolate bridged catalysts. Some

reviews on aromatic dithiolate-bridges incorporated in [2Fe2S] mimics have highlighted the interest in these compounds [104,105] due to: i) their structural robustness and rigidity that enhance the integrity of the reduced [2Fe2S] cluster, stabilize hydride intermediates and avoid dimerization or degradation by loss of CO ligands; ii) the tunability of redox properties by substituents at the conjugated bridges; iii) the exhibition of reversible reduction processes in the absence of substrate; iv) the possibility of incorporation, encapsulation or chemisorption in supramolecular scaffolds, heterogeneous supports or electrodes for subsequent application in electro- and photocatalytic processes.

Substituted benzenedithiolate (bdt) bridges incorporated in diiron complexes have been mainly investigated for their redox-tunable properties and high synthetic yields [106,107]. In 2008, Ott et al. investigated the electron-withdrawing effect in diiron arenedithiolate complexes ($[\text{Fe}_2(\mu\text{-S}_2\text{Ar})(\text{CO})_6]$) that featured different aromatic moieties (Ar), *i.e.* benzene, toluene, 3,6-dichlorobenzene and quinoxaline. The decreased electron content of the bridging ligands resulted in a lower stability of the complexes as a consequence of weaker Fe-S bonds. A direct relationship was found between increased electron-withdrawing character of the bridging ligands and a lower electron density of the diiron core, resulting in a decreased applied potential that is needed for electrocatalytic proton reduction [108]. Later, Felton et al. [109] corroborated this study by evaluating analogous diiron bdt systems with chlorine substituents as electron-withdrawing groups. Some representative examples of [2Fe2S] with bridgehead aromatic substituents applied in hydrogen photoproduction are shown in **Figure 7 (7-10)**. Building on their previous findings, Ott and co-workers reported the use of $[\text{Fe}_2(\mu\text{-Cl}_2\text{bdt})(\text{CO})_6]$ (Cl_2bdt =3,6-dichlorobenzene-1,2-dithiolate) complex **7** with two electron-withdrawing chloride substituents as catalyst for light-driven hydrogen evolution [110]. The photochemical system consisted of **7**, $\text{Ru}(\text{bpy})_3^{2+}$ as a PS and AscO^- as a sacrificial ED in a DMF/H₂O mixture to ensure the complete solubility of all reaction components. Under optimal conditions, a TON of 200 and a TOF of 2.7 min⁻¹ was obtained (**Table 1**, entry 8). DFT calculations and transient absorption spectroscopy suggested that the catalytic cycle occurred by intramolecular electron transfer. The delivery of the second electron to **7** was found to be the limiting step. The analogous complex **8**, *i.e.* $[\text{FeFe}](\text{dcbdt})(\text{CO})_6$ (dcbdt =1,4-dicarboxylbenzene-2,3-dithiolate), contained two carboxylic groups at the aromatic ring [111], offering the possibility for incorporation in heterogeneous system (see **Section 7**). This photocatalyst

was first evaluated in a completely water-soluble photosystem using $\text{Ru}(\text{bpy})_3^{2+}$ as PS and AscO^- as ED in an acetate buffer medium at $\text{pH} = 5.0$, but low TON values were obtained (**Table 1**, entry 9).

Tolyl-functionalized monophosphine substituted diiron complexes were synthesized by Jang et al. to study how distinct monophosphine ligands effect the reduction potentials for catalytic hydrogen production [112]. Using a different photocatalytic system, tetraphenylporphyrin (TPP) covalently linked to graphene oxide (GO) as a PS and cysteine were used to further simulate the protein environment in the [FeFe]-hydrogenase enzyme [113]. The analysis of the diiron complex by UV/Vis, fluorescence emission and time-resolved fluorescence techniques suggested that the high absorptivity and electrical conductivity of the GO improved electron transfer from the photosensitizer to the catalyst. The tolyl-functionalized diiron complex with a monophosphine ligand $[\text{Fe}_2(\text{CO})_5(\text{L})\{\mu\text{-SC}_6\text{H}_3(\text{CH}_3)\text{S}\}]$ ($\text{L}=\text{Ph}_2\text{P}(2\text{-C}_5\text{H}_4\text{N})$) represented as **9** in **Figure 7** showed the lowest reduction potential for catalytic H_2 evolution. With a TON of 2.82, **9** exhibited superior photocatalytic results (**Table 1**, entry 10) compared to the other diiron complexes synthesized in this work. The experimental results demonstrated that the presence of the N heteroatom in pyridine plays a fundamental role in accelerating proton transfer to the catalytic center, thereby enhancing photocatalytic hydrogen production.

A new contribution in diiron complexes with substituted bridgehead aromatic dithiolate compounds was reported in 2016 by Hou et al. who synthesized the biomimetic complex **10** $[(\mu\text{-BNT})\text{Fe}_2(\text{CO})_6]$ ($\text{BNT}=(\text{R})\text{-1,1'}$ -binaphthalene-2,2'-dithiol) with a binaphthalene-derived ligand with a high electron-withdrawing capacity [114]. The diiron complex **10** produced hydrogen with high efficiency under visible light irradiation in a homogeneous photocatalytic system consisting of **10**, Eosin Y xanthene PS (EY^{2-}) and TEA as sacrificial ED in $\text{MeCN}:\text{H}_2\text{O}$ (1:1) solution. Fluorescence experiments elucidated the electron transfer pathway via the reductive quenching mechanism between the $^3\text{*EY}^{2-}$ triplet excited state and TEA as reported previously [101]. By optimizing key photoreaction parameters, a TON of 224 per catalyst was obtained (**Table 1**, entry 11), the highest value for [2Fe2S] compounds with bridgehead aromatic substituents applied in light-driven hydrogen evolution.

Another subset of [2Fe2S] complexes are those with hydrophilic groups incorporated in the bridging dithiolate ligand. These compounds are more stable and soluble in aqueous solution. Wu and co-workers designed

water-soluble [2Fe2S] complexes by introducing hydrophilic sulfonate groups into the dithiolate bridge (**Figure 7, 11** and **12**). In 2012, they reported complex **11** incorporating a propane sulfonate group linked to the dithiolate ligand [115]. The photosystem using a Ru(bpy)₃²⁺ photosensitizer and AscOH as an ED and proton source was evaluated in aqueous solution, organic phase or in a mixture of organic solvent and water in order to observe the effect of reaction media on the efficiency of light-driven hydrogen evolution. Under optimal conditions (**Table 1**, entry 12), the highest photocatalytic performance was obtained using water as a homogeneous solvent system, achieving a TON of 88 based on **11**. The rationale for the higher activity in water than in organic solvents was clarified by spectroscopic analysis and electrochemical studies. The reduction potential of **11** was more positive in water and so favored the electron transfer (ET) from the PS to the photocatalytic diiron center. In addition, the extended lifetime of the reduced state of the PS generated through reductive quenching and the facile release of protons and AscO⁻ reducing species from the sacrificial ED further contributed to the efficiency of the photocatalytic system for hydrogen production in water.

Four years later, this research group reported an attractive comparative study of light-induced hydrogen production using a water-soluble homogeneous photosystem consisting of: 1) the previous [2Fe2S] **11** or a new [FeFe]-hydrogenase active site model with two sulfonate groups incorporated in the dithiolate site (**Figure 7, 12**) as proton reduction catalyst, 2), cadmium-selenide quantum dot (CdSe QDs) or molecular Ru(bpy)₃²⁺ as photosensitizers and 3) AscOH as the ED [116]. Motivated by the unparalleled record TON (505) obtained using CdTe QDs (**Table 1**, entry 7), Wu et al. selected this type of photosensitizers due to their wide absorption in the visible spectrum and dispersibility in water [117,118]. The photocatalytic activity of [2Fe2S] **12** using the Ru(bpy)₃²⁺ photosensitizer showed an increase in TON up to 178 (**Table 1**, entry 14) compared to the TON of 88 obtained for [2Fe2S] **11** in the earlier work [115]. The oxidative quenching of the CdSe QDs system by the diiron complexes **11** and **12** with hydrophilic sulfonate substituents is characterized by a high driving force for electron transfer, resulting in enhanced photocatalysis compared that using Ru(bpy)₃²⁺ as PS. The TON values of the CdSe QDs system were as high as 18800 and 26500 for **11** and **12**, respectively (**Table 1**, entry 13 and 15), the best catalytic performance reported in bimolecular photocatalytic reactions.

5.2.1.3. Photosensitizer-[2Fe2S] dyads: [PS-2Fe2S]

Biomimetic models of the [FeFe]-hydrogenase active site have been covalently linked to molecular photosensitizers for light-induced hydrogen production. Photosensitizer-[2Fe2S] dyads, [PS-2Fe2S], organize both components with high space and distance control. These multicomponent complexes promote fast intramolecular electron transfers and charge separation, and can avoid recombination between the redox states generated during the photocatalytic cycle.

The initial step for photochemical hydrogen production in covalently linked dyads is often the formation of reduced $\text{Fe}^{\text{I}}\text{Fe}^0$ species by oxidative quenching, whereas bimolecular systems often operate through the reductive quenching of the excited PS^* by an ED [89]. The molecular engineering of [PS-2Fe2S] is based on two different design strategies: (1) In the first approach, the PS and the catalytic cluster [2Fe2S] are connected through the organic dithiolate bridge, or (2) the PS is coordinated directly to one of the iron centres through a ligand in the first coordination sphere (**Figure 8**).

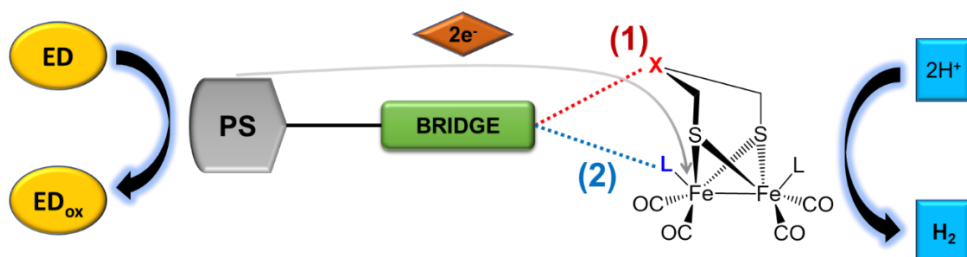


Figure 8. Schematic representation of photosensitizer-[2Fe2S]-hydrogenase dyads [PS-2Fe2S] structures for light-driven hydrogen production.

The first example of strategy (1) was reported already in 2003, when ruthenium (II) bipyridine PS were covalently linked to [2Fe2S] systems through their organic dithiolate bridges (**Figure 9, 13 and 14**). [PS-2Fe2S] **13** [119] was synthesized via palladium-mediated cross-coupling protocols using an acetylene-functionalized ruthenium bis(terpyridine) complex with well-defined geometry [120] and an adt-bridged dinuclear iron complex. Spectroscopic and electrochemical studies of [PS-2Fe2S] **13** revealed that oxidative quenching of the photoexcited $^*[\text{Ru}(\text{terpy})_2]^{2+}$ by the diiron complex was uphill by 0.59 eV [121]. [PS-2Fe2S] **14** consisting of an

amino-functionalized complex of the diiron active site linked to a carboxylic acid of a ruthenium (II) tris-bipyridine PS was prepared by the same group, and laid out the concept for light-driven hydrogen evolution from dyad systems [45]. Hydrogen formation by an oxidative quenching mechanism of the Ru excited states was however not feasible due to the reduction potentials of the [2Fe2S] sites being too negative. Consequently, the free energy change for photo-driven electron transfer was positive and the reduced state of the [2Fe2S] catalytic unit thermodynamically out of reach.

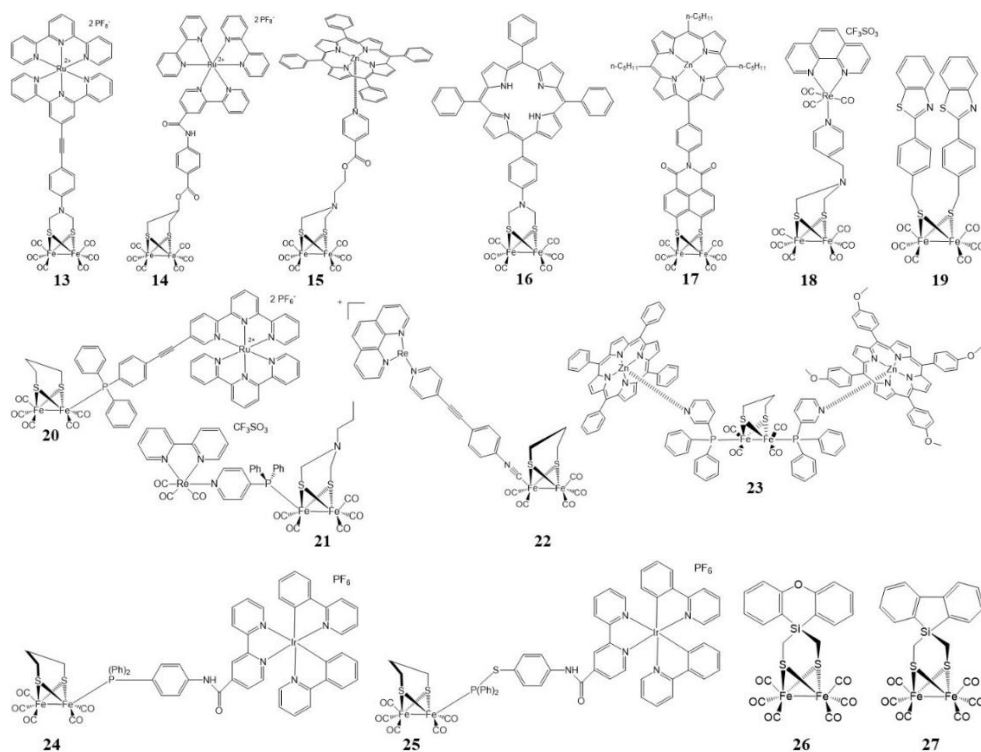


Figure 9. Structures of photosensitizer-[2Fe₂S]-hydrogenase dyads [PS-2Fe₂S] reported in literature.

Following strategy (1) and based on the synthesis of a [PS-2Fe₂S] previously proposed by Song et al. [122], Sun and co-workers prepared the [PS-2Fe₂S] assembly **15**, consisting of a metalloporphyrin (zinc tetraphenylporphyrin) and a pyridyl-functionalized [2Fe₂S] that are tethered through an axial coordination bond (**Figure 9**) [123]. Porphyrins as photosensitizers offer multiple advantages, including their ability to absorb high proportions of the solar spectrum, while also having long

lifetimes of their triplet excited states [124,125]. The non-covalent interactions in this dyad system provide a great opportunity to obtain a long-lived charge separation, as demonstrated by lifetime fluorescence experiments. Both subunits in the dyad remain in dynamic equilibrium, which is advantageous to effectively avoid fast charge recombination after photo-induced electron transfer. Transient absorption studies by nanosecond flash photolysis were carried out, confirming the intramolecular electron transfer from the excited singlet state of the molecular metalloporphyrin to the [2Fe2S] center. Based on this, it was found that visible light drove hydrogen evolution using [PS-2Fe2S] **15**, 2-mercaptobenzoic acid (ArSH) as sacrificial ED and trifluoroacetic acid (TFA) in dichloromethane solution, albeit with low catalytic activity (**Table 2**, entry 1). Despite of a TON of 0.16, this system gained special interest by being the first photoactive dyad [PS-2Fe2S] for hydrogen formation based on the self-assembly principle.

Song and co-workers pursued an alternative design in [PS-2Fe2S] **16** where a photosensitizing tetraphenylporphyrin was covalently attached to the nitrogen heteroatom of a diiron adt complex (**Figure 9**) [126,127]. This covalently assembled system was found to be photoactive for hydrogen production under suitable conditions through an intramolecular electron transfer process. However, its photocatalytic performance using ethanethiol (EtSH) as the sacrificial ED and TFA as the proton source remained low, with a TON of 0.31 (**Table 2**, entry 2).

The [PS-2Fe2S] **17** (**Figure 9**), analogues to **15** and **16**, was constructed by Wasielewski et al. through covalent linking a naphthalene monoamide dithiolate ligand of a diiron complex to a zinc porphyrin PS [128]. Incorporating the strongly electron-withdrawing naphthalene-imide stabilized the reduced diiron complex. This resulted in a less negative reduction potential, making the photoinduced electron transfer from the PS to the catalytic center thermodynamically feasible. Nevertheless, the slight increase in TON to 0.45 was still low for photocatalytic hydrogen formation reactions (**Table 2**, entry 3).

Hou and co-workers recently synthesized the [PS-2Fe2S] dyad **19** (**Figure 9**) through covalent interaction of a [2Fe2S] complex with two organic chromophores through bridging thiolates [129]. Photo-induced intramolecular electron transfer from the photoexcited organic chromophores to [2Fe2S] was demonstrated by electrochemical and spectroscopic studies to be thermodynamically favorable. This inexpensive

and easily accessible [PS-2Fe2S] **19** had the highest photocatalytic performance amongst the dyads synthesized by strategy (1) (**Figure 5**), where the PS is connected to the catalytic center through the dithiolate bridge (**Figure 9, 13-19**). The construct achieved a TON of 31.8 in the presence of EtSH as sacrificial ED and TFA as proton source under visible-light irradiation (**Table 2**, entry 5).

Strategy (2) towards [PS-2Fe2S] dyads was first described by Ott et al. in 2006. In this study, the PS was decorated with a phosphine functionality which was used as a ligand to one of the iron atoms of $[\text{Fe}_2(\text{pdt})(\text{CO})_6]$ (pdt = propyldithiolate) [130] (**Figure 5, 20**). Two years later, Sun and co-workers synthesized [PS-2Fe2S] dyad **21** by coordination of an aminodiphenylphosphine-functionalized $[\text{Re}(\text{bpy})(\text{CO})_3\text{py}]^+$ PS to an azadithiolate (adt)-bridge diiron complex $[\text{Fe}_2\text{adt}(\text{CO})_6]$ [131]. A drawback of the Re complex in the $[\text{Fe}_2\text{adt}(\text{CO})_6]$ -containing dyad **21** was its exclusive absorption in the UV spectral region, a part of the spectrum that was found destructive to the diiron site. The presence of the electron-donating phosphine ligand in the coordination sphere of both dyads **20** and **21** caused a cathodic shift of the oxidation and reduction potentials of around 300 mV compared to all-CO diiron complexes, rendering the oxidative quenching from the excited state of the photosensitizer (*PS) to the [2Fe2S] site thermodynamically unfavorable. In fact, there is a thermodynamic driving force for the reverse electron flow, *i.e.* the reductive quenching of the *PS by the [2Fe2S] center, giving rise to transient oxidized [2Fe2S] sites that are known to be structurally unstable. The possibility of an oxidative quenching mechanism in the rhenium-based dyad **21** was similarly difficult, considering the negative reduction potential of the [2Fe2S] site in this system. Alternatively, electron transfer in these [PS-2Fe2S] systems could proceed by reductive quenching in the presence of an easily oxidizable sacrificial external ED to produce a photogenerated reduced PS. Additionally, the incorporation of a second electron donor ligand (cyanide or phosphine) in the [2Fe2S] coordination sphere is suggested to generate protonation sites and shift the reduction potential to milder values in both dyads. In this way, structurally similar complexes may be active in photocatalytic hydrogen generation, while **20** and **21** have not yet been evaluated in light-induced reactions.

Further studies on rhenium-based dyads were reported in subsequent years. Several [PS-2Fe2S] systems were synthesized by coordination of various rhenium complexes to one of the iron centers in $[\mu-$

$S_2(CH_2)_3Fe_2(CO)_5CN$ [132]. The highest TON of 0.14 was obtained for [PS-2Fe2S] **22** (Figure 9) in a mixture of solvents (MeCN/MeOH/H₂O) in which MeOH was used as sacrificial ED (Table 2, entry 6). Spectroscopic studies revealed that the ³MLCT state of the Re(I) complex in the dyad was completely quenched by intramolecular electron transfer from the diiron catalytic center. Subsequent studies by Liu et al. showed improved photocatalytic hydrogen production using rhenium-based dyads. These authors synthesized [PS-2Fe2S] **18** (Figure 9) by covalent binding of a rhenium PS to the pyridyl-attached azadithiolate diiron complex (strategy 1, Figure 5) obtaining a TON of 11.8 (Table 2, entry 4) [133].

Another approach by Reek et al. assembled the chromophore-associated structure [PS-2Fe2S] **23** (Figure 9) by connecting two different types of zinc(II) porphyrin to a pyridyl-functionalized phosphine ligand coordinated to the diiron core [134]. Under certain reaction conditions (Table 2, entry 7), a TON of 1.96 was obtained using [NiPr₂EtH][OAc] ionic liquid as ED. This study was modular in design and enabled optimization of photocatalytic hydrogen evolution efficiency by altering the building blocks while keeping a controlled distance.

Chen et al. introduced a novel [PS-2Fe2S] dyad system, **24** and **25** (Figure 9), by covalent anchoring of a photosensitizing iridium molecular complex to a [2Fe2S] complex via amide bonds [135]. Both molecular photocatalysts, **24** and **25**, showed a high yield for photoinduced hydrogen production under visible light (> 400 nm) with TON values of 82 and 127, respectively, using TEA as ED in an acetonitrile/water mixture (Table 2, entry 8 and 9). Replacing TEA by TEOA reduced the catalytic activity in the system, demonstrating the superior electron donor ability of TEA in light-driven hydrogen evolution using iridium-based photosensitizers [98,136]. The difference in hydrogen generation performance by dyads **24** and **25** stems from the addition of an S atom in structure **25** that changes the coordination configuration and electron distribution with respect to dyad **24**. Density functional theory (DFT) studies and spectroscopic measurements showed that the presence of the sulfur atom in the second coordination sphere of [PS-2Fe2S] **25** reduces the charge density and conjugation in the diiron core. The resultant greater electron-accepting ability prevents the unwanted back electron-transfer and increases light-induced hydrogen formation.

Table 2. Photosensitizer-[2Fe2S]-hydrogenase dyads [PS-2Fe2S] in light-induced hydrogen formation and the selected conditions.

Entry	[PS-2Fe2S]	Selected conditions ¹	Light	Time (h)	TON ²	Ref.
1	15	DCM, 25 μ M 15; 5 mM ArSH, 1 mM TFA	Xe lamp (500 W), $\lambda > 400$ nm	2	0.16	[123]
2	16	DCM, 0.1 mM 16, 10 mM EtSH, 10 mM TFA	Hg lamp (500 W), $\lambda > 400$ nm	1	0.31	[127]
3	17	Toluene, 1 mM 17, 1 M TFA	Xe lamp (100 W), $\lambda = 500-800$ nm	Unspecified time	0.45	[128]
4	18	MeCN, 18 (concentration value not available), 500 eq TEA	Xe lamp (500 W), $\lambda > 400$ nm	6.5	11.8	[133]
5	19	MeCN, 2.5 mM 18, 0.01 M EtSH, 0.01 M HOAc	Xe lamp (500 W), $\lambda = 355$ nm	4	31.6	[129]
6	22	MeCN/MeOH/H ₂ O (3:2:1), 0.33 mM 21, 0.10 mM HOAc (10mM)	Hg lamp (500 W), $\lambda > 400$ nm	2	0.14	[132]
7	23	Toluene, 1mM 22, 10 mM ionic liquid [N ⁺ Pr ₂ EtH][OAc]	Xe lamp (180 W), $\lambda > 390$ nm	1.3	1.96	[134]
8	24	MeCN/H ₂ O, 0.2 mM 26, 5 % TEA, pH=10	Xe lamp (500 W), $\lambda > 400$ nm	4	82	[135]
9	25	MeCN/H ₂ O, 0.2 mM 26, 5 % TEA, pH=10	Xe lamp (500 W), $\lambda > 400$ nm	4	127	[135]
10	27	MeCN, 0.15 mM 27, 0.25 mM TEA, 0.25 mM TFA	Hg lamp (15 W), $\lambda = 254$ nm	13	29	[142]
11	26	MeCN, 10 μ M 26, 100 mM TEA, 50 mM TFA, pH=10	Hg lamp (15 W), $\lambda = 254$ nm	7	389	[143]
12	27	MeCN, 10 μ M 27, 100 mM TEA, 50 mM TFA, pH=10	Hg lamp (15 W), $\lambda = 254$ nm	7	539	[143]

¹Solvents and reagents abbreviations: DCM: dichloromethane, MeCN: acetonitrile, MeOH: methanol, H₂O: water, ArSH: 2-mercaptobenzoic acid, EtSH: ethanethiol, TFA: trifluoroacetic acid, HOAc: acetic acid, TEA: triethylamine.

² TON based on [2Fe2S] catalyst

In view of the moderate activities for hydrogen production obtained under light irradiation using dyads containing ruthenium- or rhenium-based photosensitizers or organic fluorophores, a new class of dyads that is based on silicon-containing [2Fe2S] complexes has emerged in recent years [137,138]. A compact, heavy-metal-free PS in direct proximity to diiron active site is an advantageous property of these systems. Silicon-aromatic compounds have attracted great interest for their broad light emission and absorption range, electroluminescent properties and physicochemical

characteristics [139–141]. Based on this, Weigand et al. prepared silicon-containing [2Fe2S] complexes by reacting 1,1'-bis-(chloromethyl)-1-silafluorene and the diiron complex $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]$ affording [PS-2Fe2S] **27** (Figure 9) [142]. Electrochemical measurements, electroluminescence studies and DFT calculations demonstrated that the silicon-aromatic compound promoted effective photo-induced intramolecular electron transfer to the [2Fe2S] site. The dyad generated hydrogen photochemically using TFA as a proton source and TEA as the ED. The TON of **27** after 13 h of irradiation (Table 2, entry 10) can be considered a significant improvement compared to many of the other dyads. In 2017, Weigand et al. proposed an enhanced photocatalytic system using the same [PS-2Fe2S] **27** and modified concentrations of TFA and TEA, respectively (Table 2, entry 12) [143]. After 7 h of illumination, a TON of 539 and a TOF of 77 h^{-1} was obtained under optimal reaction conditions. The TOF is the highest reported catalytic rate for dyad systems with a diiron complex directly coordinated to a molecular PS. The same work presented an additional dyad consisting of a [2Fe2S] complex tethered to an alternative silafluorene unit, affording the [PS-2Fe2S] **26** (Figure 9). Light-induced hydrogen evolution was evaluated under the optimal reaction conditions, achieving a TON of 389 (Table 2, entry 11). Additionally, DFT calculations, spectroscopic measurements and electrochemical analysis assigned the photocatalytic mechanism in these systems to an EECC pathway (where "E" represents an electrochemical reduction and "C" a chemical protonation) [73].

5.2.1.4. Molecular triads based on [2Fe2S] complexes [ED-PS-2Fe2S]

Triad systems [ED-PS-2Fe2S] integrate the electron donor, the photosensitizer, and the [2Fe2S] cluster, and thereby constitute the closest functional mimics to the natural [FeFe]-hydrogenase enzyme. The realization of fully functional artificial triad systems however presents numerous challenges. Apart from the obvious synthetic challenges, the main objective is to develop molecular building blocks that promote rapid electron transfer between the different functional units of the triad system. Competitive photophysical phenomena such as the recombination of charges in the sequential steps of photo-induced electron transfer (PET) must be avoided to achieve long-lived charge separation for photocatalytic hydrogen evolution.

Considering the design requirements, Wu et al. synthesized a molecular triad [ED-PS-2Fe2S] **30** consisting of a [2Fe2S] complex, [144]

a Re-based PS and a ferrocene donor, together with the reference [2Fe2S] complex (**28**) and the rhenium (I) complex (**29**) (**Figure 10**) [145]. The three components were chosen to exhibit a strong driving force for photo-driven electron transfer, while the long distance between the terminal ferrocene and the [2Fe2S] site as well as the weak electronic coupling between them were anticipated to prevent charge recombination during the photocatalytic reaction. Triad **30** and diiron complex **28** exhibited similar UV/Vis absorption bands characteristic of [2Fe2S] complexes at 300–400 nm and 450–600 nm and typical infrared vibrations corresponding to the CO ligands coordinated to the [2Fe2S] core. In contrast, complex **29** showed only two weak absorption peaks common to rhenium-based complexes at <350 nm and >400 nm attributed to ligand-to-ligand charge transfer (LLCT) and the $d\pi(\text{Re}) \rightarrow \pi^*(\text{N-N})$ ¹MLCT state, respectively [146]. These results indicated that the ferrocene-appended rhenium(I) complex did not have significant electronic interaction with the [2Fe2S] cluster in the ground state. Electrochemical studies [147] corroborated the thermodynamic feasibility of a photo-induced electron transfer (PET) cascade to form the fully charge separated state with a reduced diiron site and an oxidized ferrocene donor. The PET dynamics were further examined by time-resolved absorption spectroscopy and electrochemical data. For the reference system, addition of the [2Fe2S] complex **28** to a solution of **29** resulted in a new transient absorption at 400 nm very similar to that observed also for the triad **30**. This absorption band is characteristic for [Fe^IFe⁰] species, and agrees well with reference spectra obtained by electrochemical reduction of diiron complexes [148–150]. A significantly longer lifetime of the [Fe^IFe⁰] species was shown for the triad **30** (> 2 ms) compared to that of the combination of **28** and **29** (708 μs), highlighting the stability of the formed species. Accordingly, a decreased rate for back electron transfer was observed ($k_{\text{CR}} = <0.5 \times 10^2 \text{ s}^{-1}$) for triad **30** compared to that of the combination of **28** and **29** ($k_{\text{CR}} = 1.41 \times 10^3 \text{ s}^{-1}$). Thus, the [ED-PS-2Fe2S] **30** was anticipated to be a powerful photosystem candidate for light-induced hydrogen evolution. Indeed, triad **30** showed a higher TON (TON = 0.35 based on [2Fe2S] catalyst concentration) than the combination of **28** and **29** (TON = 0.04) for hydrogen evolution using AscOH as a proton and electron source. Despite not being a catalytic process (TON <1), a multistep PET chain was established by assembling a ferrocene donor, a rhenium chromophore and a diiron catalyst for light-assisted hydrogen production.

The same group reported dyad **31** (**Figure 10**) by fusing [2Fe2S] **28** with a complex derived from **29** without the ferrocene group. Characteristic

transient absorptions of $[\text{Fe}^{\text{I}}\text{Fe}^0]$ species analogous to those shown in the triad **30** could be observed upon laser excitation [151]. Hydrogen evolution experiments with 1,4-dihydropyridine as sacrificial ED and proton source were carried out with improved photocatalytic performance, resulting in a TON of 34 for dyad **31** and up to 47 for triad **30**.

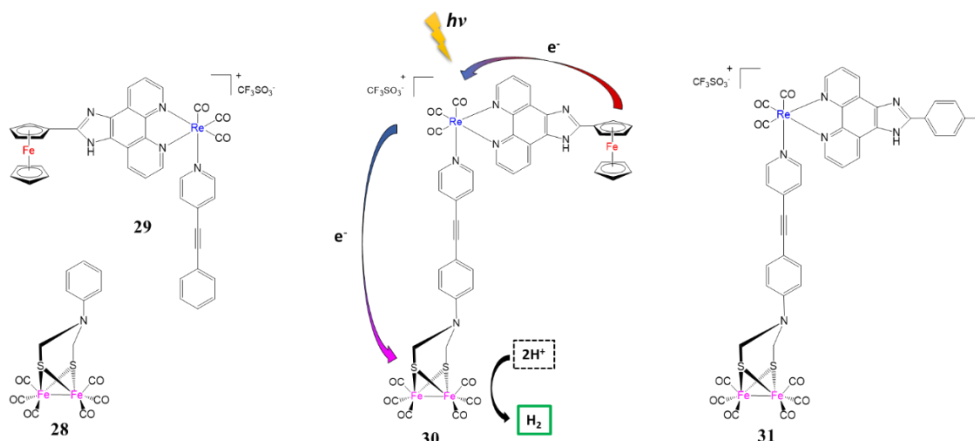


Figure 10. Molecular structures of triad **30** based on ferrocene-Re(I) complex-[2Fe₂S] mimic and its reference complexes **28**, **29** and **31** [145].

In parallel, Wasielewski and co-workers developed [ED-PS-2Fe₂S] systems **32** and **33** (**Figure 11**) composed of a naphthalene monoamide (NMI) diiron complex $[\text{NMI-Fe}_2\text{S}_2(\text{CO})_6]$, and a ferrocene electron donor that is covalently linked to a zinc metalloporphyrin (ZnTPP) via one or two phenyl groups, respectively [152]. In these triads, the lifetime of the charge separated state was envisaged to be longer as compared to that in the previously reported dyad **17** [128] (see **Section 3**, **Figure 9**). Interestingly, upon laser excitation to form the PS excited state, two competing pathways are observed. While in **32**, the main deactivation pathway for $^1\text{ZnTPP}^*$ was energy transfer to ferrocene, the extra phenyl spacer in **33** decreased the electronic coupling between ferrocene and ZnTPP, thereby promoting the productive electron transfer to the diiron site instead. Consequently, the quantum yield for the fully charge separated state differ dramatically, amounting to 13 and 71 % for **32** and **33**, respectively. Owing to the extra phenyl spacer in **33**, also the lifetime of the charge separated state is considerably longer with to $\tau_{\text{CR}} = 67 \pm 2$ ns as compared to that of triad **32** (to $\tau_{\text{CR}} = 9 \pm 1$ ns). The increased charge separation lifetime was the main factor for triad **33** to catalyzed photo-driven hydrogen production (100 W

Xe lamp, $\lambda=500\text{--}800$ nm light). Unfortunately, a TON (based on catalyst) of only 0.56 was obtained after 14 h in CH_2Cl_2 , which was explained by the decomposition of the photosystem, as evidenced by the detection of CO using gas chromatography (GC) and ESI-MS. When 2-mercaptobenzoic acid was tested as sacrificial ED, hydrogen generation did not increase as the oxidation potential of this ED is nearly identical to that of ferrocene [153].

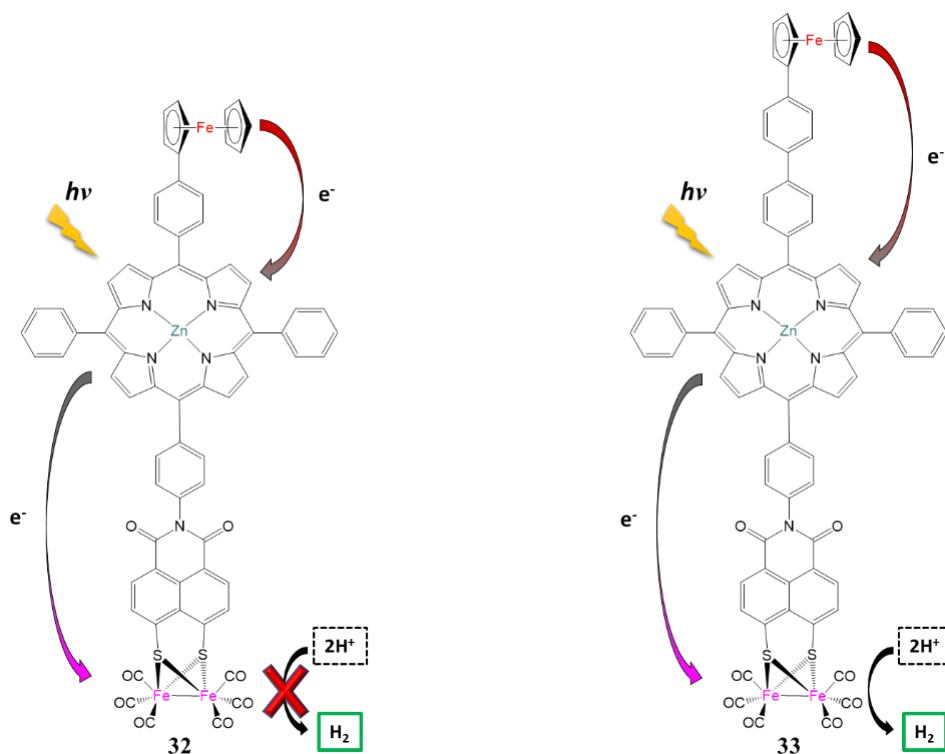


Figure 11. Molecular structures of triad **32** and **33** based on ferrocene-Zn metalloporphyrin complex-[2Fe2S] mimic for photocatalytic H_2 production [152].

The research papers discussed above show that a biomimetic [FeFe]-hydrogenase active site model can be covalently linked to a molecular PS and ferrocene ED. The resultant triads form an integrated artificial photocatalytic system with a multistep PET chain that can sustain long-lived reduced states at the [2Fe2S] site, which is key for efficient light-driven hydrogen production.

5.2.1.5. Supramolecular assemblies of [FeFe]-hydrogenase active site mimics

The assembly of supramolecular systems relies on non-covalent interactions between substrate and receptor molecules [154–157]. Molecular recognition, supramolecular catalysis and selective transport processes as concepts in these systems opened the door for chemists to gain precise control over matter and information at the supramolecular level [158]. With appropriate subunits integrated into a supramolecular complex, efficient and selective catalytic reactions could be carried out. Analogous to an enzyme's extended coordination sphere, supramolecular assemblies could be used to precisely create substrate and product channels, redox tuning, and specially tuned microenvironments for optimized catalysis.

With this goal in mind, supramolecular strategies have been implemented in the design of biomimetic models of the [FeFe] hydrogenase active site through non-covalent intermolecular interactions. Structural and electronic considerations in the construction of a supramolecular assembly for [2Fe2S] clusters are: 1) solubility and/or functionality in water, 2) buried sites for the diiron catalyst to avoid deactivation by oxygen, 3) proton-coupled electron transfer pathways in the outer coordination sphere. The scientific community has developed numerous approaches to analyze the influence of a protein matrix or supramolecular structure on [FeFe]-hydrogenase active site mimics.

5.2.1.5.1. Physical entrapment of [2Fe2S] active sites in supramolecular assemblies

5.2.1.5.1.1. Confinement of [2Fe2S] complexes in oligosaccharides and polysaccharides

The enzymatic conversion of starch produces cyclodextrins (CyD), cyclic oligosaccharides consisting of macrocyclic rings of 6 (α), 7 (β), and 8 (γ) subunits of D-glucose linked by α -[1,4] glycosidic bonds giving rise to toroidal and rigid molecular structures with specific volumes. The hydrophobic interior cavity allows the inclusion of smaller molecules forming host-guest complexes, in which the guest molecule is encapsulated in the host CyD. The hydrophilic exterior renders the system water soluble while protecting the trapped complex in its interior.

Darensbourg and co-workers pursued the approach to insert molecular [2Fe2S] complexes into CyD macrostructures, and demonstrated the self-assembly of a sulfonate-functionalized [2Fe2S] complex **34** (**Figure 14**) and β -CyD by spectroscopic studies and X-ray diffraction analysis. The resulting complex was stable in water. However, there was a decrease in electrocatalytic performance for proton reduction compared to that of the free complexes. Hindered by the insulating layer of β -CyD, large cathodic potentials were required to drive electron transfer processes [159,160]. Further studies by Sun et al. were reported for host-guest complexes with the same sulfonate-functionalized diiron complex **34** encapsulated into β -CyD and γ -CyD (**Figure 12a**). Halogenated organic dyes were included as photosensitizers for photocatalytic hydrogen production in aqueous solution [161]. The diffusion and interaction of the xanthene-derived dye with the macromolecular cyclodextrin was intended to increase their electronic interaction. Under light irradiation using Eosin Y as PS and TEA as sacrificial ED at pH=10, the β -CyD supramolecular system (**34**/ β -CyD-EY) showed the best photocatalytic performance obtaining a TON of 75 after 24 h (**Table 3**, entry 1). This system resulted in 9-fold increase in TON, 16-fold improvement in quantum efficiency and 3-fold extension in lifetime compared to the system lacking cyclodextrin for light-induced hydrogen generation in aqueous medium.

This research group further used the same [2Fe2S] complex **34** and CdSe quantum dots (QDs). Both components were embedded on a thiolato-functionalized β -cyclodextrin (β -CyD-6-SH), establishing close proximity for the diiron catalyst and the PS (**Figure 12b**) [162]. The incorporation of the diiron catalyst into the β -CyD-6-SH cavity improved the photocatalytic process and stability of the water-soluble hybrid system. Photocatalytic H₂ evolution experiments for the **34**/ β -CyD-6-S-CdSe QDs supramolecular system using AscOH as ED demonstrated a maximum TON of 2370 after 30 h (**Table 3**, entry 2) and a TOF of up to 150 h⁻¹ in the initial 10 h of the reaction. Maintaining a close distance between the CdSe QDs and the diiron complex through β -CyD-6-SH resulted in optimal electron transfer and charge separation between both functional units.

In acidic medium, the natural chitosan polysaccharide provides a chelating capacity through its polycationic character arising from the protonation of primary amines. The [2Fe2S] complex **1** (see **Section 2**, **Figure 7**) and 3-mercaptopropionic acid (MPA)-capped CdTe quantum dots (MPA-CdTe QDs) with negative surface charges were incorporated

into cationic chitosan (**Figure 12c**) [163]. The supramolecular hybrid system was evaluated for photocatalytic hydrogen production using AscOH as ED in a methanol/water mixture (1:3) at pH = 4.5. In addition, AscOH was crucial as proton source for the amine groups of chitosan and the catalytic intermediate of the diiron photoreduced complex. The self-assembled system (**1/chitosan-MPA-CdTe QDs**) showed a TON of up to 52800 (**Table 3**, entry 3) and an initial TOF of 1.40 s^{-1} . Improvement in stability and catalytic performance from 8 to 60 h was especially dramatic, showing a 4160-fold increase in TON compared to the same system without chitosan.

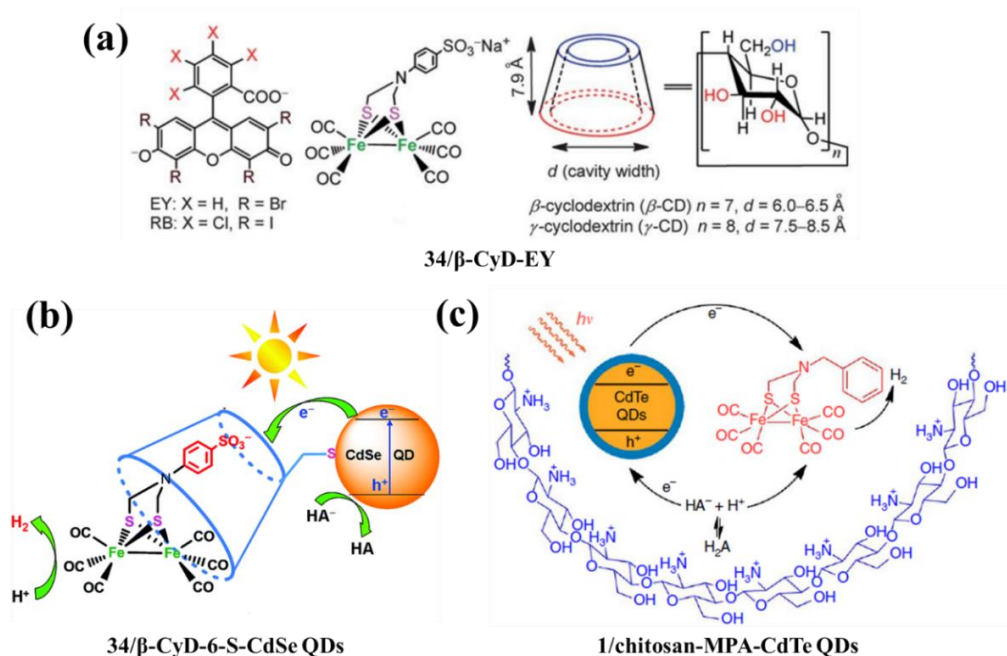


Figure 12. (a) Cyclodextrin host-guest inclusions formed by incorporation of [2Fe₂S] complex **34** and an organic halogenated xanthene dye (reproduced and modified from Ref. [161] with permission from The Royal Society of Chemistry), (b) Hybrid assembly of [2Fe₂S] complex **34** and CdSe quantum dot linked through a thiolato-functionalized β-cyclodextrin for photocatalytic hydrogen evolution (reproduced and modified from Ref. [162] with permission from The Royal Society of Chemistry), and (c) chitosan-confined [2Fe₂S] complex **1** and CdTe quantum dots for hydrogen photogeneration (reproduced and modified from Ref. [163] with permission of Springer Nature).

5.2.1.5.1.2. Confinement of [2Fe2S] complexes in micelles

Micelles are spherical macromolecular structures with an apolar interior that are formed from amphipathic molecules with surface polar groups. In the past decade, aqueous micelles prepared from surfactants have been used to simulate cell membranes to disperse [FeFe]-hydrogenase active site mimics in water. Some common surfactants used to form these micelles were sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and dodecyltrimethylammonium bromide (DTAB), all featuring a charged surface and a hydrophobic cavity. Aqueous SDS-based micelles with negatively charged surfaces encapsulating water-insoluble diiron bdt complexes **35** (**Figure 14**) were reported to be electrocatalytic for proton reduction in aqueous solutions [164,165]. Another study examined the molecular environment of complex **38** ($\text{Fe}_2(\text{pdt})(\text{CO})_6$, pdt = propanedithiolate) (**Figure 14**) encapsulated in an aqueous DTAB-based supramolecular structure by infrared spectroscopy techniques. The results suggested that the diiron complex **38** was found in two environments: one that hydrogen bonds with water molecules penetrating the surfactant layer and the second similar to that of the complex in heptane solution. Additionally, this study revealed that water access to the interior of the hydrophobic micellar cavity was limited by the micelle size [166].

In 2010, Wu et al. carried out the first attempt at photocatalytic hydrogen evolution using an aqueous SDS-based micelle to incorporate the hydrophobic [2Fe2S] complex **1** (see **Section 2, Figure 7**) and a rhenium-based PS [167]. Although the micelles promoted water solubility of the diiron complex, a very low TON value of 0.13 was obtained for the photosystem **1/SDS-Re(1)** in presence of AscOH as sacrificial ED (**Table 3**, entry 4). Diiron benzenedithiolate complexes $[(\text{Fe}_2(\text{bdt})(\text{CO})_4(\text{L}))_2, \text{L}=\text{P}(\text{OMe})_3]$ relevant to [FeFe] hydrogenases (**35-37**) (**Figure 14**) were tested in combination with organic xanthene photosensitizers in aqueous SDS-based micelles for photochemical hydrogen production using TEA as the ED under alkaline conditions [168]. The supramolecular micellar photosystem **35/SDS-EY** achieved a TON of up to 117 and a TOF of 1.1 min^{-1} (**Table 3**, entry 5).

Recently, Wu and co-workers prepared a novel amphiphilic polymeric micelle (APM) from a polynorbornene random copolymer based on a hydrophobic alkyl chain (C_{12}) and three oligo(ethyleneglycol) chains with hydrophilic moieties [169]. This self-assembled macromolecular structure was used as a microreactor to confine the hydrophobic diiron

propanedithiolate complex **38** $[(\text{Fe}_2(\text{pdt})(\text{CO})_6)]$. Under optimized reaction conditions, the photosystem **38/APM-Ru(bpy) $_3$ $^{2+}$** achieved a TON of 133 using $\text{Ru}(\text{bpy})_3^{2+}$ as a PS and AscOH as ED in acidic aqueous solution at pH = 4.0 (**Table 3**, entry 6). The amphiphilic polymeric micellar system promotes interaction between the PS and the diiron catalyst in the microreactor pocket, improving the proton migration rate and thereby the efficiency of the photocatalytic process.

In another approach, $[2\text{Fe}2\text{S}]$ complexes were tethered to a silafluorene sensitizer **27** (see **Section 3, Figure 9**) and encapsulated in micelles formed by SDS (**27-SDS**) or CTAB (**27-CTAB**) [143]. The construct was evaluated for photochemical hydrogen generation in aqueous solution, using TEA as a sacrificial ED and TFA (2:1). The TONs of 139 and 148 achieved for **27-SDS** and **27-CTAB**, respectively, were the highest reported for micellar systems (**Table 3**, entries 7 and 8).

5.2.1.5.1.3. Adsorption of $[2\text{Fe}2\text{S}]$ complexes into self-assembled vesicle membranes

Functionalized vesicles with membrane-incorporated photosensitizers and $[\text{FeFe}]$ -hydrogenase active site mimics have been developed for catalysis in aqueous solutions [170]. König et al. prepared self-assembled phospholipid vesicles with functionalized membranes by adsorption of the diiron complex **34** (**Figure 14**) and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ photosensitizer onto the membrane (**Figure 13a**). In a second approach, the amphiphilic ruthenium bipyridine photosensitizers ($[\text{Ru}(\text{bpy})_2(\text{bpy}(\text{CONHC}_{12}\text{H}_{25})_2)]\text{Cl}_2$ or $[\text{Ru}(\text{bpy})_2(\text{bpy}(\text{CONHC}_{12}\text{H}_{25})_2)]\text{PF}_6$) (**Figure 13b**) were embedded in the membrane, while keeping **34** as the catalyst [171]. The integration of the PSs in close proximity to the diiron complex at the vesicular interface promoted strong electronic interaction, enhancing light-induced hydrogen production. Membrane functionalization with the catalytic subunit **34** and the photosensitizer $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ was studied for the production of hydrogen in acetonitrile/water (1:1) or pure water, with a TON of 4.2 and 3.5, respectively. In contrast, a TON of 20 was obtained using DOPC vesicles (dioleoyl-sn-glycero-3-phosphocholine) to encapsulate the catalyst and PS. The highest catalytic activity was achieved for the photosystem **34/DMPC-Ru(bpy) $_3$ $^{2+}$** composed of $[\text{Ru}(\text{bpy})_2(\text{bpy}(\text{CONHC}_{12}\text{H}_{25})_2)]\text{PF}_6$ and the diiron complex **34** adsorbed on the vesicle prepared from the lipid DMPC (1,2-dimyristoyl- sn-glycero-

3-phosphocholine). A TON of 59 was achieved using AscOH as sacrificial ED in acidic water (pH = 2.6) (**Table 3**, entry 9). Strongly acidic conditions favor the protonation of photoreduced $[\text{Fe}^{\text{I}}\text{Fe}^{\text{0}}]$ species, a crucial intermediate in the catalytic cycle for hydrogen evolution, but decrease the formation of the AscO^{\ominus} ($\text{p}K_{\text{a},1} = 4.17$), which is key in regenerating the PS. The highly acidic pH of 2.6 in this study was due to the change in $\text{p}K_{\text{a}}$ and polarity values at the aqueous lipid interface, suggesting some influence on the electron-proton transfer features of AscOH which shifted the optimal pH to more acidic values. In parallel, the same research group functionalized DOPC and DSPC (1,2-distearoyl-sn-glycero-3-phosphocholine) vesicles by co-embedding hydrophobic oleic acid-capped cadmium selenide quantum dots (OA-CdSe QDs), known for their excellent light-harvesting properties, and the sulfonate-functionalized $[\text{2Fe2S}]$ complex **39** (**Figure 14**) [172]. Under optimized conditions, the bio-inspired photosystem **39/DOPC-OA-CdSe QDs** (**Figure 13c**) exhibited exceptional light-driven hydrogen evolution, achieving a maximum TON of 651 in purely aqueous AscOH solution (**Table 3**, entry 10).

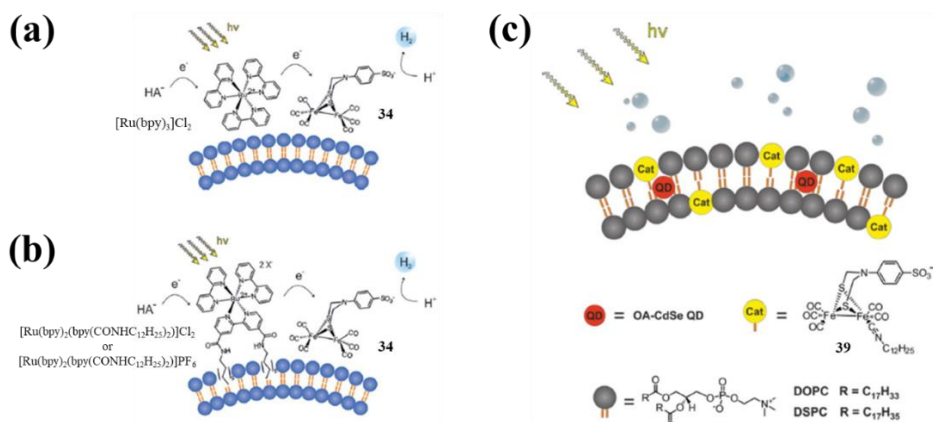


Figure 13. Schematic representation of functionalized vesicular supramolecular systems prepared from (a) photosensitizer $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ and diiron complex **34**, both adsorbed to the phospholipid membranes, (b) embedded ruthenium-based photosensitizers and adsorbed diiron complex **34** into phospholipid membranes, and (c) oleic acid capped CdSe quantum dots (OA-CdSe QDs) and proton reduction catalysts **39** incorporated into phospholipid membranes for light-induced hydrogen evolution. Reprinted and modified from Refs. [171,172] with permission from John Wiley and Sons.

5.2.1.5.1.4. Immobilization of [2Fe2S] complexes into hydrogels

Hydrogels have shown promise in addressing the challenge of introducing [FeFe]-hydrogenase mimics to aqueous solutions using a non-covalent strategy. Commonly known as polymer gels, hydrogels have a wide range of applications due to their low cost, structural tunability, and high surface area. They possess a stable internal network that is compatible with the immobilization of [2Fe2S] active sites, facilitating the dispersion of these hydrophobic complexes in water [173].

Pickett et al. reported a self-supporting supramolecular gel by non-covalent encapsulation of the diiron active site complex **40** [$(\mu\text{-pdt})\text{Fe}_2(\text{CO})_4(\text{PMe}_3)_2$] (**Figure 14**) in an Fmoc-Leu-Leu dipeptide hydrogel. This group studied the effect of the chemical environment and the interaction of the [2Fe2S] cluster with the polymer gel peptide side chains in the hydrophobic cavity [174]. Compound **40** was chosen as the [2Fe2S] complex since the replacement of CO by two trimethylphosphine ligands (PMe_3) provided an electron-rich metal center that promotes facile protonation [175,176]. This investigation showed the potential scope of this system to form a rigid H-bonding network and prevent isomerization processes caused by CO ligands in the gel.

Considering the relevant properties of hydrogels as macromolecular supports for artificial enzyme complexes, Li and co-workers used polyvinylpyrrolidone copolymer (PVP) to create a chemically inert amphipathic hydrogel by UV-induced self-crosslinking to non-covalently incorporate [2Fe2S] complex **41** (**Figure 14**) [177]. This resulted in a photocatalytic hydrogen production system fabricated from the initial preparation of a composite catalyst **41/PVP** followed by the subsequent addition of the $\text{Ru}(\text{bpy})_3^{2+}$ PS and AscOH as ED. The amphipathic PVP hydrogel provided a suitable scaffold to keep the diiron complex **41** and the ruthenium PS close, thus facilitating intermolecular electron transfer. The photosystem (**41/PVP-Ru(bpy) $_3^{2+}$**) photocatalytically produced hydrogen in aqueous solution at pH = 4 with an outstanding TON of 780 after 12 h and a TOF of 214 h^{-1} in the first hour of irradiation (**Table 3**, entry 11).

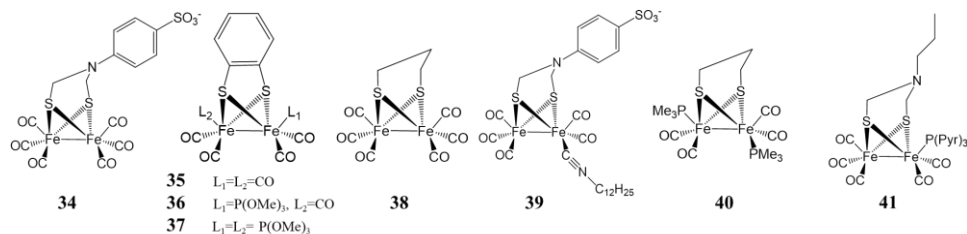


Figure 14. Molecular structures of diiron compounds used in supramolecular systems.

5.2.1.5.2. Covalent attachment of $[2Fe_2S]$ complexes on supramolecular assemblies

5.2.1.5.2.1. Immobilization of $[2Fe_2S]$ complexes into hydrogels

Inspired by nature, artificial metalloenzymes are hybrid catalysts constructed by incorporation of a catalytically active metal complex into a biosupramolecular scaffold [178–180]. $[FeFe]$ -hydrogenase active site models have been successfully incorporated into peptides and protein matrices with the aim of enhancing water compatibility and catalytic performance in terms of selectivity, specificity and efficiency [181]. The synthetic procedure consists of covalently attaching the diiron complex to a peptide chain through cysteine-derived amino acids with thiolate ligands or by introducing artificial amino acids containing bridging dithiolate groups into the polypeptide backbone.

In 2007, Jones et al. were the first to report the coordination of a diiron entity $Fe_2(CO)_6$ to the surface of an α -helical peptide through the thiol group of cysteine in the CXXC motif (C=cysteine and X= any amino acid) [182]. Construct **42** (**Figure 15**) was the first protein-organometallic hybrid system based on synthetic models of the $[FeFe]$ -hydrogenase active site, inspiring further peptide engineering to fine-tune the properties of such systems.

Hayashi and co-workers developed two methodologies to synthesize artificial metalloenzymes with catalytically active diiron complexes incorporated into appropriately positioned CXXC peptide fragments that established a dithiolate bridge. The group designed a hybrid system by constructing the $[2S_2Fe]$ complex in the native CXXC motif using Cys14 and Cys17 in the cytochrome c protein matrix affording **43/cytochrome c** $[Fe_2(\mu-S(Cys))(CO)_6]$ (**Figure 15**) [183]. Simulating

electron transfer in the respiratory mitochondrial system, the water-soluble intermolecular photosystem (**43/Cytc-Ru(bpy)₃²⁺**) was evaluated for photocatalytic hydrogen production yielding a TON of 80 over 2 h with a maximum TOF of 2.1 min⁻¹ in the presence of Ru(bpy)₃²⁺ and AscO[□] at pH = 4.7 (**Table 3**, entry 13).

An alternative route was reported by the same group in the construction of a peptide platform containing both a datively anchored [Fe₂(μ-S(Cys))(CO)₆] diiron complex **42** and a Ru-based PS [184]. The octadecapeptide Pep-18 (YIGKACGNCHENFRDKEG) contained in the sequence of cytochrome c556 (*Rhodospseudomonas palustris*) was selected as the matrix. The [2Fe2S] cluster was attached to the cysteine thiols and the ruthenium complex to a histidine within the CXXCH peptide fragment. Photochemical hydrogen evolution experiments demonstrated intramolecular electron transfer from the photoexcited ruthenium species to the [2Fe2S] core within photosystem **42/Cytc₅₅₆@Ru(bpy)(tpy)**, obtaining a TON of 9 and a TOF of up to 0.19 min⁻¹ calculated from the initial rate of hydrogen production (**Table 3**, entry 12). When the photocatalytic reaction was performed using **42/Cytc₅₅₆** and externally incorporating [Ru(tpy)(bpy)(Im)]²⁺ (Im = imidazole) as a PS under similar experimental conditions, H₂ evolution was not observed, verifying the crucial role of the ruthenium complex residing within the cavity of the protein matrix.

To investigate the engineering of the outer coordination sphere, Jones et al. reported a new route using an artificial amino acid for immobilization of a diiron complex on the peptide chain. The synthetic procedure involved modifying the primary amine functional group with a 1,3-dithiol moiety via on-resin coupling in solid-phase peptide synthesis to covalently anchor the [2Fe2S] **44** (**Figure 15**) [185]. This synthetic strategy provided a general methodology for the covalent binding of a [2Fe2S] entity to any peptide framework with a primary amine group. However, the selectivity for the targeted amino acid during the multistep process was not ideal. In subsequent work carried out by the same group, an analogous diiron complex was incorporated into the above peptide sequence by coordination through a phosphine ligand incorporated at the distal iron atom. The synthesized structure **45** (**Figure 15**) with phosphine-containing peptides was useful to increase the water solubility and served as a model strategy for the synthesis of a wide variety of biomimetic peptide-based models of [FeFe]-hydrogenases [186].

Inspired by this approach, Ghirlanda et al. prepared an artificial amino acid bearing a 1,3-dithiol moiety to covalently anchor the [2Fe2S] cluster **46** (**Figure 15**) and the C terminal lysine 19 at the *i* and *i* + 3 positions of a helical peptide scaffold (**46/pepK16Dt**), simulating the H-cluster in *Clostridium pasteurianum* hydrogenase [187]. The hydrophobic protein environment promoted the stabilization of the catalytically active ‘rotated’ structure of the [2Fe2S] cluster. In the presence of the Ru(bpy)₃²⁺ and AscO[□], the photosystem **46/PepK16Dt-Ru(bpy)₃²⁺** showed catalytic activity for photo-driven hydrogen production with a TON of 84 after 2 h reaction at pH = 4.5 (**Table 3**, entry 14).

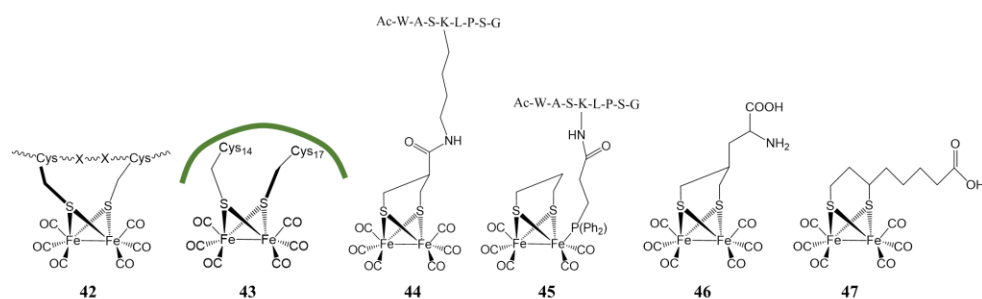


Figure 15. Molecular structures of diiron complexes anchored within peptide and protein scaffolds.

In 2014, Hayashi and co-workers reported a biomimetic model of the [FeFe]-hydrogenase active site supported on a protein scaffold. The [2Fe2S] complex Fe₂(μ-S)₂(CO)₆ with a maleimide moiety attached to the dithiol bridgehead **4** (see **Section 2**, **Figure 7**) was covalently embedded into the cavity of a β-barrel nitrobindin (NB) protein matrix by maleimide coupling to cysteine residues [188]. Photochemical hydrogen production experiments were performed in the presence of a Ru(bpy)₃²⁺ with excess AscO[□] in an aqueous acidic solution of Tris/HCl at pH = 4. A high photocatalytic activity was obtained using the hybrid system **4/NB-Ru(bpy)₃²⁺**, yielding a TON of 130 after 6 h and an initial TOF of 2.3 min⁻¹ (**Table 3**, entry 15). The rigid NB protein support provided an isolated specific site for the diiron complex to operate in aqueous solution and maintain the photostability of the [2Fe2S] cluster. However, the catalytic activity of the system after 2 hours was slightly lower compared to that of the free diiron compound under near-identical experimental reaction conditions. Nonetheless, the protein environment maintains catalytic activity for a longer time. Another challenge to be addressed is the inaccessibility of the ruthenium PS within the rigid cavity of the NB protein

where the [2Fe2S] site is located, causing a decrease in photocatalytic hydrogen production rate.

Recently, Feng and co-workers prepared a supramolecular photosystem that integrates a ruthenium-based PS Rudpqp ($[\text{Ru}(\text{bpy})_2(\text{dpqp})]^{2+}$), containing bipyridine and phenanthroline ligands, and the diiron catalyst **47** (**Figure 15**) within the inner hydrophobic cavity of a single apoferritin (apo-HSF) via noncovalent interactions [189]. This biomimetic system presented the following advantages: stability and dispersibility in aqueous solution, tuneable **47**:PS ratio within the protein structure and close proximity of both units to promote electron transfer. The nanocomposite **47/apo-HSF@Rudpqp** synthesized with a Rudpqp:**47** concentration ratio of 2.79:1 exhibited the highest H₂ generation rate without significant leaching, providing a TON of 5 per catalyst over 4 h under visible light irradiation (**Table 3**, entry 16), which is tenfold that of the protein-free homogeneous photocatalytic system.

5.2.1.5.2.2. Polymer-supported [2Fe2S] systems

Metallopolymers have been developed in which [2Fe2S] clusters are incorporated in polymeric macrostructures either by covalent binding or intermolecular non-covalent interactions. These studies are based on knowledge from polymer chemistry that provides perspectives on suitable design and functionalization methods to tune and isolate the [2Fe2S] clusters.

Appropriate macromolecular engineering of the metallopolymers by tuning the outer coordination sphere of the [2Fe2S] complex enables the construct to operate in an aqueous medium, increases the stability under experimental reaction conditions, and improves charge transport in photocatalytic processes. Various approaches have been developed using polymer-supported [2Fe2S] systems, but only a few have succeeded in designing a functional [2Fe2S]-polymer conjugate for light-driven hydrogen production.

5.2.1.5.2.2.1. Poly(acrylic acid) (PAA) and polyethylenimine (PEI) polymers

Poly(acrylic acid) (PAA) is a commercial hydrophilic polymer with carboxylic acid groups along the polymeric chain that promote water solubility and offer modification sites for functionalization. Wu and co-

workers reported the incorporation of the amine-modified [2Fe2S] **48** on the PAA polymer [190]. This functionalized polymer **48/PAA** (**Figure 16**) was evaluated for photocatalytic hydrogen production in water using 3-mercaptopropionic acid (MPA) stabilized CdSe QDs (MPA-CdSe QDs) as PS and AscOH as source of protons and electrons (**Table 3**, entry 17). Under these conditions, the system achieved a splendid TON of 27135 for 8 h and a TOF of up to 3.6 s^{-1} . Besides promoting water solubility for the diiron complex **48**, the carboxyl groups of the grafted-polymer **48/PAA** coordinated the cadmium ions of CdSe QDs, preventing the formation of QD aggregates and maintaining the catalyst close to the PS. This proximity boosted photoinduced electron transfer ($k_{\text{ET}} = 6.15 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$) from photoexcited *MPA-CdSe QDs to **48**.

In subsequent work, Wu's group designed the metallopolymer **49/PEI** (**Figure 16**) by grafting a carboxylate-functionalized diiron complex **49** onto the side chains of a branched polyethylenimine polymer (PEI, MW=600 g mol^{-1}) [191]. The branched PEI is a water-soluble polymer capable of simulating the environment of biological systems. It contains a large number of amino groups that can be protonated over a wide pH range and covalently coordinate [2Fe2S] model complexes. The **49/PEI** system was stable in aqueous solution even in neutral conditions, showing high photocatalytic H₂ production with a TON of up to 10,600 after 44 h of reaction time in the presence of a MPA-CdSe QD PS and AscOH as the sacrificial ED and proton source (**Table 3**, entry 18). Although a higher rate was obtained under acidic conditions at pH = 4 in the first 4 h, the system showed durable hydrogen production for prolonged times at neutral conditions, as is the case of the enzymatic active site that is buried within the [FeFe] hydrogenase. The high degree of protonation of the amine groups increases the self-buffering capacity and stabilizing ability of PEI that protects CdSe QDs from aggregation over a broad pH range to enhance photocatalytic activity.

Wu and colleagues have delved into the investigation of these [2Fe2S] catalysts and CdSe QDs based multi-component systems. In their previous study [190], they found that the grafted **48** on the PAA chain suffered from poor stability since the hole transfer rate was slower than the electron transfer rate. The hole electron transfer rate from CdSe QDs to AscOH was threefold slower than the electron transfer rate from CdSe QDs to **48**, slowing down hydrogen evolution as holes accumulated in the valence band of CdSe QDs. To overcome this, this research group

combined the branched PEI and the previous **48/PAA** system, creating a secondary coordination sphere and taking advantage of the supramolecular interaction of both polymers. This resulted in a 30-fold acceleration of the hole transfer without affecting the electron transfer rate, improving the stability and catalytic activity [192]. The photocatalytic hydrogen evolution system (**48/PAA-PEI-CdSe QDs**) (**Figure 16**) exhibited an excellent TON of 83600, which is so far the highest performance obtained from the use of [2Fe2S] complexes as catalysts for photocatalytic hydrogen production (**Table 3**, entry 19).

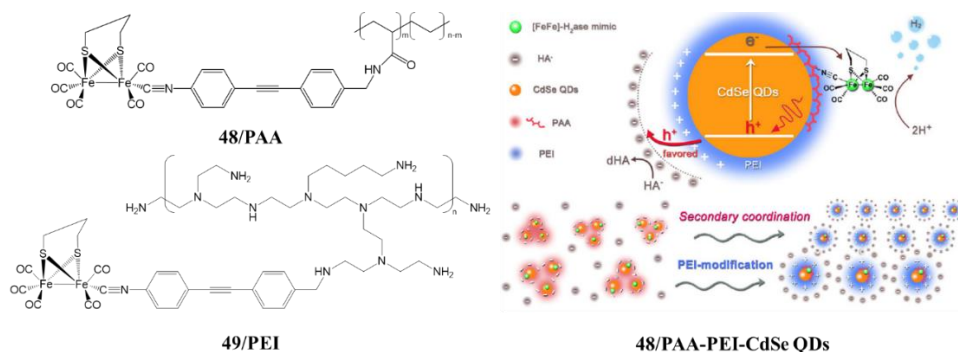


Figure 16. Structures of water-soluble [2Fe₂S]-metallopolymers for the light-induced hydrogen generation. Adapted from Refs. [192] with permission from Springe Nature.

5.2.1.5.2.2.2. Dendritic macropolymers

Dendrimers, three-dimensional hierarchically branched macromolecules of tree-like structure, can be used for a wide variety of applications. Their high water solubility and ability to form host-guest systems, among other relevant properties, have made them attractive candidates for applications in catalysis, artificial enzymes and biomedicine [193–195]. Several investigations have also demonstrated the light-harvesting ability of dendrimers for photoenergy conversions [196–198].

Li and co-workers reported an elegant strategy to stabilize a simple [2Fe₂S] complex in a hydrophobic pocket within a macromolecular dendritic architecture [199]. Four generations of benzyl ether-based Fréchet-type dendrons (G_n; generation number; n = 1–4) were attached to the [(μ-S)₂Fe₂(CO)₆] diiron core **50** by covalent interaction of the sulfide ligands with the ether groups in the dendrite (**Figure 17**).

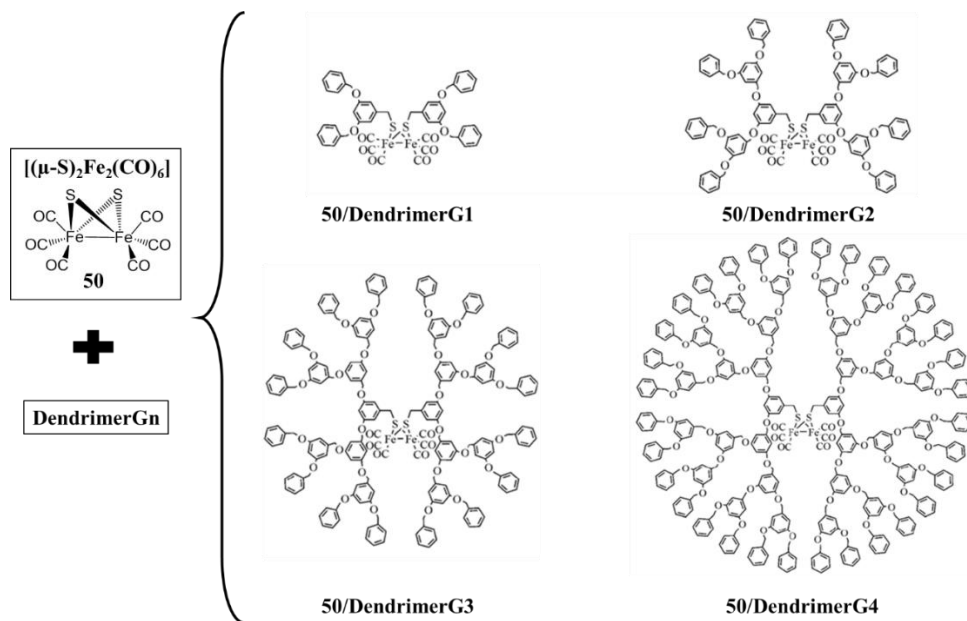


Figure 17. Structures of dendritic hydrogenase mimics (**50/DendrimerGn**, Gn=Generation Number; n=1-4) with the diiron active site **50** $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]$. Reproduced and modified from Refs. [199] with permission from John Wiley and Sons.

Dendrimer catalysts functionalized with $[2\text{Fe}2\text{S}]$ were then evaluated in a photocatalytic system containing a molecular complex of Ir(III) $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ as a PS and TEA as a sacrificial ED in an acetone/water mixture (9:1, v/v) to solubilize all components. **50/dendrimerGn-Ir(III)** showed excellent hydrogen productivity under visible-light irradiation with TONs of up to 18100, 19000, 21500 and 22200 after 8 h, initial TOFs of up to 6190, 6360, 7000, and 7240 h^{-1} , and quantum efficiencies of 0.18%, 0.21%, 0.24% and 0.28% for the dendritic diiron complexes of generations 1–4, respectively (**Table 3**, entry 20). Hydrogen generation increased with the size/generation of the dendritic metallopolymer architecture. The highest value of TOF and total TON was found for the system with the largest dendritic structure (**50/DendrimerG4-Ir(III)**), which also exhibited the longest lifetime of the $[2\text{Fe}2\text{S}]^-$ intermediate (86.3 μs estimated from transient absorption spectroscopy).

Thus, the dendritic framework encapsulating the $[2\text{Fe}2\text{S}]$ complex protects the active sites similarly to enzyme microenvironments that

regulate electron transfer and provide effective charge separation. Although this experimental procedure is a promising approach in the design of enzyme-based artificial photocatalysts towards the conversion of solar energy into hydrogen, future advances should aim to incorporate modifications in the dendritic periphery to improve water solubility.

Table 3. Supramolecular assemblies for [FeFe]-hydrogenase active-site mimics evaluated in light-driven hydrogen production.

Entry	SA ¹	Supramolecular photocatalytic system	Selected conditions ²	Light	Time (h)	TON ²	Ref.
1	Oligo- and polysaccharides	34/ β -CyD-EY	Water, 0.5 mM 34 ; 0.5 mM EY, 10 equiv. β -CyD, 10% TEA, pH=10	Xe lamp (500 W), $\lambda > 450$ nm	24	75	[161]
2		34/ β -CyD-6-S-CdSe QDs	Water, 1 μ M 34 , 100 μ M β -CyD-6-S-CdSe QDs, 0.28 M AscOH, pH=4.5	Xe lamp (300 W), $\lambda > 400$ nm	30	2370	[162]
3		1/chitosan-MPA-CdTe QDs	MeOH/Water (1:3), 1 μ M 1 , 1.71 μ M MPA-CdTe QDs, 1 g/L chitosan, 0.2 M AscOH, pH=4.5	LED, $\lambda = 410$ nm	60	52800	[163]
4	Micelles	1/SDS-Re(1)	Water, 0.18 mM 1 , 0.18 mM Re(I) complex, 0.1 M AscOH, 0.166 M SDS	Hg lamp (300 W), $\lambda > 400$ nm	2	0.13	[167]
5		35/SDS-EY	Water, 0.1 mM 35 , 0.2 mM EY, 10% TEA, 10 mM SDS, pH=10.5	LED (0.3 W), $\lambda = 455$ nm	4.5	117	[168]
6		38/APM-Ru(bpy) ₃ ²⁺	Water/APM, 0.03 mM 36 , 0.3 mM Ru(bpy) ₃ ²⁺ , 45 mM AscOH, pH=4.0-4.1	LED, $\lambda = 450$ nm	2	133	[169]
7		27-SDS	Water/SDS, 10 μ M 27 , 100 mM TEA, 50 mM TFA, pH=10	Hg lamp (15 W), $\lambda = 254$ nm	4	139	[143]
8		27-CTAB	Water/CTAB, 10 μ M 27 , 100 mM TEA, 50 mM TFA, pH=10	Hg lamp (15 W), $\lambda = 254$ nm	4	148	[143]
9	Vesicle membranes	34/DMPC-Ru(bpy) ₃ ²⁺	Water, 0.1 mM 34 , 0.1 mM Ru(bpy) ₃ ²⁺ , 100 mM AscOH, 0.9 mM DMPC, pH=2.6, 19 °C	LED (91 mW/cm ²), $\lambda = 455$ nm	1.5	59	[171]
10		39/DOPC-OA-CdSe QDs	Water, 50 μ M 39 , 0.2 μ M OA-CdSe QDs, 200 mM AscOH, 0.9 mM DOPC, pH=4, 19 °C	LED (91 mW/cm ²), $\lambda = 455$ nm	72	651	[172]
11	Hydrogels	41/PVP-Ru(bpy) ₃ ²⁺	Water, 1 μ M 41 , 0.5 mM Ru(bpy) ₃ ²⁺ , 0.2 M AscOH, 10 mg PVP, pH=4	Xe lamp (300 W), $\lambda = 400-780$ nm	12	780	[177]
12	Peptides and proteins	42/Cytc _{ss6} @Ru(bpy)(tpy)	Water, 140 μ M 42/Cytc_{ss6}@Ru(bpy)(tpy) , 100 mM AscO, 50 mM Tris/HCl, pH=8.5, 25 °C	Xe lamp (500 W), $\lambda = 410-770$ nm	2	9	[184]
13		43/Cytc-Ru(bpy) ₃ ²⁺	Water, 14 μ M 43/Cytc , 140 μ M Ru(bpy) ₃ ²⁺ , 100 mM AscO, 50 mM Tris/HCl, pH=4.7, 25 °C	Xe lamp (500 W), $\lambda = 410-770$ nm	2	80	[183]

14		46/PepK16Dt-Ru(bpy)₃²⁺	Water, 9.33 μ M 46/PepK16Dt , 150 μ M Ru(bpy) ₃ ²⁺ , 50 mM AscO ⁻ , 50 mM citrate buffer, pH=4.5	Xe lamp (450 W), λ =410-770 nm	2.3	84	[187]
15		4/NB-Ru(bpy)₃²⁺	Water, 7.8 μ M 4/NB , 140 μ M Ru(bpy) ₃ ²⁺ , 100 mM AscO ⁻ , 50 mM Tris/HCl, pH=4.0, 25 °C	Xe lamp (500 W), λ =410-770 nm	6	130	[188]
16		47/apo-HSF@Rudpqp	Water, 11.3 μ M 47 , 31.6 μ M Ru(bpy) ₃ ²⁺ , 100 mM AscOH, pH=5.3.	Xe lamp (300 W), λ >420 nm	4	5	[189]
17	Metallopolymers	48/PAA-MPA-CdSe QDs	Water, 0.25 mg/mL 47/PAA , 0.08 mg/mL MPA-CdSe QDs, 0.1 M AscOH, pH=4.0	LED, λ =450 nm	8	27135	[190]
18		49/PEI-MPA-CdSe QDs	Water, 1.46 μ M 48/PEI , 0.08 mg/mL MPA-CdSe QDs, 0.125 M AscOH, pH=6.5	LED (3W), λ =410 nm	44	10600	[191]
19		48/PAA-PEI-CdSe QDs	Water, 0.25 g/L 47/PAA , 5.8 μ M CdSe QDs, 0.46 g/L PEI, 0.1 M AscOH, pH=4.1	LED (3W), λ =450 nm	28	83600	[192]
20		50/DendrimerG4-Ir(III)	Acetone/Water (9:1), 1 μ M 49/DendrimerG4 , 0.5 mM Ir(III) complex, 0.6 M TEA	Xe lamp (300 W), λ =400-800 nm	8	22200	[199]

¹Supramolecular assembly; ²Solvents and reagents abbreviations: MeOH: methanol, AscOH: ascorbic acid, AscO⁻: ascorbate, TFA: trifluoroacetic acid, TEA: triethylamine.

² TON based on [2Fe2S] catalyst

5.2.1.6. Direct assembly of [2Fe2S] compounds on inorganic hybrid semiconductor nanoparticles

Artificial photosynthetic systems using semiconductors as light-harvesters in combination with a fuel-forming catalyst such as biomimetic models of the [FeFe]-hydrogenase active site (**Figure 18**) are promising candidates for solar fuel conversion.

The assembly of an appropriate catalyst onto a semiconductor can promote highly efficient charge separation, a fast electron transfer rate and decreased activation energy or overpotential, all key aspects to enhancing performance in light-driven hydrogen production. Functional groups on the catalyst are often essential for increased loading and reliable assembly on the semiconductor.

The interaction of *Clostridium acetobutylicum* [FeFe]-hydrogenase (CaI) with quantum dots of CdTe or CdS [200,201], or *Clostridium perfringens* SM09 [FeFe]-hydrogenase (CpHydA) with TiO₂

semiconductors [202] has been investigated for photocatalytic hydrogen formation. Even [NiFeSe]-hydrogenases from *Desulfomicrobium baculatum* (Db-[NiFeSe]) attached to TiO₂ nanoparticles [203] or organic polymeric carbon nitride (CN_x) [204] have been used as photosystems showing excellent performance in the light-assisted hydrogen generation. However, only a few studies have demonstrated the combination of [2Fe2S] complexes on semiconductor or semiconductor nanoparticles and their subsequent application in photocatalytic hydrogen production.

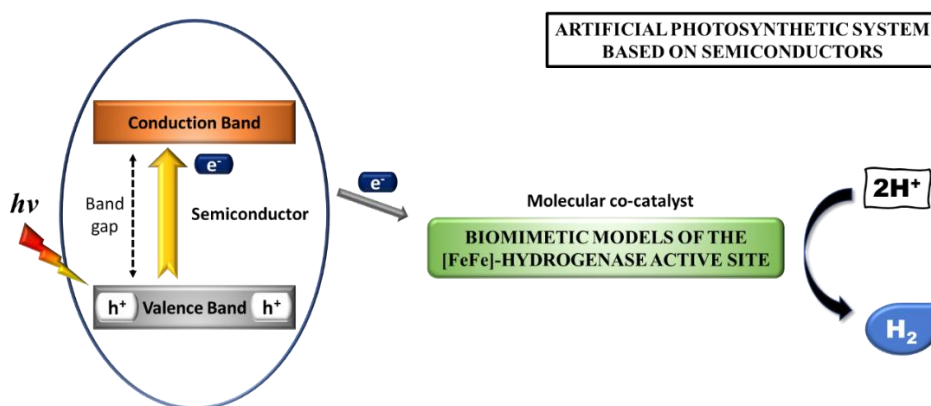


Figure 18. Schematic representation of light-driven hydrogen production in artificial photosynthetic system using semiconductors.

Wu and co-workers used CdSe QD semiconductors to build a water-soluble system by interface-directed assembly of the [2Fe2S] complex **50** onto MPA-CdSe nanocrystals [205]. The ideal characteristics of CdSe QDs such as light-harvesting, charge separation, effective quantum confinement, rich chemistry for surface functionalization and large surface-to-volume ratio [206,207] make them potential candidates in combination with [2Fe2S] complexes for hydrogen evolution in aqueous solution. Under optimized reaction conditions, the **50/MPA-CdSe** photosystem in combination with AscOH (pH = 4) exhibited a TON of 8781 after 82 h of visible-light irradiation in water, with a TOF of up to 596 h⁻¹ in the first 4 h (Table 4, entry 1). This study demonstrated that the interface-directed assembly facilitated electron transfer from the excited *CdSe to the [2Fe2S] cluster **50** and allowed the catalytic center to operate in water. Both benefits, together with the strong interaction and direct contact between the functional units, were crucial to obtain high photocatalytic hydrogen performance.

Zinc sulfide (ZnS) nanoparticles are wide-band-gap II-VI semiconductors (3.6-3.8 V) commonly used as light-harvesters in photocatalysis. However, their photocatalytic applicability has several restrictions such as fast recombination of electron/hole pairs and light absorption only in the ultraviolet region [208]. Several strategies have been used to improve catalytic activity using these nanomaterials, such as increasing the surface area, changing the morphology to mediate closer contact with reagents, promoting the absorption of visible light through doping processes, and forming heterojunctions with a cocatalyst (semiconductors or metals) to reduce the electron-hole recombination rate [209,210].

Li and colleagues reported a noble-metal-free hybrid photocatalytic system made by physical adsorption of the amino groups of the organometallic diiron hydrogenase catalyst **51** $[(\mu\text{-SPh-4-NH}_2)_2\text{Fe}_2(\text{CO})_6]$ onto ZnS semiconductor nanoparticles for photocatalytic hydrogen evolution using AscOH as ED (**Figure 19a**) [211]. Efficient transfer of the photogenerated electrons from ZnS to the [2Fe2S] cluster was achieved in the **51/ZnS** photosystem resulting in a TON of 2607 for 38 h and an initial TOF of 100 h^{-1} (**Table 4**, entry 2). These results demonstrate the remarkable performance and stability of this catalytic system, which showed an even higher catalytic rate than a platinum ZnS (Pt/ZnS) reference system.

In 2014, Chen et al. assembled the two structural analogues **52** and **53** to the surface of a ZnS nanomaterial [212]. While **52** is directly coordinated to the unsaturated Zn ions on the surface of ZnS through a carboxy linkage, complex **53** is physically adsorbed through the dangling S atoms at the ZnS interface (**Figure 19b**). Photocatalytic experiments were carried out using TEOA as ED in organic alkaline solution (DMF/H₂O, 9:1), with a 3- and 5-fold improved catalytic activity upon addition of **52** and **53**, respectively, compared to pristine ZnS. Under irradiation for 38 h, a TON of 3400 was obtained by the carboxy-functionalized mimic **52** in combination with ZnS (**52/ZnS**). A TON of 4950 was achieved for the diiron complex **53** without carboxyl group incorporated in the same ZnS nanomaterial (**53/ZnS**) (**Table 4**, entry 3 and 4). The TOFs shown in the first 4 h were 151 and 282 h^{-1} for **52/ZnS** and **53/ZnS**, respectively. The disparity in the hydrogen production rate by the hybrid photosystems was attributed to the different absorption modes of each [2Fe2S] catalyst on the ZnS nanoparticles.

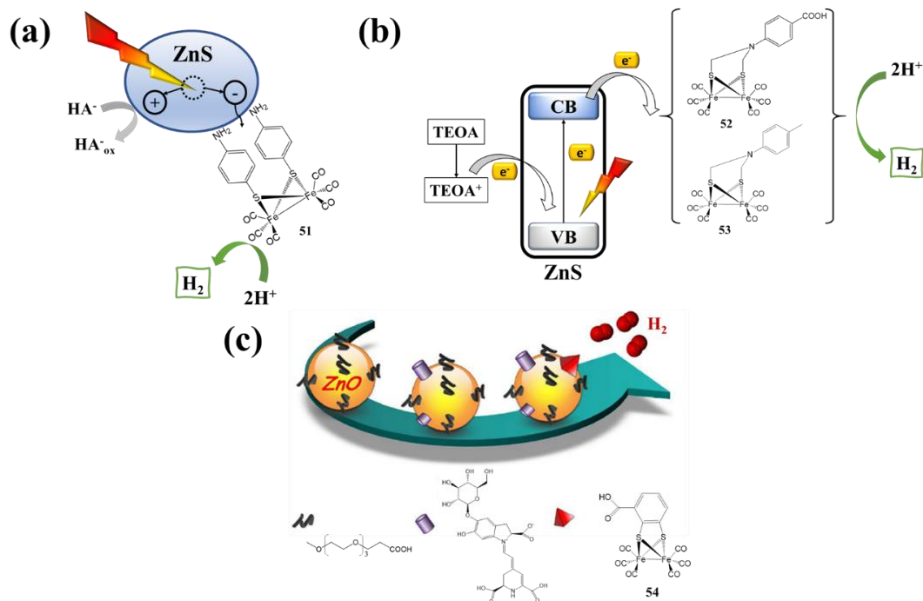


Figure 19. Schematic representation of hybrid photocatalytic systems engineered by (a) integrating ZnS semiconductor nanoparticles and the [2Fe₂S] complex **51** (reproduced and modified from Ref. [211] with permission from John Wiley and Sons), (b) assembling biomimetic diiron complexes **52** and **53** on the surface of ZnS (reproduced and modified from Ref. [212] with permission from John Wiley and Sons), and (c) anchoring betanin (B) and the synthetic diiron catalyst **54** to ZnO-OEG, for photocatalytic hydrogen evolution (reproduced and modified from Ref. [213] with permission from The Royal Society of Chemistry).

Another type of zinc-based nanoparticulate semiconductors incorporating an [2Fe₂S] complex has recently been reported by Sá and co-workers [213]. Ultra-stable ZnO nanocrystals, modified with an oligoethylene carboxylate glycol shell (ZnO-OEG), provided extended electron lifetime and stabilization of the photo-generated hole, thereby slowing down charge recombination in aqueous solution [214]. The nano-hybrid photocatalytic system **ZnO-OEG@B-54** was created by anchoring the natural light-harvesting pigment betanin (B), capable of injecting two electrons per adsorbed photon into the conduction band of ZnO in a few picoseconds, and **54** [FeFe(mcbdt)(CO)₆] (mcbdt = 3-carboxybenzene-1,2-dithiolate) (**Figure 19b**) [213]. Hydrogen evolution experiments under visible-light irradiation using TFA as a proton source demonstrated a TON of 11 in 4 h (**Table 4**, entry 5). FTIR spectroscopy revealed the construct

is remarkably stable, with more than 95% of the initial [FeFe(mcbdt)(CO)₆] catalyst remaining intact after one day of photocatalysis. A second reaction cycle resulted in approximately 70% of the initial hydrogen production under the same experimental conditions for 4 h. Therefore, the ZnO-OEG nanohybrid semiconductor was an effective scaffold for achieving accumulative charge separation and prolonging the stability of the PS and [2Fe2S] **54**.

Table 4. Inorganic hybrid semiconductor systems with attached [2Fe2S] complexes for light-driven hydrogen production.

Entry	Semiconductor photocatalytic hybrid system	Selected conditions ¹	Light	Time (h)	TON ²	Ref.
1	50/MPA-CdSe	Water, 2.3 μM 49 , 6.3 μM MPA-CdSe, 85 mM AscOH, pH=4.0	LED (160 mW/cm ²), λ>405 nm	8	8781	[205]
2	51/ZnS	DMF/H ₂ O (9:1), 3.9 μM 50 , 0.2 g ZnS, 85.2 mM AscOH	Xe lamp (300 W), λ=not available	38	2607	[211]
3	52/ZnS	DMF/H ₂ O (9:1), 4 μM 51 , 10 mg ZnS, 2.5% (v/v) TEOA, pH=11	Xe lamp (300 W), λ=not available	30	3400	[212]
4	53/ZnS	DMF/H ₂ O (9:1), 4 μM 52 , 10 mg ZnS, 2.5% (v/v) TEOA, pH=11	Xe lamp (300 W), λ not specified	30	4950	[212]
5	ZnO-OEG@B-54	ZnO-OEG@B-53 , TFA. Concentration data not available	Continuous wave (CW) laser, λ=532 nm	4	11	[213]

¹Solvents and reagents abbreviations: DMF: N,N-dimethylformamide, AscOH: ascorbic acid, TFA: trifluoroacetic acid, TEOA: triethanolamine.

² TON based on [2Fe2S] catalyst

5.2.1.7. [FeFe]-hydrogenase active site models anchored onto heterogeneous supports

The use of a heterogeneous matrix for the immobilization of [2Fe2S] clusters via their outer coordination sphere is an appealing approach to increase structural stability of all reaction partners. These supports can provide well-ordered tailorable pores or channels, very high internal surface areas, well-defined structures, electrostatic microenvironments and hydrophobic cavities. Water-insoluble [2Fe2S] catalysts can be isolated in specially designed sites that are accessible throughout the matrix and

capable of operating efficiently in aqueous media. The precise design of these platforms allows the creation of solid heterogeneous photocatalytic systems with enhanced stability, simple separation after reaction and efficient recycling for light-induced hydrogen production processes.

Metal-organic frameworks (MOFs), mesoporous molecular sieves (MCM-41), periodic mesoporous organosilicas (PMOs), silica nanoparticles and graphene-based supports have been used as matrices for the incorporation of diiron catalysts, PSs and/or EDs to be applied in hydrogen evolution schemes.

5.2.1.8.1. Metal-organic frameworks platforms for [2Fe2S] complexes

MOFs are 3D porous coordination polymers formed from metal clusters and organic linker molecules. Almost limitless combinations of metal nodes and available organic linkers have sparked the use of MOFs in a wide variety of fields such as gas storage, separation, heterogeneous catalysis, drug delivery, and chemical sensing [215–218]. The use of MOFs as a support in photocatalytic applications is particularly interesting because they have well-defined structures, exceptionally high internal surface areas, remarkable chemical stability, structural flexibility and tunability [219–221]. MOFs as enzymatic platforms for hydrogen production must: i) be water stable under catalytic conditions in a wide pH range, and ii) have functional sites where the molecular catalyst can be incorporated during the framework synthesis, or through postsynthetic modification (PSM) or postsynthetic linker exchange (PSE) [222,223]. In addition, iii) the MOF must either possess pore diameters that are sufficiently large to allow transport of the PS and the ED to the active sites, or be capable of electron transport to wire catalytic sites in the interior of the crystals [224]. In the latter scenario, electrons may be generated in a light-driven process in solution, and then transferred into the MOF through the crystal surface [225].

Catalyst-containing MOFs offer improved stability, especially if organic co-linkers in the MOF backbone contain functional groups that can interact with the catalyst to enhance its selectivity and/or activity [226,227]. Photocatalytic MOFs can be built using several approaches: a) immobilization of the catalyst and external incorporation of the PS in solution, b) incorporation of a photoactive MOF with light-harvesting organic ligands or metallic clusters and external incorporation of the

catalyst in solution, c) combination of both functional units in the MOF or d) creation of active hetero-junctions in MOF composite materials [226]. Only a few examples of [2Fe2S] complexes immobilized in heterogeneous MOF platforms have been reported, mainly designed following approaches a) and c).

In 2013, Cohen and Ott et al. incorporated the [2Fe2S] catalyst **8** ([FeFe]-(dcbdt)(CO)₆) into a thermally robust Zr(IV)-based UiO-66 MOF by PSE of 1,4-benzenedicarboxylate (bdc) ligands [111]. UiO-66 is a highly crystalline framework with a large surface area ($S_{\text{BET}} = 1475 \text{ m}^2 \text{ g}^{-1}$) and tetrahedral and octahedral cages with pore widths of ~ 8 and $\sim 11 \text{ \AA}$, respectively. Proton nuclear magnetic resonance spectroscopy (¹H NMR) and energy-dispersed X-ray spectroscopy (EDX) confirmed a degree of bdc linker exchange of 14%. The resulting **8@UiO-66** demonstrated enhanced photocatalytic hydrogen production when combined with the [Ru(bpy)₃]²⁺ PS and AscO[□] as ED in aqueous acetate buffer at pH = 5 (**Figure 20a**). A TON of 5.9 (**Table 5**, entry 1) was obtained, higher than that of the molecular catalyst **8** in homogeneous phase (TON = 1.7, see **Section 2**). The homogeneous reference decomposed by releasing the coordinated CO ligands from the diiron core under photoirradiation conditions. The UiO-66 matrix served to increase the stability of the catalytic diiron unit **8** within the MOF crystals, thus achieving higher TONs than the homogeneous photosystem.

The reactivity of the confined molecular catalyst **8** in a UiO-66 MOF was modified by replacement of CO ligands by phosphines of different sizes (**Figure 20b**) [228]. Small phosphines (PX₃, X = Me, Et) can be introduced to the diiron complex within the MOF structure in yields of 50-80%. These [FeFe-(dcbdt)(CO)₄(PX₃)₂] complexes in the UiO-66 platform were reduced at more cathodic potentials than the analogous [FeFe-(dcbdt)(CO)₆] and formed hydride species under acidic conditions. Recently, Hammarström et al. proposed intra-crystal linker scrambling in the photochemical hydrogen evolution with **8@UiO-66** [229]. Under the reaction conditions shown in **Table 5** (entry 1), hydrogen production ceased after a period of 3 h under visible-light irradiation. However, the molecular catalyst **8** in the MOF maintained its structural integrity after the reaction and the photocatalytic activity could be restored after a resting period of 60 minutes. Interestingly, recovered **8@UiO66** showed similar catalytic activity as the original photocatalysis experiment during 9 reaction cycles with 45 minutes of light irradiation (**Figure 20c**).

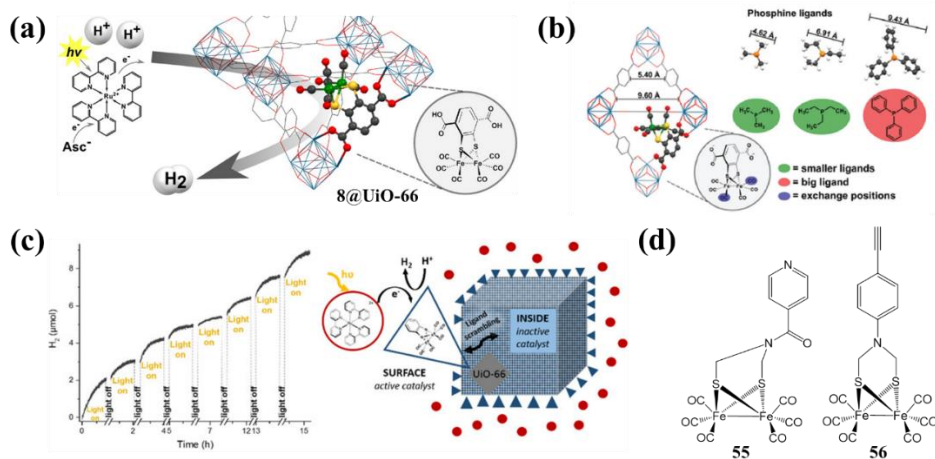


Figure 20. (a) Reaction scheme of photochemical hydrogen evolution using $8@UiO-66$ catalyst (adapted from Ref. [111]. Copyright (2013) American Chemical Society) with , (b) schematic representation of CO ligand exchange with different phosphine ligands in $8@UiO-66$ (reprinted from Ref. [228] with permission from The Royal Chemical Society), (c) self-recovery of photocatalytic hydrogen production with $8@UiO-66$ by intra-crystal linker scrambling (reprinted from Ref. [229] with permission from John Wiley and Sons), and d) structures of diiron mimetic compounds **55** and **56** incorporated into ZrPF and UiO-MOF, respectively.

The same group reported a functionalized MIL-101 (Cr) MOF with a larger pore diameter (29–34 Å) compared to that in UiO-66 (8–11 Å) for the covalent attachment of the diiron compound **54** [$FeFe(mcbdt)(CO)_6$] affording $54@MIL-101$ [228]. The easy accessibility to these pores with windows of 12–14.5 Å, compared to the 6 Å in UiO-66, enabled increased catalyst loading throughout the entire MOF matrix. The pore size of MIL-101 allows chemical reduction of the catalyst by stabilizing the reduced catalyst intermediate in the MOF structure for hours. However, ion pairing phenomena were observed between the reduced species $[FeFe]^{2-}$ and oxidized cobaltocene reducing agent $[Cp_2Co]^+$ that clogged MOF channels and limited fast and efficient accessibility to the catalyst. This effect was less pronounced in MIL-101 with a lower loading of **54**. The performance of three $54@MIL-101$ materials with different catalyst loadings was evaluated in photochemical hydrogen evolution experiments, demonstrating better catalytic activity than the homogeneous reference system with the diiron compound **8** ($[FeFe]-(dcbdt)(CO)_6$). The hydrogen productivity was linearly dependent on the loading of **54** within the MOF

and showed a similar TON for the three systems, although the highest value was obtained for the medium loading **54@MIL-101** catalyst, reaching a TON of 18.5 after 2.3 h (**Table 5**, entry 2).

Feng and co-workers took the alternative strategy c) consisting of simultaneous incorporation of the PS and the diiron catalyst into the MOF support [230]. The group used a light-harvesting zinc porphyrin complex (ZnTPP) that was linked to Zr (IV)-based metal cluster nodes. The [2Fe2S] complex **55** with a pendant pyridyl group (**Figure 20d**) was anchored to the zinc center in the porphyrin. The direct coordination of both functional units provided intimate contact between the PS and the diiron catalyst, facilitating the visible-light-driven intramolecular electron transfer from singlet excited state $^1\text{ZnTPP}$ to **55** without the need for an electron mediator. The heterogeneous **55@ZrPF** system showed high efficiency for photochemical hydrogen production, yielding 3.5 μmol of H_2 after 2 h in an aqueous acetate buffer solution (pH = 5) with AscO^\square as a sacrificial ED (**Table 5**, entry 3). The MOF matrix provided improved stability for the anchored [2Fe2S] cluster, as the homogeneous system was stable for only 40 min under the same photoreaction conditions.

In another effort to simultaneously immobilize the PS and [2Fe2S] complex in a MOF platform, Yuan and colleagues designed the **56@UiO-MOF** consisting of a mixture of $[\text{Ru}(\text{bpy})_3]^{2+}$ -derived dicarboxylate linkers as light harvesters and azide-modified dicarboxylate ligands that provided covalent anchor sites for the diiron catalyst **56** (**Figure 20d**) by a facile click reaction [231]. The closeness of both functional units in the MOF support led to an enhancement of the electron transfer efficiency and a decent photocatalytic hydrogen evolution performance. The incorporation of **56** in the UiO framework promoted the stability of the [2Fe2S] catalyst in water. Using AscOH as the sacrificial ED, the **56@UiO-MOF** photosystem exhibited decent catalytic activity, reaching a TON of up to 16 for 50 h of reaction time in an acetate buffer (pH = 5) (**Table 5**, entry 4).

5.2.1.8.2. Silica-based heterogeneous supports for [FeFe]-hydrogenase active site mimics

Silica-based mesoporous molecular sieves offer tunability of the pore size (2-50 nm), high surface area, simple synthesis, an electrostatic microenvironment, water stability, and the ability to stabilize charge-separated states in catalytic processes [232,233]. An ordered mesoporous

K⁺-exchanged molecular sieve MCM-41 has been used to immobilize hydrophobic [2Fe2S] complexes, improving the stability of the diiron catalyst in photochemical hydrogen evolution experiments in aqueous solution. This work by Li and Yu et al. incorporated the diiron complex **57** [$\{(\mu\text{-SCH}_2)_2\text{N}(\text{CH}_2\text{-C}_6\text{H}_5)\}\text{Fe}_2(\text{CO})_5\text{P}(\text{Pyr})_3$] into K⁺-exchanged molecular sieve MCM-41 via electrostatic interactions [234]. The resulting **57@MCM-41** system catalyzed light-induced proton reduction in water by using an iridium-based photosensitizer ([Ir(ppy)₂bpy]Cl) and TEA as a sacrificial ED (**Figure 21a**). Under optimized reaction conditions, a TON of 18.3 was achieved during 1 hour of irradiation under visible light (**Table 5**, entry 5), demonstrating that this strategy can stabilize and disperse a hydrophobic diiron catalyst in aqueous solution. The photochemical hydrogen evolution was limited by the degradation of the PS, since re-addition of more iridium PS led to recovery of the catalytic activity. In an advanced approach, the same group reported the electrostatic immobilization of a PS-[2Fe2S] dyad (**58-Ir**) into the ordered mesoporous K⁺-exchanged molecular sieve MCM-41 (**Figure 21b**) [235]. The heterogeneous system **58-Ir@MCM-41** exhibited an enhanced photocatalytic activity, 3-fold higher than that of the dyad **57-Ir** without the MCM-41 matrix, obtaining a TON of 5 in MeCN/H₂O (9:1) under visible-light irradiation (**Table 5**, entry 6). This enhanced catalytic performance was attributed to the stabilization of the diiron catalyst in the molecular sieve, which was further confirmed by transient absorption studies.

Periodic mesoporous organosilicas (PMOs) are a class of silica-based hybrid materials prepared by the combination of a surfactant as template and a silsesquioxane as the organosilica precursor. PMOs exhibit the typical ordering of mesoporous silicas, and the diversity of synthetic procedures provides a range of functionalities which suggest these systems for applications as catalysts, adsorbents (metal ions, toxic organic compounds and even gasses), chromatography phases, and biological/biomedical supports, among others [236]. In 2018, Inagaki and co-workers designed a heterogeneous photochemical system by covalently anchoring a [2Fe2S] complex tethered with a maleimide group (**4**) on the pore surface of a thiol-functionalized PMO (SH-PMO) [100,237]. The **4@SH-PMO** showed photocatalytic hydrogen production (**Figure 21c**) without the decomposition of the diiron center, achieving a high TON of 310 over 2 h in an aqueous solution containing the photosensitizer [Ru(bpy)₃]²⁺ and the AscO[□] ED (**Table 5**, entry 7). This heterogeneous system had higher photocatalytic activity than the corresponding

homogeneous reference complex **4** (TON = 180, see **Section 2**) under analogous experimental conditions. It also out-performed the [2Fe2S] systems immobilized on MOFs and mesoporous silica MCM-41 (TON = 6-19), described earlier in this section. The enhanced hydrogen generation rate was attributed to the periodic mesostructure of the PMO that provided a robust and rigid solid matrix to stabilize the immobilized **4**, overcoming water solubility and photostability issues associated with the [2Fe2S] catalyst.

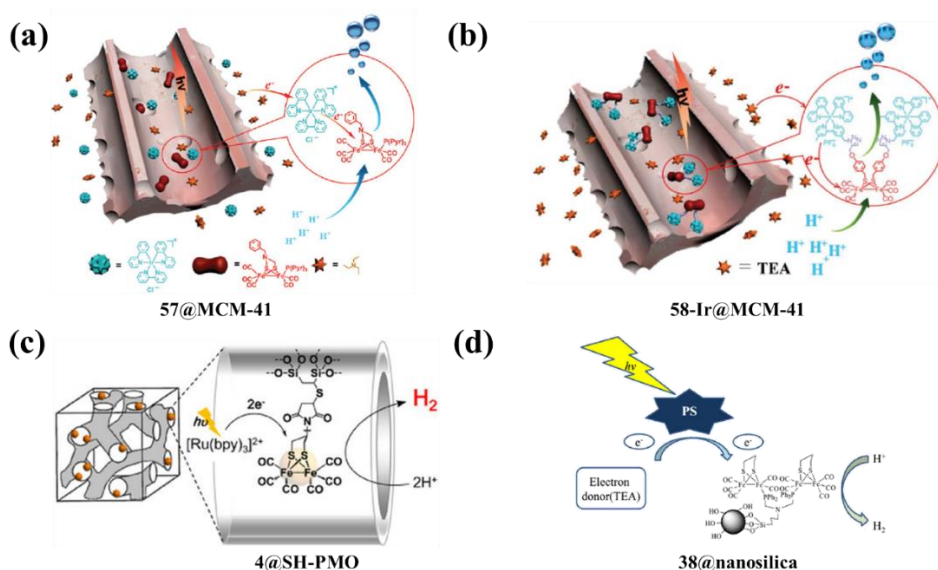


Figure 21. Schematic illustration of the light-driven hydrogen production by (a) **57@MCM-41** (reproduced and modified from Ref. [234] with permission from John Wiley and Sons), (b) **58-Ir@MCM-41** (reproduced and modified from Ref. [235] with permission from The Royal Society of Chemistry), (c) **4@SH-PMO** (reproduced and modified from Ref. [100] with permission from John Wiley and Sons), and (d) **38@nanosilica** (reproduced and modified from Ref. [238] with permission from Elsevier).

This work was extended by co-immobilizing diiron catalyst **4** and a $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer functionalized with a maleimide on PMO via covalent coupling by thiol groups affording **4-Ru@SH-PMO**. This all-solid-state photocatalyst with a loading of 250 and 115 $\mu\text{mol/g}$ of **4** and Ru, respectively, showed photoinduced hydrogen production with a TON of 1.3 (**Table 5**, entry 8.). This was higher than the **4@SH-PMO** reference system (TON = 0.6) with the homogeneous $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer in

solution, even with a Ru/4 ratio analogous to that of **4-Ru@SH-PMO**. Indeed, the difference in TON obtained for the heterogeneous **4@SH-PMO** and **4-Ru@SH-PMO** systems was attributed to vastly different Ru/4 ratios in the two systems of 67 and 0.46, respectively.

Recently, the use of nanosilica as a solid support for anchoring diiron catalysts has been reported by Wang et al [238]. The heterogeneous system **38@nanosilica** consisting of complex **38**, $[\text{Fe}_2(\text{pdt})(\text{CO})_6]$, immobilized on modified nanosilica was used in a photocatalytic system in conjunction with $[\text{Ir}(\text{ppy})_2(\text{bpy})]\text{PF}_6$ as a PS, TEA as a sacrificial ED, H_2O as a proton source and MeCN as the solvent (**Figure 21d**). After irradiation for 5 h with visible light, a TON of 324 per catalyst was achieved (**Table 5**, entry 9). The degradation of the catalyst after the reaction was demonstrated by IT spectroscopy. Furthermore, a decreased iron content (1.18%) with respect to the original loading (1.39%) on the nanosilica was observed by atomic absorption spectroscopy (AAS), thus corroborating the decomposition and associated leaching of the diiron complex.

5.2.1.8.3. Graphene-based [FeFe]-hydrogenase active site model nanohybrids

In recent years, a novel approach for the preparation of a heterogeneous photosystem containing a $[2\text{Fe}2\text{S}]$ catalyst and a molecular PS immobilized on graphene oxide (GO) was reported [239]. GO has extraordinary physicochemical and structural properties used in wide-ranging applications such as photocatalysis, energy conversion or biosensing [240]. Surface oxygen-containing groups (carboxylic, hydroxy and epoxy) provide high water solubility and reactive sites for chemical modification.

Jang and colleagues developed a graphene-based nanohybrid (**38-Fc-TPP@GO**) composed of the $[2\text{Fe}2\text{S}]$ complex (**38**) bound to a ferrocene group (**Fc**) forming (**38-Fc**) and a porphyrin light harvester (**TPP**). Both functional units were anchored on the GO nanosheets to assemble a photocatalytic system in aqueous solution (**Figure 22**) [239].

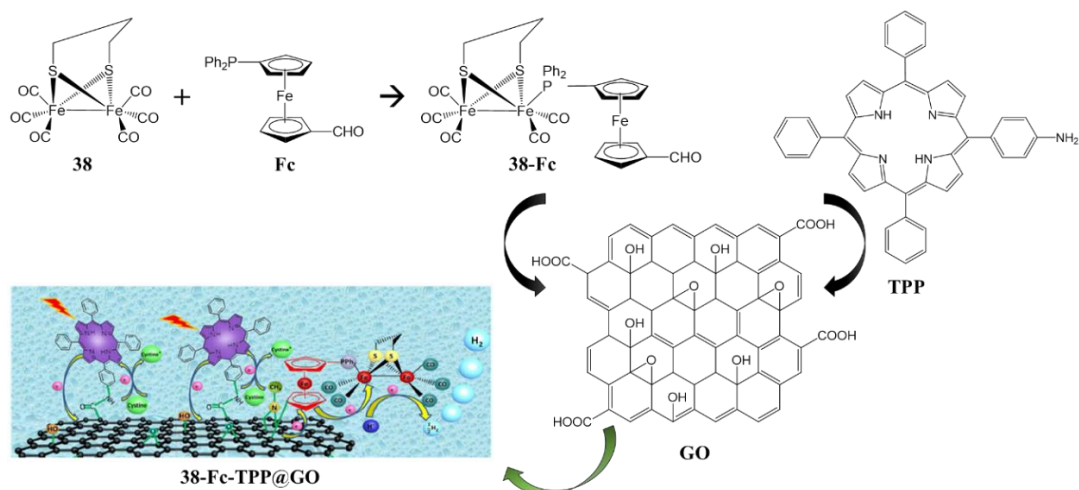


Figure 22. Synthetic route towards a graphene-based [2Fe₂S] system for photocatalytic hydrogen evolution in aqueous solution. Schematic representation adapted from Ref. [239] with permission from Elsevier.

The **38-Fc** unit operates at mild redox potentials and mimics the [4Fe₄S] cubane cluster present in the [FeFe]-hydrogenase enzyme [241]. Photochemical hydrogen production experiments were carried out with **38-Fc-TPP@GO**, and a light-induced electron transfer was demonstrated by emission fluorescence data. A variety of common sacrificial EDs were evaluated (AscOH, TEOA, glucose or Na₂S₂O₃) but the best efficiency for hydrogen generation was found in cysteine, an amino acid present in the natural metalloenzyme. Under visible light irradiation, the **38-Fc-TPP@GO** nano-hybrid system exhibited a TON of 3.9 over 5 h in the presence of cysteine in an aqueous solution at pH = 1 (**Table 5**, entry 10). This catalytic activity surpassed that of the intramolecular (**38-Fc-TPP**) or intermolecular (**38-Fc** + TPP and **38-Fc** + TPP@GO) photocatalytic reference systems.

These results corroborated the crucial role of GO for enhancing electron transfer to increase the photoinduced hydrogen productivity in water. The stability of **38-Fc-TPP@GO** was studied by reusing the material in repeated photoreaction experiments. Hydrogen evolution was maintained at 86.5% of the initial value after the third reaction cycle with a remaining [2Fe₂S] content of 81.7% calculated by ICP-AES, confirming the reusability of this nano-hybrid system.

Table 5. Biomimetic models of the [FeFe]-hydrogenase active site anchored on heterogeneous supports for light-driven hydrogen production.

Entry	Heterogeneous photocatalytic system	Selected conditions ¹	Light	Time (h)	TON ²	Ref.
1	8 @UiO-66	Water, 5 mg 8 @UiO-66 (0.59 μmol 8), 0.5 mM [Ru(bpy) ₃] ²⁺ , 100 mM AscO ⁻ , 1 M acetate buffer, pH=5.0	LED (850 μE), $\lambda > 470$ nm	2.5	5.9	[111]
2	54 @MIL-101	Water, 1.5 mg 53 @MIL-101 (0.15 μmol 53), 0.5 mM [Ru(bpy) ₃] ²⁺ , 100 mM AscO ⁻ , 1 M acetate buffer, pH=4.9	LED, $\lambda > 470$ nm	2.3	18.5	[228]
3	55 @MOF-ZrPF	Water, 54 @MOF-ZrPF (2 μM 54), 20 mM AscOH, 1 M acetate buffer, pH=5.0	Xe lamp (300 W), $\lambda > 420$ nm	2	Insufficient data for calculation	[230]
4	56 @UiO-MOF	Water, 15 mg 55 -Ru@UiO-MOF (2 μmol 55), 100 mM AscOH, 1 M acetate buffer, pH=5.0	Solid-state white light source, $\lambda > 420$ nm	50	16	[231]
5	57 @MCM-41	Water, 4.5 mg 56 @MCM-41 (43 $\mu\text{mol/g}$ 56), 0.25 mM [Ir(ppy) ₂ bpy], 0.28 M TEA	Xe lamp (300 W), $\lambda = 400\text{-}800$ nm	1	18.3	[234]
6	58 -Ir@MCM-41	MeCN/H ₂ O (9:1), 5.5 mg 57 -Ir@MCM-41 (19.1 $\mu\text{mol/g}$ 57), 0.8 M TEA, pH=10	Xe lamp (300 W), $\lambda = 400\text{-}800$ nm	8	5	[235]
7	4 @SH-PMO	Water, 0.3 mg 4 @SH-PMO (21 nmol 4), 140 μM [Ru(bpy) ₃] ²⁺ , 200 mM AscO ⁻ , pH=4.5	Hg lamp, ($\lambda > 400$ nm)	2	310	[100]
8	4 -Ru@SH-PMO	Water, 0.5 mg 4 -Ru@SH-PMO (250 $\mu\text{mol/g}$ 4 , 115 $\mu\text{mol/g}$ Ru), 200 mM AscO ⁻ , pH=4.5	Hg lamp, ($\lambda > 400$ nm)	2	1.3	[100]
9	38 @nanosilica	MeCN/H ₂ O/TEA (7:1:2), 30 mg 38 @NanoSilica (1.86 μmol 38), 0.9978 mM [Ir(ppy) ₂ (bpy)]PF ₆	Xe lamp (300 W), $\lambda > 400$ nm	5	324	[238]
10	38 -Fc-TPP@GO	Water, 0.1 mg 38 -TPP@GO (12 μM 38), 3Fe ₂ S, 5.8 μM TPP, 1.8 mM cysteine, pH=1.0	Hg lamp (450 W), $\lambda > 380$ nm	5	3.9	[239]

¹Solvents and reagents abbreviations: MeCN: Acetonitrile, TEA: triethylamine.

² TON based on [2Fe₂S] catalyst

5.2.1.9. Photocathodes based on [FeFe]-hydrogenase active site mimics

Water-splitting photoelectrochemical (PEC) cells are comprised of two electrode compartments in which the oxidation and reduction half-reactions occur. The energy for the thermodynamically uphill half-reactions comes from the absorption of photons from visible light, potentially complemented by an external applied bias. Light absorption is ensured by semiconductor materials that either absorb visible photons directly through band gap excitation, or that are decorated with PS molecules for light absorption. In the latter case, electron or hole injection from the PS excited state into the conduction and valence band of the semiconductor, respectively, will produce oxidized or reduced PS that drive the half-reactions. While, in principle, only one of the two electrodes need to be light-driven to qualify as a PEC device, tandem PEC devices in which both electrodes are photo-active offer higher theoretic efficiencies (**Figure 23**) [242].

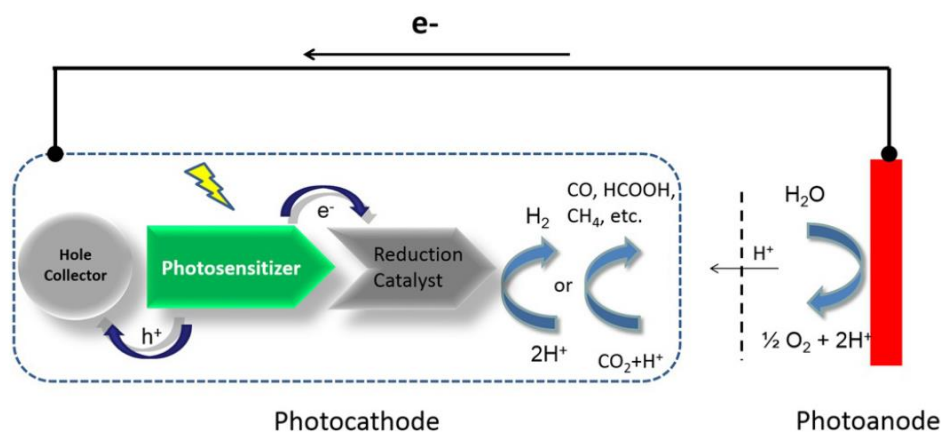


Figure 23. Schematic representation of a tandem PEC device. Reprinted from Ref. [242] with permission from John Wiley and Sons.

In analogy to the examples in the previous sections, photoanode and photocathode are often investigated separately in the laboratory. An electrochemical potential can be applied to complement the available energy from the photo-electrodes, and such systems thus omit the need for sacrificial reagents.

For optimal function, precise engineering of the catalyst/semiconductor interface is crucial to achieve decent performance

of molecular PEC devices. Factors to consider in particular include interfacial stability, suitable light-absorptivity of the semiconductor electrode, efficient charge separation and electron transfer enhanced at the interface [243–245].

In this section, we focus on photocathodes for H₂ evolution based on catalysts that mimic the [FeFe] hydrogenase active site. Photocathodes for CO₂ reduction and photoanodes for water oxidation are reviewed elsewhere [246–250]. [2Fe2S] complexes have been used as catalysts at photocathodes in which the photoactive component is either a light-absorbing p-type inorganic semiconductor (**Section 8.1**) or a molecular PS deposited on a p-type semiconductor (**Section 8.2**).

5.2.1.9.1. [2Fe2S] catalysts immobilized on light-absorbing p-type inorganic semiconductors

Molecular catalysts based on the [2Fe2S] motif anchored directly on the surface of a light-harvesting p-type solid-state inorganic semiconductor constitutes a first group of photoelectrochemical architectures for hydrogen evolution [251]. Typically, these photoelectrodes use low bandgap p-type semiconductors that absorb visible-light (InP, Si, GaP or Cu₂O, among others) and have a conduction band potential below the equilibrium thermodynamic potential of the H⁺/H₂ couple to provide effective transfer of the excited electrons in the conduction band to the [2Fe2S] catalyst [242,252].

The first example of this design by Nann, Pickett and co-workers in 2010 reported a photocathode that was composed of a gold substrate with indium phosphide (InP) nanocrystals that were cross-linked by 1,4-benzenedithiolates and decorated with the [2Fe2S] catalyst **50** via sulfide bridges (**Figure 24a**) [253]. The driving force for electron transfer between the conduction band of the InP semiconductor and catalyst **50** was found exergonic by 0.1 V. Photoelectrochemical hydrogen production was performed in a three-electrode system (**Figure 24b**) under irradiation at 395 nm using a LED array with a bias potential of -0.4 V versus Ag/AgCl, reaching photocurrents of 250 nA/cm² in 0.1 M NaBF₄ electrolyte solution. After 1 hour of light-driven electrolysis, a faradaic efficiency of 60 % was obtained.

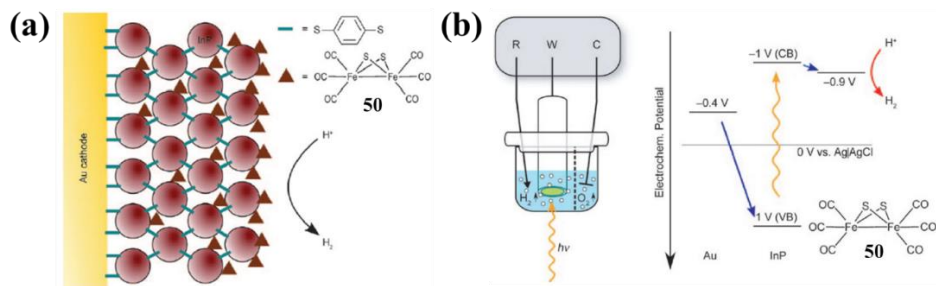


Figure 24. (a) InP nanocrystal-modified gold photocathode with diiron complex **50** integrated. (b) Electrochemical cell used and energy levels (R: reference electrode, W: working electrode, C: counter electrode, CB: conduction band, VB: valence band). Reproduced and modified from Ref. [253] with permission of John Wiley and Sons.

Subsequently, Ott, Kubiak and co-workers prepared a photoelectrochemical system for homogeneous catalytic proton reduction based on p-type silicon (p-Si) photocathode with a narrow band gap of 1.8–2.2 eV, diiron benzenedithiolate catalyst **35** [(bdt)Fe₂(CO)₆], and HClO₄ as a proton source [254]. Reduction of the [2Fe2S] complex was achieved at an illuminated p-type Si at a reduction potential 0.5 V less negative than that at a glassy carbon electrode. Homogeneous photocatalytic reduction of protons to molecular H₂ was achieved with 100 % Faradaic efficiency, a high current density of 38 mA cm⁻², and a light conversion efficiency of 8 % under light-visible illumination at $\lambda = 661$ nm for five hours at -900 mV versus Fc⁺/Fc⁰ (ferrocenium/ferrocene redox couple).

Further work based on p-Si in combination with [FeFe] hydrogenase active site mimics by Nann, Voelcker and co-workers reported hierarchically nanostructured photocathodes in which a porous p-Si electrode was sensitized with InP quantum dots and [2Fe2S] complex **50** [255]. The obtained photocurrent density was -1.2 mA/cm² at low bias potentials of 0.5 V. The applied bias photo-to-current efficiency (ABPE) was calculated to 0.63%. Unfortunately, this photocurrent density was lower compared to the results previously obtained by Ott et al. [254] although hydrogen generation and the protection of the electrode surface against possible oxidation processes were demonstrated.

Recently, Gu et al. investigated the activity and electrochemical decomposition pathways of catalyst **59** covalently attached to a p-Si photocathode [256]. Contact angle measurement and GATR-FTIR were

used to monitor the modifications on the semiconductor-catalyst interface in the different synthesis steps, in order to confirm the effectiveness of the procedure and to analyse the distribution of [2Fe2S] **59** along the surface of the p-Si (**Figure 25**). The integration of this molecular catalyst passivates the silicon interface, preventing the growth of undesirable native SiO₂ for more than 300 h, and thus improves the stability of the device. Photoelectrochemical hydrogen production of the electrode under illumination was as high as $2.31 \times 10^{-5} \text{ mol h}^{-1} \text{ cm}^{-2}$ at -0.78 V versus RHE. Compared to the unmodified hydrogen-terminated Si photoelectrode, the presence of the [2Fe2S] catalyst gives rise to a reduced overpotential of 100 mV to reach a current density of 10 mA cm^{-2} under illumination. Spectroscopic surface analysis techniques (XPS and GATR-FTIR) were useful tools to reveal the structural rearrangement produced in the photocathode due to degradation of the catalyst by dissociation of the Fe-S bond after 1 hour of electrolysis. This study enables the detailed elucidation of the decomposition pathways for the photoelectrode-catalyst interface which will allow the preparation of more active and efficient photocathodes in the future.

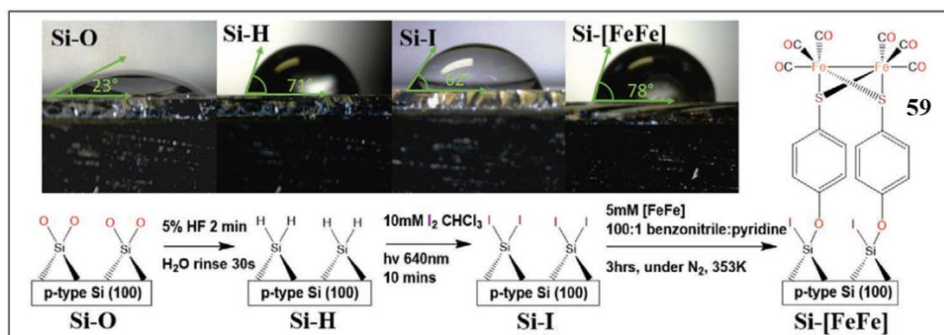


Figure 25. Schematic modification strategy for preparation of photocathode with [2Fe2S] **59** covalently bonded and contact angle measurements in the different synthesis steps. Reproduced and modified from Ref. [256] with permission from John Wiley and Sons.

5.2.1.9.2. [2Fe2S] catalysts anchored on dye-sensitized NiO photocathodes

p-Type dye-sensitized solar cells (p-DSSCs) have served as inspiration for the design of dye-sensitized p-type semiconductor photocathodes [242,252,257]. In analogy to the working principle of p-DSSCs, excitation of the PS on the photocathode results in hole injection

into the valence band of the metal oxide. The thereby generated reduced PS transfers an electron to the hydrogen generation catalyst. An alternative mechanism includes charge separation between photosensitizer and the catalyst prior to hole injection into the VB of the semiconductor. In the last decade, p-type NiO semiconductor has been commonly used as electrode substrate to anchor both photosensitizer and [2Fe2S] catalysts.

In 2012, Hammarström, Ott and co-workers made the first attempt in this field with the development of a dye-sensitized photocathode by co-adsorption of the Coumarin-343 (C343) photosensitizer and a mononuclear iron dithiolate complex on the surface of mesoporous NiO films [258]. Light-driven electron transfer from the reduced dye to the proton reduction catalyst was spectroscopically demonstrated. The reversible reduction of the catalyst after dye excitation occurred within 50 ns, while the interfacial charge recombination between the reduced H₂-evolving catalyst and the valence band holes in NiO occurred on a 100 μs time scale following a non-exponential kinetics. This research represented an essential proof-of-concept for the preparation of dye-sensitized NiO photocathodes by a co-grafting strategy and its application for photoelectrochemical hydrogen evolution in the absence of sacrificial donor reagents.

Subsequently, an advanced study reported by the same group showed ultrafast electron transfer from the reduced C343 dye to the [2Fe2S] catalyst **60** (**Figure 26**) on the co-sensitized surface of p-type NiO films [259]. Transient optical spectroscopy revealed that hole injection occurred on a femtosecond time scale (200 fs) from NiO to the excited dye followed by the rapid surface electron transfer from reduced dye to the [2Fe2S] catalyst ($t_{1/2} \approx 10$ ps). Charge recombination between the reduced catalyst **60** and the NiO holes was considerably slower (several tens of μs) compared to previous research. The obtained long-lived charge separation state and the resulting ultrafast electron transfer between dye and catalyst, both co-immobilized on NiO, were crucial for the subsequent design of efficient photocathodes incorporated into p-DSSCs for the electrochemical reduction of protons to H₂.

Based on these works, Hammarström's group reported the first dye-sensitized solar fuel device (DSSFD) based on a [2Fe2S] complex. The employed [2Fe2S] complex **61** (**Figure 26**) has a molecular structure analogous to that of complex **60** but with a pendant phosphonate group binding on the C343-sensitized NiO photocathode [260]. Subpicosecond hole injection from the excited dye to NiO mesoporous films ($t_{50\%} \sim 6$ ps)

followed by ultrafast surface electron transfer led to catalyst reduction with an approximate yield of 70% as verified by femtosecond transient absorption spectroscopy. The slow charge recombination of the reduced catalyst ($2\mu\text{s}$ - 20ms) made protonation and second reduction step of the catalyst feasible. The device containing the C343:**61**/ NiO photocathode showed activity in the photoelectrochemical hydrogen production with a Faradaic efficiency of $\sim 50\%$. Unfortunately, catalyst degradation and desorption from the NiO surface were observed by infrared spectroscopy and gas chromatography techniques.

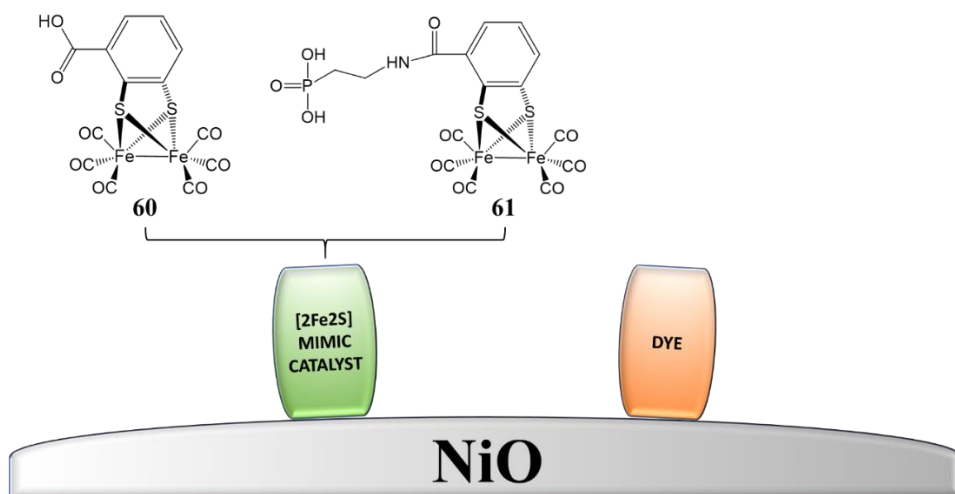


Figure 26. Schematic drawing of dye-sensitized NiO photocathodes integrating [2Fe₂S] mimics.

More recently, the same group analysed the viability of the charge transfer reactions between dye/catalyst **61** co-adsorbed on NiO photocathode by femtosecond mid-infrared transient absorption spectroscopy [261]. An organic push-pull dye (E2) and C343 dye were used as molecular photosensitizers independently. Spectroscopic signatures of the reduced **61** were monitored upon photo-excitation of the dye at a few picosecond time scales although kinetic differences were observed in the first reduction step of the catalyst depending on the dye co-adsorbed into NiO films. In the C343-sensitized NiO films, hole injection into NiO occurred prior to the catalyst **61** reduction with a lifetime $\tau > 5$ ns. In contrast, direct electron transfer occurred between the excited E2* and the catalyst in E2-sensitized NiO films with a decreased lifetime ($\tau = 50$ ps) of the singly reduced catalyst. These mechanistic changes were attributed to the different arrangement of the dye and diiron catalyst **61** on the surface

of the NiO films highlighting the importance of the dye/catalyst packing on the efficiency of co-sensitized NiO photocathodes.

An alternative approach that includes utilization of a QDs-sensitized NiO photocathode was proposed by Wu, Li and co-workers. CdSe QDs and [2Fe2S] complex **50** loaded onto a NiO substrate resulted in efficient proton reduction to H₂ at a bias ~ 0.3 V vs. NHE in neutral water [262]. Novel strategy to anchor diiron catalyst **50** on the CdSe QDs surface allowed to decrease the electrochemical energy input providing an efficient interfacial electron transfer. Therefore, a high photocurrent density of $-56 \mu\text{A cm}^{-2}$ at -0.1 V (vs. NHE) under visible-light illumination was obtained making this photoelectrode a promising candidate to enhance the performance of PEC cells.

5.2.1.10. Summary and outlook

Photocatalytic systems based on biomimetic models of the [FeFe]-hydrogenase active site have evolved substantially during the last two decades. Chemical engineering to reproduce architectures analogous to those found in the natural hydrogenase enzyme, mechanistic elucidation of the role of the hydride, and electrochemical investigation of the [2Fe2S] complexes had a decisive impact on their application as catalysts in visible-light-driven hydrogen production. The basic molecular [2Fe2S] catalysts have the general formula Fe₂S₂RL₆, where the two sulphur atoms are part of a bridging unit that tethers together the Fe cations, each of which is further coordinated by three ligands L, often carbon monoxide. These metallic clusters can be precisely modified by replacing the L ligands or the dithiolate bridge, allowing the tuning of electronic and photophysical properties of the complex for optimal employment in photocatalysis.

The wide range of reaction conditions for photocatalysis using hydrogenase active site mimics precludes a direct comparison between the catalytic performances of different [2Fe2S] complexes. Nevertheless, some conclusions can be drawn from this literature review. First, the performance of [FeFe]-hydrogenase active site mimics can clearly be modulated through the first and second coordination sphere. The replacement of CO ligands in the [2Fe2S] cluster by phosphines renders the reduction potential of the diiron species more negative, and increases the stability of the catalyst under photoreaction conditions. Aromatic bridges stabilize the complex and anodically shift the reduction potential for proton reduction, while

sulfonates in the bridgehead promote water solubility. These strategies have resulted in [2Fe2S] complexes with improved catalytic performance.

The intermolecular electron transfer between [2Fe2S] and appropriate photosensitizers can produce hydrogen using light in the presence of electron donors by a reductive quenching mechanism. *Intramolecular* electron transfer processes can be carried out using molecular dyads bearing photosensitizers directly linked to [2Fe2S] compounds. Furthermore, triads with an electron donor appended to PS-[2Fe2S] complexes have demonstrated a strong driving force for photoinduced electron transfer from the photosensitizer to the diiron center via oxidative quenching. The enhanced charge separation combats undesirable recombination processes, providing a longer lifetime of the reduced $\text{Fe}^{\text{I}}\text{Fe}^{\text{0}}$ species essential for hydrogen evolution. Future efforts in the design of dyads and triads should offer production of strong reducing equivalents, optimized redox properties, enhanced electron transfer efficiency, and photostability.

Supramolecular assemblies incorporating synthetic [2Fe2S] clusters have been used to tune the outer coordination sphere and promote strong interactions and efficient electron transfer between the PS and the diiron compound in an environment mimicking that of the native metalloenzyme. Supramolecular platforms provide hydrophobic hydrogenase-like isolation sites that stabilize the charge-separated state and/or reactive intermediates, and improve water solubility. Particularly, the elegantly designed artificial hydrogenases immobilized on polysaccharides and metallopolymers in combination with quantum dot light harvesters exhibit significant stability and high photocatalytic activity for hydrogen production in aqueous solution under visible light irradiation.

Hybrid photocatalytic systems consisting of the biomimetic diiron catalyst assembled on semiconductor nanoparticles have been successfully applied in light-induced hydrogen generation reactions. In addition, the anchoring of [2Fe2S] catalysts on the surface of QD constitutes an alternative strategy for the design of a water-soluble artificial photosynthetic [2Fe2S] system. Outstanding hydrogen productivity rates have been achieved due to the broad and tunable spectral absorption range of these materials, as well as the structural stability of the molecular catalyst and the effective electron transfer and charge separation from the photoexcited semiconductor to the diiron cluster [2Fe2S].

Novel pathways have been pursued using ordered heterogeneous structures for embedding or immobilizing [2Fe2S] complexes, raising the possibility to increase the stability of the diiron molecular catalyst for large-scale applications. Metal-organic frameworks (MOFs), silica mesoporous platforms and graphene-based supports are easily separable and recyclable hybrid materials. Regarding MOFs, their well-ordered structures can provide the appropriate hydrophobic environment for anchoring [2Fe2S] sites, while promoting accessibility to the catalyst through facile diffusion of reactants and products through the framework pores. The development of future catalytic MOFs requires further catalyst design and precise engineering of transport channels. The appropriate distance between the catalytically active unit and the photosensitizer within the framework is essential for efficient charge transfer in the photocatalytic process. It is not always clear where catalysis occurs in a MOF since the substrate, reducing equivalents and protons may not always be accessible to all catalytic units, in particular those that are deeply buried in the MOF crystals, thereby decreasing overall efficacy. Silica-based heterogeneous supports with immobilized [2Fe2S] complexes provide catalyst photostability and long-lived charge-separated states, crucial factors to increase photocatalytic hydrogen generation activity. The use of graphene-based materials to immobilize both photosensitizer and diiron catalyst is a promising alternative strategy to design a suitable electronic and stable configuration that improves intramolecular electron transfer between anchored functional units and thus enhances photoinduced hydrogen production.

The synergistic hybridization of catalysts based on [2Fe2S] complexes and solid supports in the correct environment is a promising research avenue to develop enhanced photocatalytic systems for hydrogen production by harnessing inspiration from nature.

The challenge in the future of biomimetic catalysis is coupling reductive and oxidative half-reactions to build complete artificial photosynthetic water-splitting systems for the conversion of solar energy to chemical fuels. The rational combination of a synthetic hydrogenase photosystem capable of carrying out proton reduction together with a system capable of catalyzing the water oxidation half-reaction is being evaluated in whole cell conditions and in photoelectrochemical devices [263–266]. In this field, PEC cells containing photocathodes based on p-type semiconductor with immobilized H₂-evolving [2Fe2S] mimic catalysts have emerged enormously in recent years as potentially

inexpensive, robust and non-toxic devices for efficient photoelectrochemical proton reduction applications. These efforts will put forward new inspiration and technologies based on the fascinating world of photocatalysis and biomimicry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

J. A.-G., D. E. and F. J. R.-S. wish to acknowledge financial support from Ramon Areces Foundation, Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981) and Project RTI2018-101611-B-100, Andalusian Regional Government (FQM-346 group), and Feder Funds. H.T. wants to acknowledge the Olle Engkvist Foundation (200-0523), and S. O. the Swedish Research Council (2015-04640) for financial support.

5.2.1.11. References

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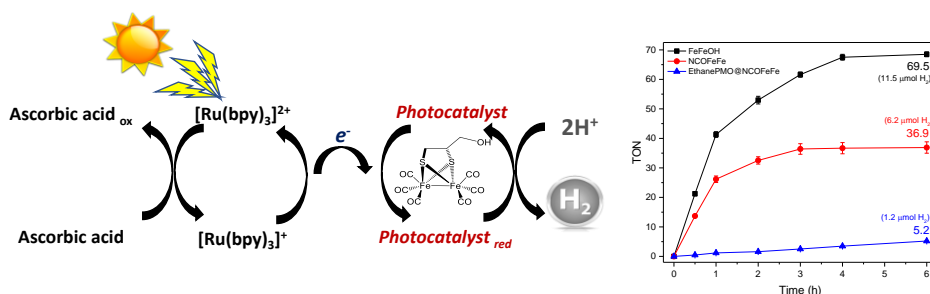
5.2.2. Hydroxyl-Decorated Diiron Complex as a [FeFe]-Hydrogenase Active Site Model Complex: Light-Driven Photocatalytic Activity and Heterogenization on Ethylene-Bridged Periodic Mesoporous Organosilica

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Published in *Catalysts*

Catalysts, 2022, vol. 12, no 3, p. 254

DOI: <https://doi.org/10.3390/catal12030254>

Abstract

A biomimetic model complex of the [FeFe]-hydrogenase active site (FeFeOH) with an ethylene bridge and a pendant hydroxyl group has been synthesized, characterized and evaluated as catalyst for the light-driven hydrogen production. The interaction of the hydroxyl group present in the complex with 3-isocyanopropyltriethoxysilane provided a carbamate triethoxysilane bearing a diiron dithiolate complex (NCOFeFe), thus becoming a potentially promising candidate for anchoring on heterogeneous supports. As a proof of concept, the NCOFeFe precursor was anchored by a grafting procedure into a periodic mesoporous organosilica with ethane bridges (EthanePMO@NCOFeFe). Both molecular and heterogenized complexes were tested as catalysts for light-driven hydrogen generation in aqueous solutions. The photocatalytic conditions were optimized for the homogenous complex by varying the reaction time, pH, amount of the catalyst or photosensitizer, photon flux, and the type of light source (light-emitting diode (LED) and Xe lamp). It was shown that the molecular FeFeOH diiron complex achieved a decent turnover number (TON) of 70 after 6 h, while NCOFeFe and EthanePMO@NCOFeFe had slightly lower activities showing TONs of 37 and 5 at 6 h, respectively.

Keywords: [FeFe]-hydrogenase; Periodic Mesoporous Organosilica; Biomimetic Chemistry; Artificial Photosynthesis; Light-Driven Hydrogen Evolution

5.2.2.1. Introduction

The current energy crisis produced by the imminent depletion of non-renewable energy sources has prompted the scientific community to carry out numerous investigations with the aim of finding inexhaustible and environmentally friendly alternative energy forms [1–3]. In this area, solar energy applied to the chemical decomposition of an abundant substrate such as water is constantly on the rise as a key strategy for obtaining hydrogen [4–8].

A large part of the energy-sustainable systems of the future is based on hydrogen as a renewable energy carrier due to its high energy density and its combustion free of polluting gases [9,10]. The naturally occurring [FeFe]-hydrogenase enzymes in certain algae and bacteria catalyze the reduction of protons to hydrogen with a very high efficiency [11–13]. Due to the low availability of natural hydrogenases, a large number of investigations have been reported in the search for biomimetic catalysts reproducing the biological activity carried out by these enzymes, with the aim of designing an artificial photocatalytic system capable of providing light-driven hydrogen production [14,15].

Bimolecular reactions where electron transfer occurs between biomimetic [2Fe2S]-hydrogenase-based catalysts and suitable photosensitizers in the presence of an electron donor have been extensively investigated [16,17]. For these photocatalytic systems, a wide variety of molecular [2Fe2S] catalysts have been designed through well-established strategies and evaluated in photocatalytic reactions for hydrogen generation. Very different catalytic performances were reported to be dependent on the biomimetic diiron model and experimental conditions set for the photocatalytic system [18–27]. Regarding [2Fe2S] active sites, the structural modifications through ligand replacement in the first coordination sphere or incorporation of functionalities via the dithiolate-bridged group in the second coordination sphere have provided some interesting characteristics to the diiron complex. Among them, it is worth mentioning that the modulation of redox properties, photostability, water solubility and the inclusion of a specific functional unit allow for the formation of supramolecular architectures or the subsequent immobilization into heterogeneous solids [28–30].

Accordingly, the scientific community has made enormous efforts to the preparation of functional biomimetic systems based on [FeFe]-

hydrogenase by modifying the first, second, or even outer coordination sphere [28,31–34], thus being capable of acting as artificial proton reduction catalysts in hydrogen evolution reactions. In fact, we have recently reported a comprehensive review of [FeFe]-hydrogenase-inspired catalysts applied in photocatalytic hydrogen production, including molecular [2Fe2S] catalysts, photosensitizer–[FeFe]-hydrogenase dyads, electron donor–photosensitizer–[FeFe]-hydrogenase triads, supramolecular entities, hybrid semiconductor assemblies, heterogeneous supports and photocathodes based on [2Fe2S] for photoelectrochemical (PEC) devices. Indeed, there exists growing interest in this research topic in order to design an efficient and effective catalytic architecture that exhibits high performance in the photochemical proton reduction to molecular hydrogen [35].

In the current work, the second coordination sphere of a hydroxyl-decorated diiron complex (FeFeOH; Figure 1a) [36] has been modified by the reaction with 3-isocyanopropyltriethoxysilane, providing a carbamate triethoxysilane bearing a diiron dithiolate biomimetic model (Figure 1b). The monosilane precursor obtained (NCOFeFe) was postulated as a promising candidate to be anchored on a silica-based support via outer coordination sphere interactions. Therefore, the precursor NCOFeFe was anchored in a periodic mesoporous organosilica (PMO) with ethylene-bridged organic groups using a grafting procedure (EthanePMO@NCOFeFe). Once characterized in detail, all the samples were tested as catalysts for light-driven hydrogen generation. The photocatalytic process was optimized in a homogeneous phase using the FeFeOH complex as the catalyst, [Ru(bpy)₃]²⁺ as the photosensitizer, and ascorbic acid as the sacrificial electron donor under the irradiation with a light-emitting diode (LED) light and operating in an organic water/acetonitrile mixture (11.8 vol%). Different parameters influencing the reaction were evaluated in order to establish the optimal experimental conditions: pH, photon flux, and the concentration of catalyst or photosensitizer. The light source was changed to a Xenon lamp with a higher irradiation power to analyze the increase in the light intensity illuminated on the active area of the sample in the hydrogen production. The maximum TON of 70 was reached after 6 h for the molecular FeFeOH complex, almost 15 times higher compared to that obtained using the LED lamp. Conversely, the NCOFeFe precursor provided approximately half of the photocatalytic activity compared to FeFeOH, resulting in a TON of 37 for 6 h, while the heterogeneous catalyst EthanePMO@NCOFeFe yielded

a lower TON of 5 after 6 h working in a pure aqueous medium. Such TONs are comparable to those reported for related systems in heterogeneous supports in the literature [35].

5.2.2.2. Materials and Methods

5.2.2.2.1. Reagents and Materials

Triiron dodecacarbonyl ($\text{Fe}_3\text{CO}_{12}$, containing 1%–10% methyl alcohol), 2,3-dimercapto-1-propanol ($\geq 98\%$, iodometric), THF (anhydrous, $\geq 99.9\%$, inhibitor-free), ethyl acetate (ACS reagent, $\geq 99.5\%$), 3-isocyanatepropyltriethoxysilane (95%), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123, average M_n : $\sim 5,800$), potassium chloride (KCl, ACS reagent, 99.0%–100.5%), hydrochloric acid (HCl, ACS reagent, 37%), 1,2-bis(triethoxysilyl)ethane (96%), L-ascorbic acid (ACS reagent, $\geq 99\%$), and tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate ($\text{Ru}(\text{bpy})_3^{2+}$, 99.5% trace metals basis) were purchased from Sigma-Aldrich (St. Louis, Missouri, United States). Hexane (alkanes mixture for analysis) was obtained from PanReac AppliChem (Barcelona, Spain). Petroleum ether (40–60 AGR), ethyl acetate (AGR, 99.5%), ethanol absolute (AGR, 96%), dichloromethane (CH_2Cl_2 , amylene as stabilizer, AGR, 99.9%), and chloroform (CHCl_3 , AGR, 98.5%) were purchased from Labbox Labware S.L. (Barcelona, Spain).

5.2.2.2.2. Synthesis of the Catalysts

The synthesis of the hydrogenase biomimetic model FeFeOH was carried out by adapting the procedure previously reported by Liu et al. [36]. In a three-neck round-bottom flask, a mixture of 2.42 g (4.8 mmol) $\text{Fe}_3\text{CO}_{12}$, 0.5 mL (4.8 mmol) 2,3-dimercapto-1-propanol, and 100 mL anhydrous THF was stirred at 70 °C for 4 h under a nitrogen atmosphere. Initially, the color of the solution was dark green, but it changed to dark red after the total reaction time was completed. After the mixture was cooled to room temperature, the solvent was evaporated with a rotary evaporator under reduced pressure. The crude product was purified by column chromatography using petroleum ether:ethyl acetate (4:1, v/v) as the eluent. The FeFeOH hydroxyl–diiron complex was crystallized from hexane/ CH_2Cl_2 (2:1, v/v) at 4 °C as a red solid (1.7 g, yield: 88%). ^1H NMR (400 MHz, CDCl_3) δ 3.63 (m, 1H, *CHH*-OH), 3.53 (m, 1H, *CHH*-OH), 2.81 (m, 1H, CH), 2.66 (dd, $J = 13.1, 7.7$ Hz, 1H, *CHH*-CH), 1.91 (dd, $J = 13.1,$

5.6 Hz, 1H, CHH-CH), 1.85 (m, 1H, OH). ^{13}C NMR (76 MHz, CDCl_3) δ 65.36 ($\text{CH}_2\text{-OH}$), 56.06 ($\text{CH}_2\text{-CH}$), 38.71 ($\text{CH}_2\text{-CH}$). IR (CHCl_3 , cm^{-1}): 1981, 2029, 2075. UV/VIS (CHCl_3 , nm): 327, 455.

The monosilane hydrogenase precursor NCOFeFe was prepared by the reaction of FeFeOH and 3-isocyanatepropyltriethoxysilane. In a three-neck round-bottom flask was placed 0.8 g of FeFeOH (2.0 mmol) dissolved in 25 mL of anhydrous THF under a nitrogen atmosphere. The yellow solution was magnetically stirred at 65 °C under reflux. Subsequently, 1 mL of 3-isocyanatepropyltriethoxysilane was slowly added dropwise. Then, the reaction was left to react under an inert atmosphere for 24 h and monitored by FTIR-ATR spectroscopy. Later, the solvent was evaporated with a rotary evaporator under reduced pressure, and the crude product was purified by column chromatography using hexane:ethyl acetate (4:1, v/v) as the eluent. The NCOFeFe monosilane precursor was obtained as a dark red viscous oil (0.9 g, yield: 67%). ^1H NMR (300 MHz, CDCl_3) δ 4.95 (s, 1H, NH), 3.94 (m, 2H, $\text{CH}_2\text{-O-}$), 3.75 (q, $J = 7.0$ Hz, 6H, $\text{O-CH}_2\text{-CH}_3$), 3.11 (q, $J = 6.8$ Hz, 2H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$), 2.83 (m, 1H, CH), 2.58 (dd, $J = 13.2, 7.7$ Hz, 1H, CHH-CH), 1.87 (dd, $J = 13.2, 5.7$ Hz, 1H, CHH-CH), 1.55 (m, 2H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$), 1.16 (t, $J = 7.1$ Hz, 9H, $\text{O-CH}_2\text{-CH}_3$), 0.55 (t, $J = 8.1$ Hz, 2H, $\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$). ^{13}C NMR (76 MHz, CDCl_3) δ 65.95 ($\text{CH}_2\text{-O}$), 59.91 ($\text{O-CH}_2\text{-CH}_3$), 52.86 ($\text{CH}_2\text{-CH}$), 43.71 ($\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$), 38.64 ($\text{CH}_2\text{-CH}$), 23.38 ($\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$), 19.23 ($\text{O-CH}_2\text{-CH}_3$), 7.85 ($\text{NH-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$). IR (CHCl_3 ; cm^{-1}): 1994, 2034, 2076. UV/VIS (CHCl_3 ; nm): 327, 455.

Periodic mesoporous organosilica EthanePMO was synthesized following the procedure reported by Yang et al. [57]. Typically, 3.3 g of P123 and 20.94 g of KCl were stirred in 99 g of HCl (2 M) and 22.5 g of H_2O at 45 °C for 24 h. After that, 1,2-bis(triethoxysilyl)ethane (7.55 mL, 21.3 mmol) was added dropwise to the formed solution. The reaction mixture was left under stirring at 45 °C for 24 h and then aged at 100 °C under static conditions for 24 h. The white suspension was filtered and washed with distilled water and ethanol. The solid was dried under vacuum at 80 °C overnight. Surfactant extraction was performed by refluxing 1 g of the as-synthesized material in a solution of 1 mL HCl in 50 mL ethanol for 24 h at 80 °C. After repeating this process twice, 3.38 g of the white solid product EthanePMO were recovered by filtration, washed with ethanol and dried under vacuum at 120 °C.

The grafting procedure of the NCOFeFe precursor on the EthanePMO matrix was similar to that described by Yang et al. [58]. Then, 6.98 g of NCOFeFe (10.8 mmol) were added dropwise into 1.28 g of EthanePMO previously dispersed in 100 mL of CHCl_3 . The suspension was kept under stirring for 5 days. Afterwards, the solid was filtered, washed repeatedly with CHCl_3 and dried under vacuum at 60 °C. The material was referred to as EthanePMO@NCOFeFe.

5.2.2.2.3. *Characterization of the Catalysts*

The $^1\text{H-NMR}$ spectra were recorded at 300 MHz on a Bruker Avance III (AVIII, Bruker Corporation, Billerica, Massachusetts, United States) at room temperature. Chemical shifts were measured relative to a tetramethylsilane standard. The UV–VIS spectroscopy for the FeFeOH complex and the NCOFeFe precursor were performed in the liquid phase with a double-beam UV/VIS 4260/50 (ZUZI, Auxilab, Beriáin, Navarra) instrument in a wavelength range of 250–700 nm. The UV/VIS diffuse reflectance spectroscopy for solid samples was measured with a Perkin Elmer Lambda 650S UV/VIS spectrometer (PerkinElmer, Inc., Waltham, Massachusetts, United States) in a wavelength range of 250–700 nm. FTIR spectra were obtained on a PerkinElmer FTIR spectrometer (PerkinElmer, Inc., Waltham, Massachusetts, United States), equipped with a high-performance Pike GladiATR monolithic diamond crystal accessory (PIKE Technologies, Fitchburg, United States) of the ATR mode. The XRD patterns of powdered solid samples were collected with a Bruker D8 Discover X-ray diffractometer using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The patterns were recorded within the 0.5–5° (2θ) range, using a step size of 0.040° and 1.05 s per step. Specific surface areas, pore sizes and pore volumes were examined from the N_2 adsorption–desorption isotherms with an Autosorb iQ/ASiQwin (Quantachrome Instruments, Moscow, Rusia). The samples were previously outgassed under vacuum at 120 °C overnight and then measured at the liquid nitrogen temperature (77 K). Surface areas were calculated using the BET method. Pore size distributions and pore volumes were obtained from the DFT method. Micropore analysis was performed by the t-plot method. TEM images were obtained on a Jeol JEM-1400 transmission electron microscope (JEOL Ltd., Akishima, Tokyo, Japón) operated at an accelerating voltage of 120 kV. Iron loading was determined by ICP-MS analysis in an ICP Mass Spectrometer model NexION™ 350X (PerkinElmer Inc., Waltham, Massachusetts, United States).

5.2.2.2.4. Photocatalytic Experiments

The optimization of photocatalytic hydrogen evolution was performed in 9 mL gastight vials containing 0.084 mM of the homogeneous catalyst, 0.5 mM of $\text{Ru}(\text{bpy})_3^{2+}$, 100 mM of ascorbic acid, and 1 M of an acetate buffer at $\text{pH} = 5.0$ in a total volume of 2 mL using the solvent $\text{ACN}/\text{H}_2\text{O}$ with a 11.8 vol% organic phase.

Firstly, the solution was purged with argon (Ar) for 20 min in order to completely remove oxygen. An LED PAR38 lamp (17W, 5000K, Zenaro Lighting GmbH, Karlsruhe, Baden-Württemberg, Germany, $\lambda = 475\text{--}750$ nm) was used as the light source. The light intensity illuminated on the active area of the sample was 50 mW cm^{-2} , as measured by a pyranometer (CM11, Kipp&Zonen, B.V., Delftechpark, XH Delft, Netherlands). The LED light source basically had a similar intensity to the standard 1 sun condition between 475 and 750 nm. After starting light irradiation, aliquots of 100 μL of the headspace were removed at different times using a gastight Hamilton syringe, and the amount of hydrogen evolved from the system was subsequently analyzed by gas chromatography (GC; PerkinElmer Clarus 500, PerkinElmer Inc., Waltham, Massachusetts, United States) using Ar as the carrier gas. The total reaction time was 2 h. The photocatalytic reactions were carried out three times, and the results were given as average values with standard deviations.

In addition, a Xenon lamp (300 W, $\lambda > 420$ nm; Ushio Inc., Tokyo, Japan) was used as the light source. In this case, the light intensity illuminated on the active area of the sample was 90 mW/cm^2 . The reaction conditions in the homogeneous phase for the FeFeOH complex and the NCOFeFe precursor were the same as those mentioned above. In the case of the heterogeneous phase, 2 mg of EthanePMO@NCOFeFe were used, maintaining the same concentrations of $[\text{Ru}(\text{bpy})_3]^{2+}$, the ascorbic acid, and the acetate buffer at $\text{pH} = 5.0$, but using a totally aqueous medium.

Once the irradiation on the samples started, aliquots of 100 μL of the headspace were withdrawn at different times using a gastight Hamilton syringe and the amount of hydrogen evolved from the system was subsequently analyzed by GC (Shimadzu GC-2010 Plus, Shimadzu Corporation, Kyoto, Japan) using He as the carrier gas. The total reaction time was 6 h. The photocatalytic reactions were carried out four times, and the results were given as average values with standard deviations.

5.2.2.3. Results and Discussion

5.2.2.3.1. Synthesis and Characterization of Diiron Catalysts

Figure 1 shows the reaction scheme for the synthesis of the FeFeOH hydroxyl–diiron complex and the monosilane precursor NCOFeFe. Firstly, FeFeOH was synthesized by the reaction of Fe₃(CO)₁₂ with 2,3-dimercapto-1-propanol in tetrahydrofuran (THF) under a nitrogen atmosphere at 70 °C for 2 h. The pendant hydroxyl group incorporated in the dithiolate bridge was of great interest due to the possibility of carrying out a subsequent functionalization. Accordingly, the monosilane precursor NCOFeFe was prepared via the reaction of FeFeOH and 3-isocyanatepropyltriethoxysilane in THF under a nitrogen atmosphere at 65 °C.

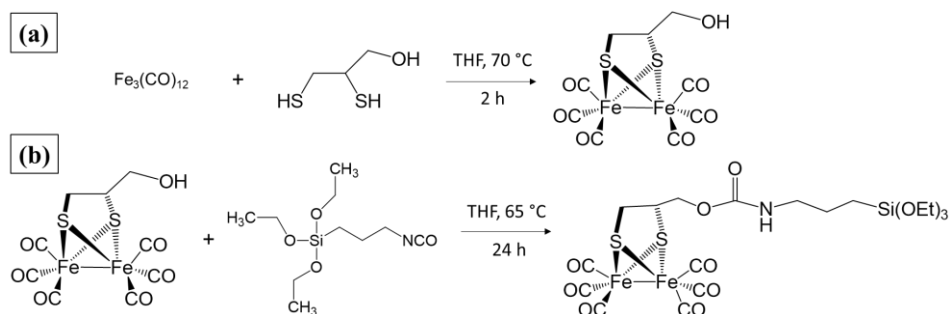


Figure 1. Schematic representation for the synthesis of the complex FeFeOH (a) and the monosilane precursor NCOFeFe (b).

The formation of the NCOFeFe precursor was monitored by FTIR-attenuated total reflection (ATR) taking aliquots of 100 μ L at different times during 24 h (**Figure S1**). The progress of the reaction was corroborated by observing the disappearance of the isocyanate band over 2300 cm^{-1} and the concurrent growth of a new band corresponding to the C=O vibration from urethane at ca. 1715–1730 cm^{-1} . The molecular structures of the FeFeOH diiron complex and the NCOFeFe precursor were confirmed by proton and carbon nuclear magnetic resonance (¹H-NMR, ¹³C-NMR, and ¹³C DEPT-NMR; **Figure S2–S5**).

The FTIR-ATR spectra of 3-isocyanatopropyltriethoxysilane, FeFeOH, and NCOFeFe are shown in **Figure 2a**. The FeFeOH spectrum showed the characteristic bands corresponding to the C–O stretching vibrations located at 1994, 2034, and 2076 cm^{-1} for the diiron–

hexacarbonyl complexes, while modes with the predominant Fe–CO characteristic appeared above 500 cm^{-1} [36,37]. The formation of the carbamate bond was confirmed by the presence of the vibration relative to the carbonyl groups C=O from the urethane group at $1715\text{--}1730\text{ cm}^{-1}$, and the disappearance of the intense band peaked at ca. 2260 cm^{-1} related to the isocyanate group (N=C=O), which was observed in the starting reagent 3-isocyanatopropyltriethoxysilane [38]. The C–O stretching vibrations were located at similar wavelengths ($1994, 2034, \text{ and } 2076\text{ cm}^{-1}$) as for FeFeOH, and the Fe–CO vibration modes were also present slightly above 500 cm^{-1} . The presence of the N–H stretching vibration in the range of $3200\text{--}3400\text{ cm}^{-1}$ and the N–H bending located above 1510 cm^{-1} were also observed. Furthermore, the C–H stretching of the hydrocarbon chain, the CO group from the carbamate, and the Si–O stretching of the triethoxysilane groups located at $2850\text{--}3000, 1235, \text{ and } 1080\text{ cm}^{-1}$, respectively, were present in the NCOFeFe precursor, similar to 3-isocyanatopropyltriethoxysilane, confirming the efficient functionalization process on the FeFeOH diiron complex.

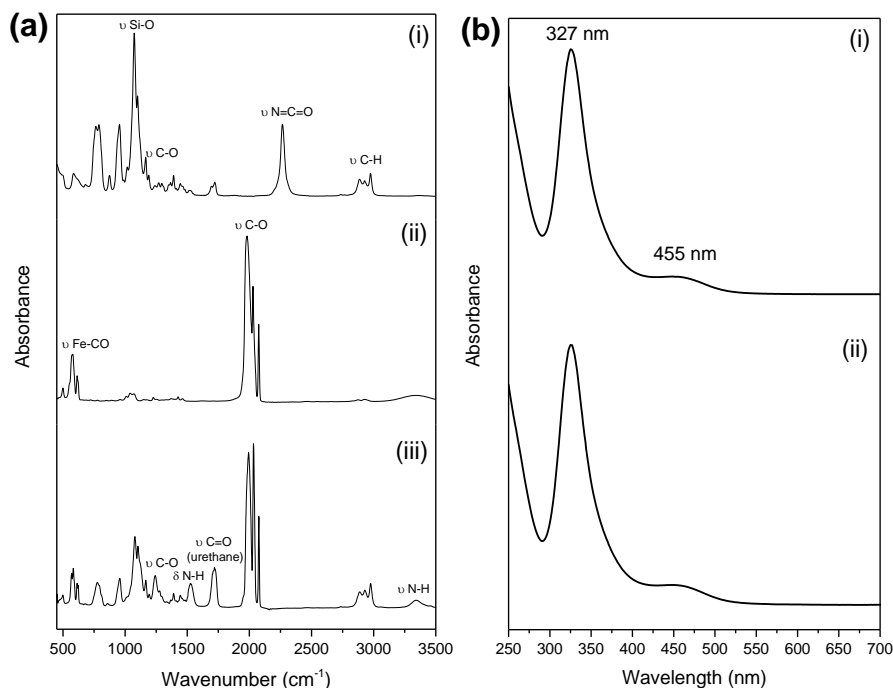


Figure 2. (a) FTIR-attenuated total reflection (ATR) spectra of 3-isocyanatopropyltriethoxysilane (i), FeFeOH (ii), and NCOFeFe (iii). (b) UV-VIS spectra of FeFeOH (i) and NCOFeFe (ii).

The UV–VIS absorption spectrum of FeFeOH and NCOFeFe were recorded in CH₂Cl₂ at room temperature. As shown in **Figure 2b**, both compounds exhibited two identical bands centered at 327 cm⁻¹ (UV region) and 455 cm⁻¹ (visible region) assigned to π – π^* electronic transitions and metal-to-ligand charge-transfer (MLCT) transitions, respectively [39–43]. Therefore, the functionalization of the FeFeOH complex did not generate significant alterations in the electron densities at the diiron core, which corroborated the results drawn from the FTIR-ATR measurements.

Periodic mesoporous organosilicas (PMOs) are organic–inorganic hybrid materials prepared by the condensation of a hydrolysable bis-silane of the type (R'O)₃-Si-R-Si-(OR')₃, where R is the organic functional linker located within the channel walls as bridges between silicon centers and R' is a hydrolysable group (normally ethoxy or methoxy), in the presence of a surfactant that acts as a structure-directing agent. Ethylene-bridged periodic mesoporous organosilicas (EthanePMO) are the most readily available materials of the PMO family. They show interesting features such as high hydrophobicity and high mechanical and hydrothermal stability in aqueous media [44]. Therefore, this material was chosen as the support for the diiron complexes. Thus, the NCOFeFe precursor was anchored onto EthanePMO by a grafting method at room temperature for five days using CHCl₃ as the solvent (**Figure 3**).

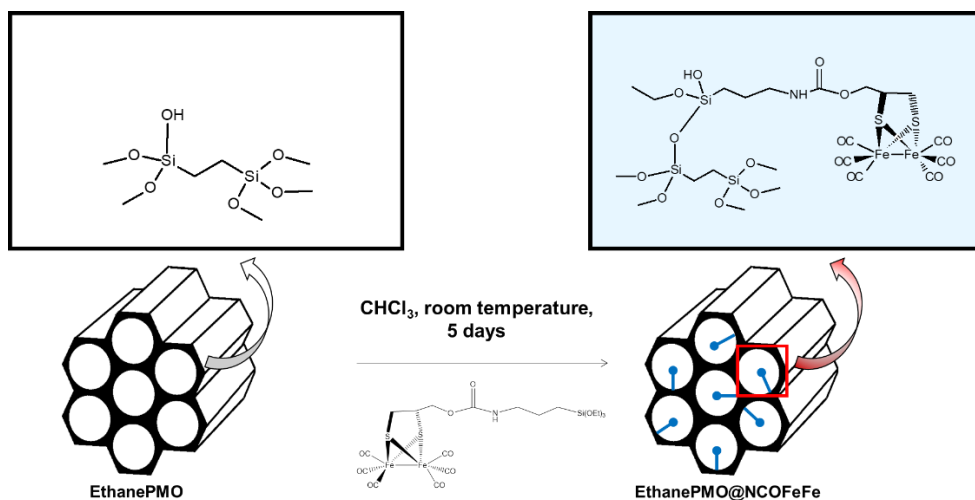


Figure 3. Scheme of the grafting procedure on the ethylene-bridged periodic mesoporous organosilicas (EthanePMO) material with the NCOFeFe precursor.

The structural analysis of EthanePMO@NCOFeFe taking the starting EthanePMO as a reference was examined by XRD, FTIR-ATR spectroscopy, UV-VIS diffuse reflectance spectroscopy, TEM, and nitrogen adsorption isotherm analyses.

The XRD patterns of EthanePMO and EthanePMO@NCOFeFe are shown in **Figure 4a**. Both diffractograms exhibited a strong reflection at a low angle ($2\theta \approx 1^\circ$) related to the (100) diffraction peak from a two-dimensional (2D) hexagonal structure and two weak well-defined diffraction peaks corresponding to (110) and (200) planes, typical of a $p6mm$ mesostructure [45]. The incorporation of the NCOFeFe monosilane precursor into the EthanePMO support was confirmed by FTIR-ATR and UV-VIS spectroscopic techniques. The FTIR-ATR spectra of EthanePMO@NCOFeFe represented in **Figure 4b** contained three prominent C–O stretching vibration bands at 1998, 2046, and 2080 cm^{-1} , while no such peaks were observed for EthanePMO in the range of 1600–2400 cm^{-1} . The solid-state UV–VIS spectra of EthanePMO@NCOFeFe (**Figure 4c**) also showed two characteristic absorption bands at 329 and 457 cm^{-1} , which were in accordance with the UV-VIS spectral features of the NCOFeFe and FeFeOH diiron complexes. No absorption bands were appreciated in the UV–VIS diffuse reflectance spectrum of EthanePMO. The results clearly confirmed that the NCOFeFe precursor was successfully attached to the surface of EthanePMO with a grafting procedure. The loading of iron in the EthanePMO@NCOFeFe material determined by inductively coupled plasma mass spectrometry (ICP-MS) was 0.235 mmol Fe/g PMO.

The nitrogen adsorption/desorption isotherms and pore size distributions of EthanePMO and EthanePMO@NCOFeFe are shown in **Figure 5**. Both materials exhibited type IV isotherms with H1-type hysteresis loops with a sharp step at P/P_0 around 0.6–0.8, typically obtained for ordered mesoporous materials with uniform pores [46,47]. These results corroborated that the ordered mesoporous structure was essentially preserved after anchoring the NCOFeFe precursor. The pore size distribution represented for both materials mainly indicated the presence of pores in the meso range and a reduced fraction of micropores. The Brunauer–Emmett–Teller (BET) surface areas (S_{BET}), density functional theory (DFT) pore diameters (D_p) and volumes (V_p), and t-plot micropore analysis data, determined from isotherms, are listed in **Table 1**. The EthanePMO@NCOFeFe material exhibited a decreased BET surface area

(481 m²/g), pore diameter (4.9 nm), and pore volume (0.55 cm³/g) compared to the pristine EthanePMO, demonstrating the efficient attachment of the NCOFeFe monosilane precursor during the grafting process. Additionally, the area and volume of micropores were also reduced, suggesting the blockage of micropores upon the incorporation of the NCOFeFe compound into the walls.

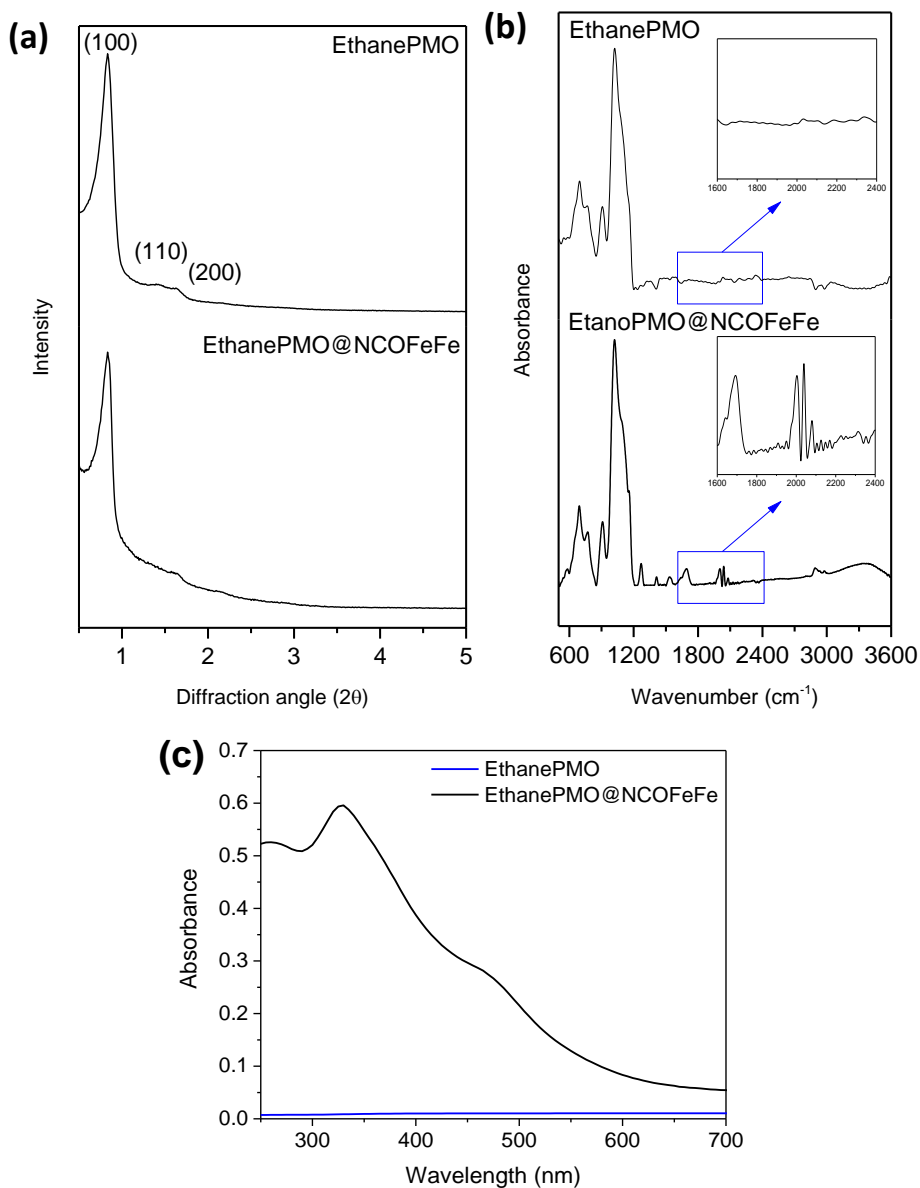


Figure 4. XRD patterns (a), FTIR-ATR spectra (b), and UV-VIS diffuse reflectance spectra (c) of EthanePMO and EthanePMO@NCOFeFe.

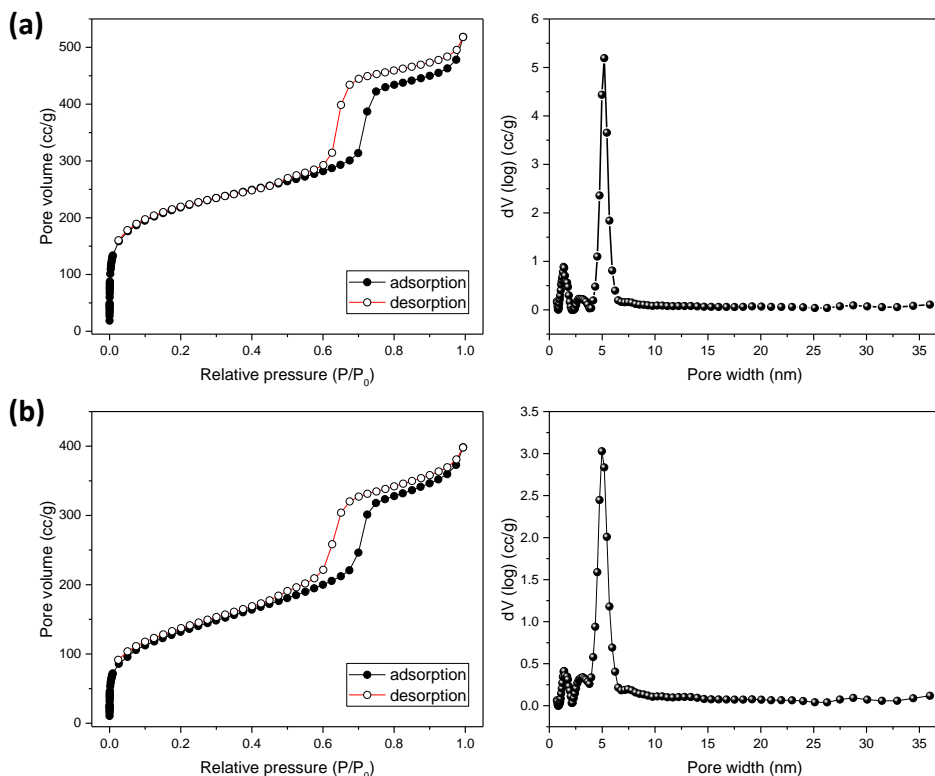


Figure 5. Nitrogen adsorption–desorption isotherms (left) and pore size distributions calculated by the density functional theory (DFT) method (right) of EthanePMO (a) and EthanePMO@NCOFeFe (b).

Table 1. Textural properties of EthanePMO and EthanePMO@NCOFeFe materials.

Sample	Brunauer– Emmett– Teller (BET) Surface Area (m ² /g)	D _p (nm) ^a	V _p (cm ³ /g) ^a	External Surface Area (m ² /g) ^b	Micropore Area (m ² /g) ^b	Micropore Volume (cm ³ /g) ^b
EthanePMO	789	5.2	0.71	363	426	0.18
EthanePMO@NCOFeFe	481	4.9	0.55	375	106	0.04

^a analysis by the DFT method. ^b t-plot method micropore analysis.

To further characterize the PMO materials, the morphology was analyzed by TEM (**Figure 6**). The TEM images clearly confirmed the preservation of the characteristic mesoporous structure after the grafting procedure, in agreement with the analysis carried out by XRD and N₂ adsorption–desorption measurements. Both the starting EthanePMO and the EthanePMO@NCOFeFe exhibited 2D parallel-aligned cylindrical

mesopore channels with a honeycomb-like arrangement, uniform sizes, and hexagonal shapes [48–50]. In addition, no particles deposited on the walls or inside the pores of the material were observed, confirming the absence of aggregates from NCOFeFe species on PMO.

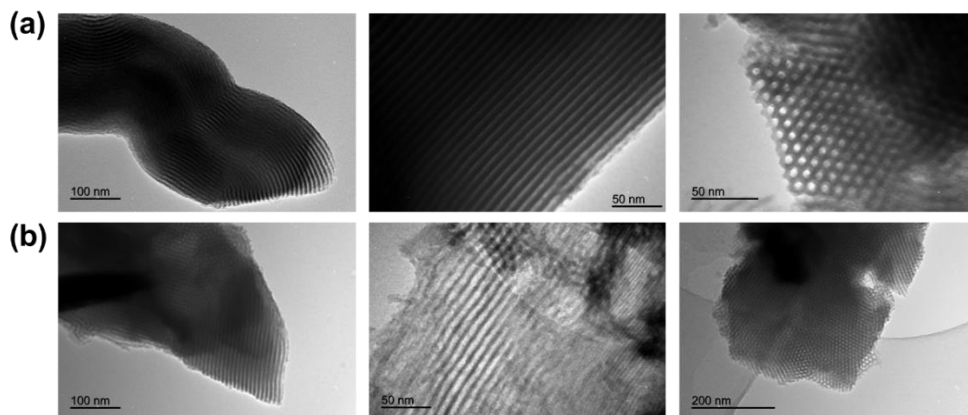


Figure 6. TEM images of EthanePMO (a) and EthanePMO@NCOFeFe (b).

5.2.2.3.2. Light-Driven Hydrogen Production

Light-driven hydrogen production was examined using FeFeOH as the catalyst, $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer, and ascorbic acid as the sacrificial electron donor under white LED irradiation ($50 \text{ mW}/\text{cm}^2$, $\lambda = 475\text{--}750 \text{ nm}$). Due to the poor solubility of the diiron complex in pure water, a slight proportion of acetonitrile (11.8 vol%) was added to the total volume of the reaction mixture in order to ensure the complete dissolution of the catalyst.

As depicted in **Figure 7**, the proposed scheme for photocatalytic proton reduction by the FeFeOH catalyst commences with the reductive quenching of excited $^*[\text{Ru}(\text{bpy})_3]^{2+}$ by the ascorbate electron donor according to the mechanism reported for other $[\text{Ru}(\text{bpy})_3]^{2+}$ /ascorbate systems [51,52]. The photogenerated $[\text{Ru}(\text{bpy})_3]^+$ successively reduces the catalyst by the transfer of one electron, recovering the original state of the photosensitizer. Once this process is repeated a second time, two electrons are accumulated at the FeFeOH diiron catalyst, and two protons will be reduced to one H_2 molecule.

This process is thermodynamically feasible based on the cathodic peak potential of FeFeOH (-1.18 V vs. Ag/AgCl) [53] which is sufficiently

mild to be accessed from the photo-produced $[\text{Ru}(\text{bpy})_3]^+$ reductant. In fact, this light-driven electron transfer process bears resemblance to other related works in which a sufficient driving force for electron transfer from photo-reduced $[\text{Ru}(\text{bpy})_3]^+$ to diiron catalysts following the photocatalytic mechanism mentioned above is established [19,24].

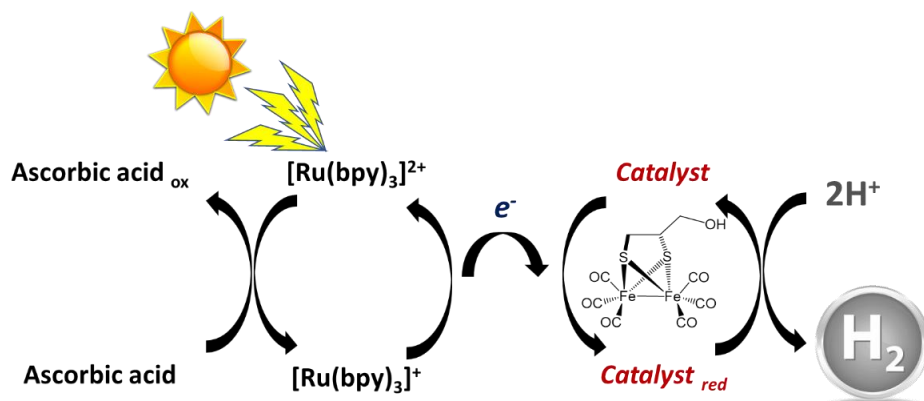


Figure 7. Schematic representation of light-driven hydrogen production by the FeFeOH catalyst.

In order to optimize the experimental conditions of the photocatalytic system, light-induced hydrogen evolution was conducted by modifying the pH, the percentage of photon flux, and the concentrations of the diiron catalyst and the photosensitizer. The pH value of the catalytic system was adjusted with a 1 M acetate buffer at pH 4.5, 5.0, and 5.5. Under standard conditions (0.084 mM of FeFeOH, 0.5 mM of $[\text{Ru}(\text{bpy})_3]^{2+}$, and 100 mM of ascorbic acid), the highest catalytic activity was accomplished at pH 5.0, resulting in a TON of 4.8 after 2 h (**Figure 8**).

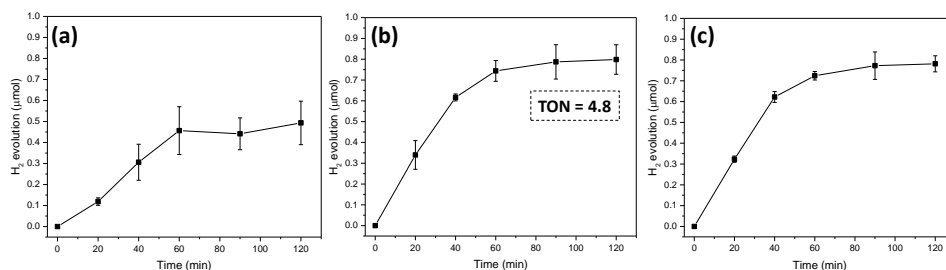


Figure 8. Photocatalytic hydrogen production as a function of the pH: (a) 4.5; (b) 5.0; and (c) 5.5.

While similar results were obtained at pH 5.5, the poorer photocatalytic performance at lower pH values (pH = 4.5) is most likely due to the increasing amount of ascorbate being in its protonated state ($pK_{a1} = 4.17$), in which it is known to be a significantly weaker donor to $^*[\text{Ru}(\text{bpy})_3]^{2+}$ than in its deprotonated state.

The photon flux was a parameter that was tuned to determine the limitation of the system related to the light intensity projected on the surface of the photocatalytic system. These experiments were carried out by placing two neutral density filters (60% transmittance and 30% transmittance) in front of the LED lamp (**Figure 9**). Minor deviations of the hydrogen evolution were observed with the 60% transmittance filter compared to the reaction without any filter (within the error). In contrast, a further decrease of the light intensity up to 30% transmittance produced a reduction of hydrogen gas evolution over 40%. Therefore, when the photon flux from the LED lamp was less than 60%, the hydrogen productivity generated by the photocatalytic system was decreased. These findings corroborated that the photocatalytic activity of FeFeOH under these conditions was limited by photon flux.

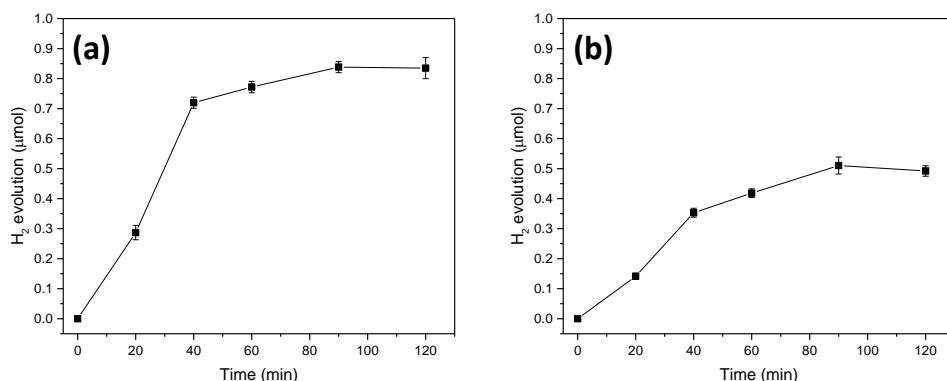


Figure 9. Hydrogen evolution data for the FeFeOH photocatalytic system at pH 5.0 with neutral density filters that transmitted 60% (0.2 mm thickness) (a) and 30% (0.5 mm thickness) (b) of the initial light.

The light-driven hydrogen evolution catalyzed by FeFeOH at different concentrations while maintaining the standard conditions of the photosensitizer and the electron donor at pH = 5.0 for 2 h is illustrated in **Figure 10a**. The results indicated that the overall hydrogen production increased linearly with the catalyst concentration from 0.0084 to 0.168

mM. This behavior favors photocatalytic performance at high catalyst concentrations for large-scale hydrogen generation [54].

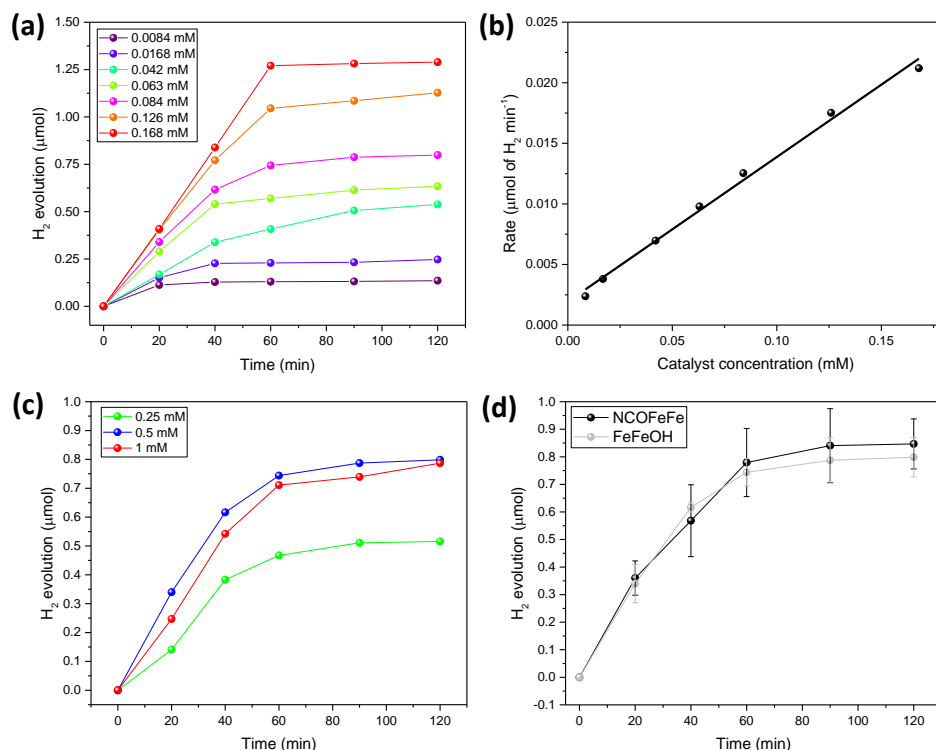


Figure 10. (a) Photocatalytic hydrogen production as a function of the FeFeOH catalyst concentration at pH = 5.0; (b) initial rate of H_2 formation versus the concentration of the FeFeOH catalyst obtained from the previous graph; (c) photocatalytic hydrogen production as a function of the $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer concentration at pH = 5.0; and (d) comparison of the photocatalytic hydrogen productions between FeFeOH and NCOFeFe catalysts at pH = 5.0.

Accordingly, **Figure 10b** shows the initial rate of H_2 formation ($\mu\text{mol of H}_2 \text{ min}^{-1}$) versus the catalyst concentration (mM). The linear dependence observed between both parameters indicated a pseudo first-order reaction [55]. The influence of $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer concentration on the photoinduced hydrogen production is represented in **Figure 10c**. Under standard conditions, hydrogen evolution decreased by 40% at a lower photosensitizer concentration. Interestingly, an increased productivity was not observed, when the photosensitizer concentration was doubled, thus suggesting that the performance of the photocatalytic reaction was not restricted by the $[\text{Ru}(\text{bpy})_3]^{2+}$ concentration.

Control experiments in the absence of the FeFeOH catalyst and the photosensitizer generated minimal amounts of hydrogen, indicating that all components were essential for hydrogen production (**Figure S6**). The photocatalytic activity of the NCOFeFe monosilane precursor was also tested. As shown in **Figure 10d**, NCOFeFe provided a similar hydrogen evolution compared to the FeFeOH diiron complex under standard conditions at pH 5.0. Therefore, the functionalization of the FeFeOH did not affect the photocatalytic performance under the standard experimental conditions established for the photocatalytic reaction.

Once the experimental conditions of the photocatalytic reaction were optimized for homogeneous catalysis, the light source was replaced by a Xenon lamp with a higher irradiation intensity to evaluate the effect of this parameter on the photocatalytic performance. The Xe lamp provided a higher light intensity illuminated on the active area of the sample of 90 mW/cm² and an increased range of wavelength ($\lambda > 420$ nm) to cover most of the maximum absorption of the photosensitizer [Ru(bpy)₃]²⁺ [56].

As can be seen in **Figure 11**, the FeFeOH complex reached the maximum TON of 70 after 6 h, which is amongst the highest reported catalytic performances of diiron catalysts under similar experimental conditions, using [Ru(bpy)₃]²⁺ as the photosensitizer and ascorbate as the sacrificial electron donor (**Table S1**). A lower TON of 37 was obtained for NCOFeFe under the same standard conditions for 6 h, demonstrating a loss of photocatalytic activity of around 50% with respect to FeFeOH. We assigned this drop in activity either to a lower intrinsic activity of the NCOFeFe catalyst or non-productive reduction events at the NCOFeFe catalyst that may involve the reduction of the carbamate tether. The FeFeOH complex displayed an excellent solubility under reaction conditions, thus providing a good accessibility of diiron active sites for promoting an efficient electron transfer from the photo-reduced [Ru(bpy)₃]⁺. The molecular aggregation phenomena of the NCOFeFe precursor might, however, occur during the photocatalytic reaction due to its hydrophobic chain, thus causing a restricted availability of diiron active sites capable of being reduced, thereby offering another potential explanation for the decreased hydrogen production performance. Obtaining an analogous TON for FeFeOH and NCOFeFe under the lighting system with an LED lamp could be explained by the lower irradiation intensity emitted on the photocatalytic system, which would cause a lower concentration of reduced [Ru(bpy)₃]⁺ species. Therefore, in both cases, sufficient diiron active sites would be present to achieve the maximum

hydrogen productivity under these conditions. Furthermore, the photodegradation of the FeFeOH and NCOFeFe catalysts was observed spectroscopically after 4 h. The maximum absorption bands of both catalysts decreased and shifted drastically (**Figure S7**), while the original carbonyl groups completely disappeared in the FTIR-ATR spectra (**Figure S8**). This would cause the deactivation of the catalysts, thus preventing further hydrogen production.

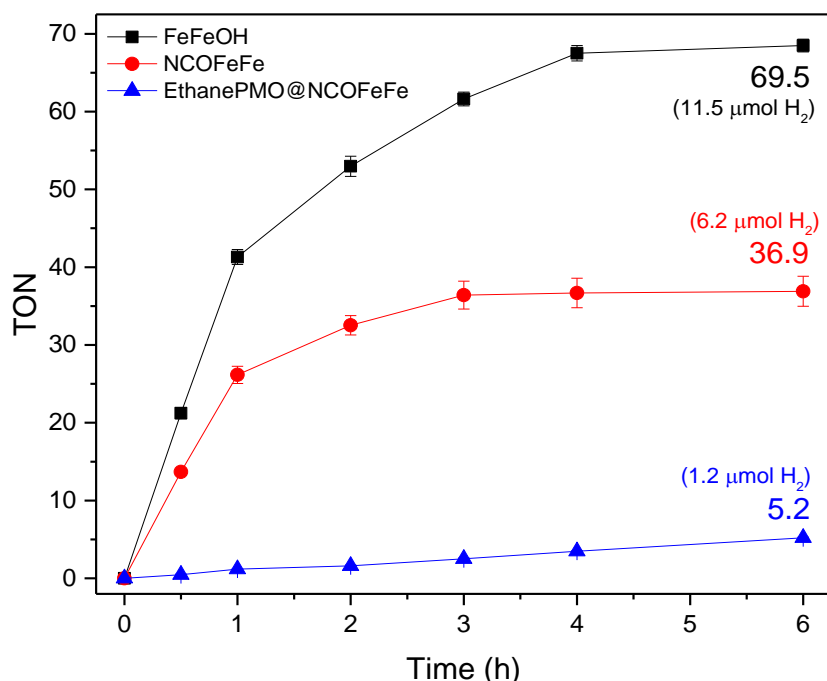


Figure 11. Photocatalytic hydrogen production under standard conditions (0.084 mM of the homogeneous catalyst, 0.5 mM of Ru(bpy)₃²⁺, 100 mM of ascorbic acid, and 1 M of the acetate buffer at pH 5.0) in the homogeneous phase (ACN/H₂O with a 11.8 vol% organic phase) using FeFeOH and NCOFeFe. Similar conditions were established in the heterogeneous phase with the only difference being the solvent, i.e., milli-Q water solution, and using 2 mg of EthanePMO@NCOFeFe.

The heterogeneous catalyst EthanePMO@NCOFeFe was also evaluated under photocatalytic conditions using the Xenon lamp as a light source. The modulation of the outer coordination sphere on the NCOFeFe precursor by anchoring to EthanePMO material allowed working in pure aqueous solutions, which is one of the advantages of using heterogeneous supports incorporating biomimetic models of the [FeFe]-hydrogenase

active site that are otherwise only soluble in organic solvents. Control experiments with pristine EthanePMO and without $[\text{Ru}(\text{bpy})_3]^{2+}$ photosensitizer in the photocatalytic system were carried out, resulting in negligible hydrogen production. Unfortunately, the high photocatalytic activities shown by the FeFeOH complex and the NCOFeFe precursor were not achieved for the heterogeneous catalyst using analogous concentrations of diiron centers. Probably, the blocking of some diiron active sites could be the cause of the low photocatalytic performance, possibly as a consequence of the hydrophobic chain folding inside the channel walls of EthanePMO. Anyway, the activity of this heterogeneous catalyst, with a TON of 5.2, was comparable to other biomimetic models of the [FeFe]-hydrogenase active site anchored on heterogeneous supports reported in the literature for light-induced hydrogen generation [35]. Moreover, the immobilization of NCOFeFe on EthanePMO support promoted the stabilization of the diiron center, extending the photocatalytic activity for hydrogen evolution beyond 4 h (**Figure S9**).

5.2.2.4. Results and Discussion

A biomimetic [FeFe]-hydrogenase active site model complex (FeFeOH) with an ethylene bridge and a pendant hydroxyl group has been successfully synthesized, characterized and investigated for the first time as a potential catalyst for light-driven hydrogen evolution.

In addition, a novel precursor based on a carbamate triethoxysilane bearing a diiron dithiolate (NCOFeFe) was designed and prepared to be incorporated on a solid support. Thus, it was efficiently anchored onto EthanePMO via a grafting procedure, obtaining the EthanePMO@NCOFeFe material with an iron loading of 0.235 mmol Fe/g PMO.

The photocatalytic hydrogen production system was adequately optimized in the homogeneous phase using the FeFeOH complex as the catalyst, $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photosensitizer, and ascorbic acid as the electron donor in a water/acetonitrile mixture (11.8 vol%) under irradiation by an LED light with an intensity of 50 mW/cm². Different variables influencing the photocatalytic reaction were investigated: pH, photon flux, catalyst concentration, and photosensitizer concentration. Under these conditions, the NCOFeFe precursor showed similar hydrogen generation compared to the FeFeOH complex.

The replacement of the lighting system by a Xenon lamp with a higher light intensity, i.e., 90 mW/cm², and an increased range of wavelength promoted an excellent improvement of the light-driven hydrogen production, achieving TONs of 70 and 37 for the FeFeOH and NCOFeFe, respectively. Molecular aggregation phenomena due to the hydrophobic nature of the NCOFeFe precursor was suggested to explain the decrease of available active diiron centers and, as a consequence, the decrease in photocatalytic activity compared to that shown by FeFeOH.

The immobilization of NCOFeFe on ethylene-bridged PMO allowed working in a completely aqueous medium but led to lower hydrogen evolution yields, likely due to some blocking of the active sites. The EthanePMO@NCOFeFe heterogeneous catalyst reached a TON of 5, indicating a lower activity than the homogeneous complexes but comparable to other immobilized [FeFe]-hydrogenase biomimetic models, which were previously reported.

Supplementary Materials

The following are available online at <https://www.mdpi.com/article/10.3390/catal12030254/s1>, **Figure S1**: FTIR-ATR monitoring of the reaction between the FeFeOH catalyst and 3-isocyanopropyltriethoxysilane, **Figure S2**: ¹H-NMR spectra of the FeFeOH diiron complex, **Figure S3**: ¹³C-NMR and ¹³C DEPT-NMR spectra of the FeFeOH diiron complex, **Figure S4**: ¹H-NMR spectra of the NCOFeFe monosilane precursor, **Figure S5**: ¹³C-NMR and ¹³C DEPT-NMR spectra of the NCOFeFe diiron complex, **Figure S6**: Control photocatalytic experiments without the FeFeOH catalyst (a) and photosensitizer (b), **Figure S7**: UV–VIS spectra of FeFeOH (A) and NCOFeFe (B) under analogous standard conditions (0.84 mM of the homogeneous catalyst, 1 M of the acetate buffer at pH 5.0, and ACN/H₂O with a 11.8 vol% organic phase) at t = 0 h and t = 4 h, **Figure S8**: FTIR-ATR spectra of 0.71 mM FeFeOH (A) and 0.71 mM NCOFeFe (B) in ACN at t = 0 h and t = 4 h, **Figure S9**: Photocatalytic hydrogen production under standard conditions (2 mg of EthanePMO@NCOFeFe, 0.5 mM of Ru(bpy)₃²⁺, 100 mM of ascorbic acid, and 1 M of the acetate buffer at pH 5.0) in the heterogeneous phase (milli-Q water solution) after 26 h, **Table S1**: Photocatalytic performance of diiron molecular catalysts in light-driven hydrogen production. References [18,19,22,24,25,27] are cited in the supplementary materials.

Author Contributions

Conceptualization, D.E., C.J.-S., H.T., S.O., and F.J.R.-S.; investigation, J.A.-G. and M.V.P.; writing—original draft preparation, J.A.-G.; writing—review and editing, J.A.-G., D.E., M.V.P., S.O., and F.J.R.-S.; supervision, C.J.-S. and H.T. All authors have read and agreed to the published version of the manuscript.

Funding

This research was funded by Ramon Areces Foundation (RAMON ARECES 16), Spanish Ministry of Science, Innovation and Universities (MICIU, FPU teaching and research fellowship (FPU17/03981), Project RTI2018-101611-B-I00), Olle Engkvist Foundation (200-0523), and Swedish Research Council (2015-04640).

Acknowledgments

J. A.-G., D.E., C.J.-S., and F. J. R.-S. wish to acknowledge the financial support from Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981) and Project RTI2018-101611-B-I00, Andalusian Regional Government (FQM-346 group), and Feder Funds. M.V.P., H.T., and S.O. wish to acknowledge the financial support from Olle Engkvist Foundation (200-0523), and Swedish Research Council (2015-04640).

Conflicts of Interest

The authors declare no conflicts of interest.

5.2.2.5. References

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Appendix III: Supplementary Information

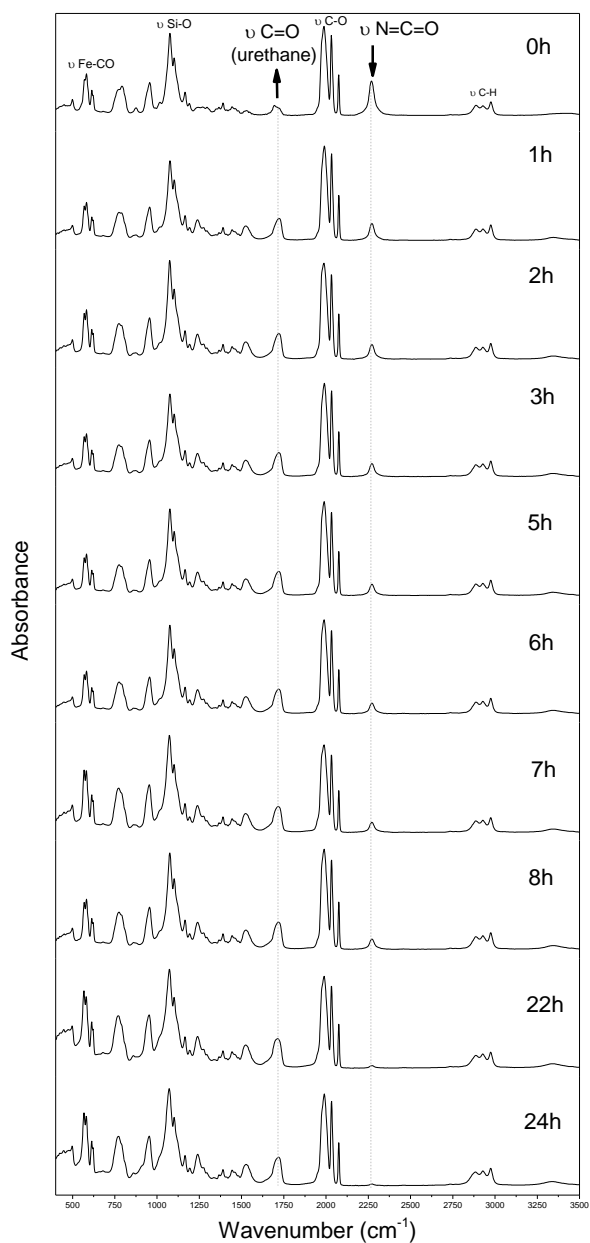


Figure S1. ATR-FTIR monitoring of the reaction between FeFeOH catalyst and 3-isocyanopropyltriethoxysilane.

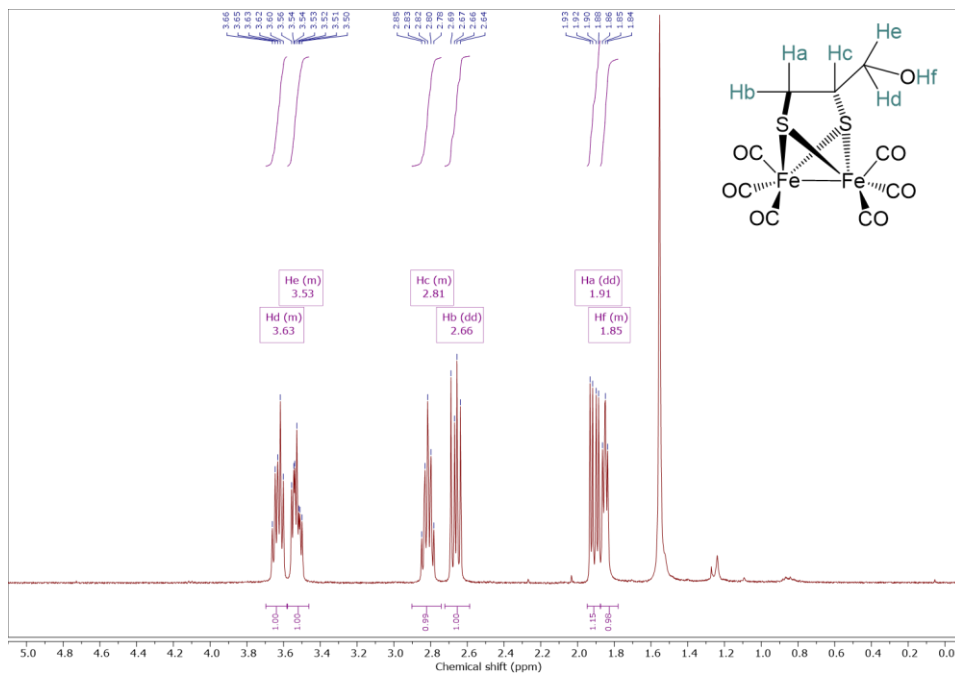


Figure S2. $^1\text{H-NMR}$ spectra of FeFeOH diiron complex

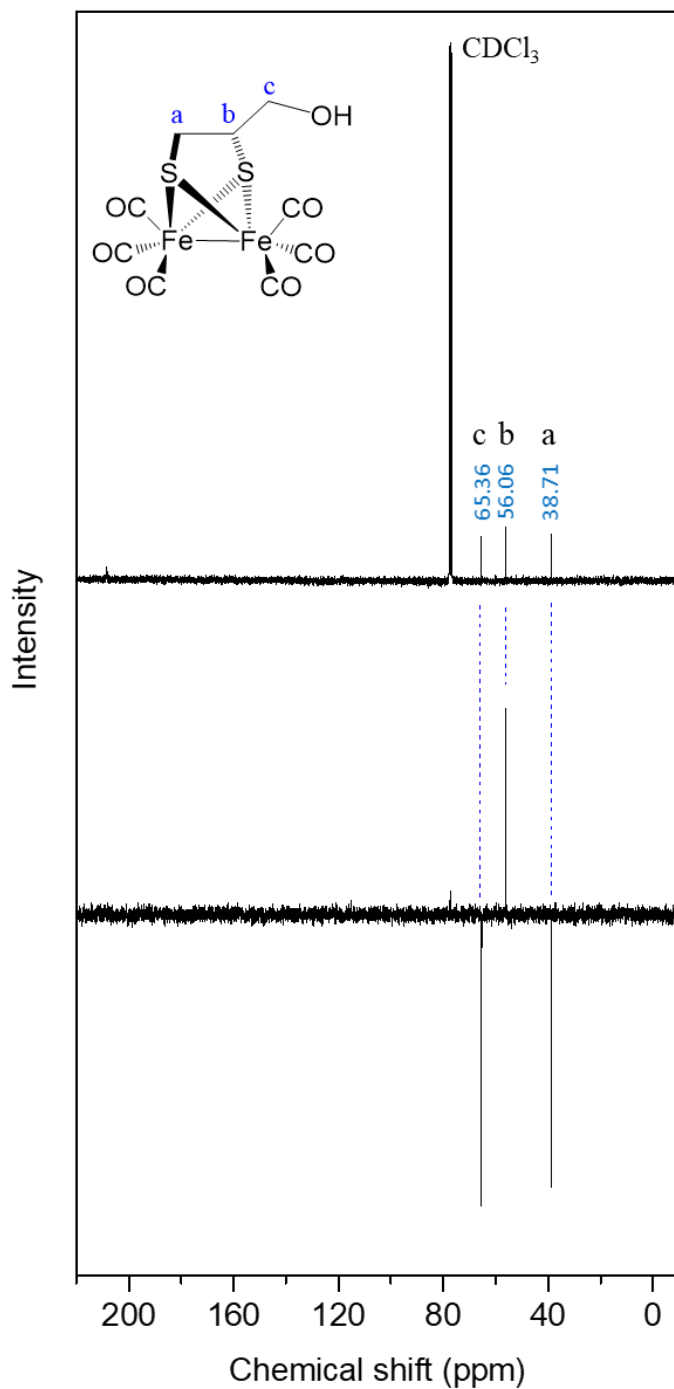


Figure S3. ^{13}C -NMR and ^{13}C DEPT-NMR spectra of FeFeOH diiron complex

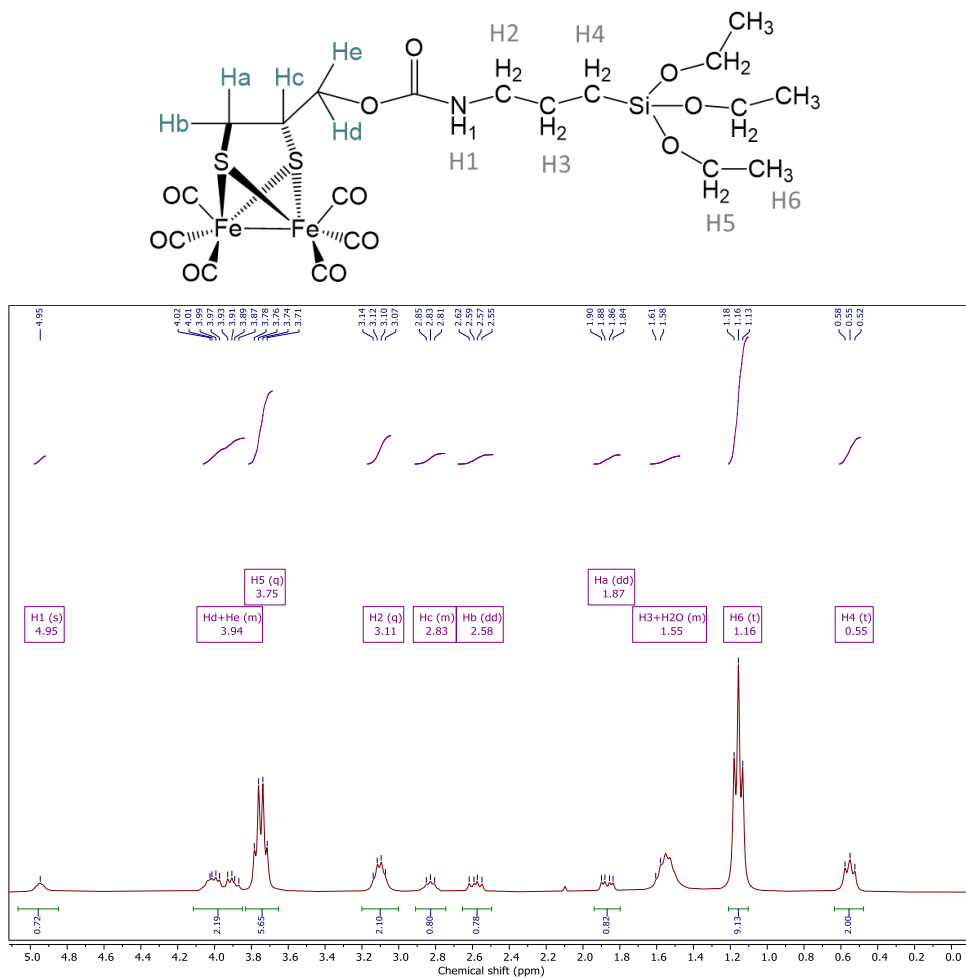


Figure S4. $^1\text{H-NMR}$ spectra of NCOFeFe monosilane precursor

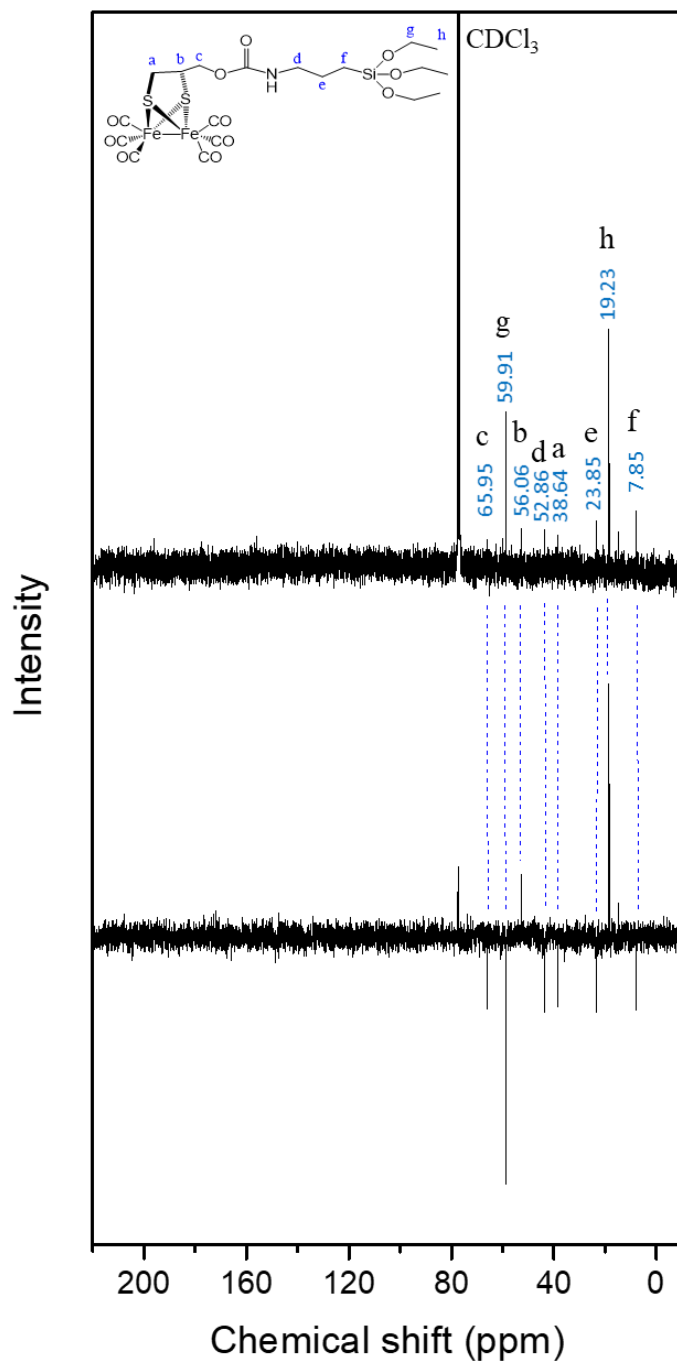


Figure S5. ^{13}C -NMR and ^{13}C DEPT-NMR spectra of NCOFeFe diiron complex

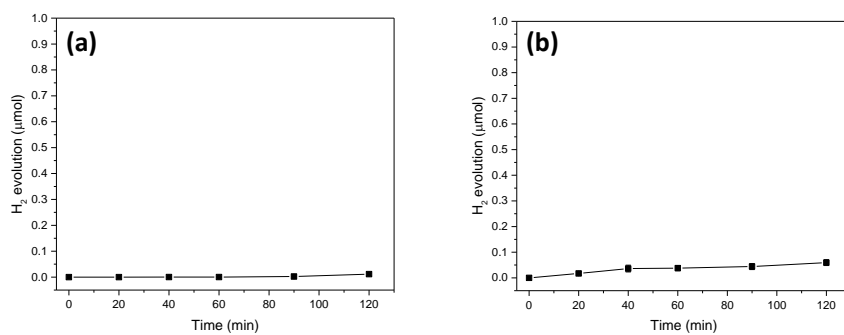


Figure S6. Control photocatalytic experiments without a) FeFeOH catalyst and b) photosensitizer

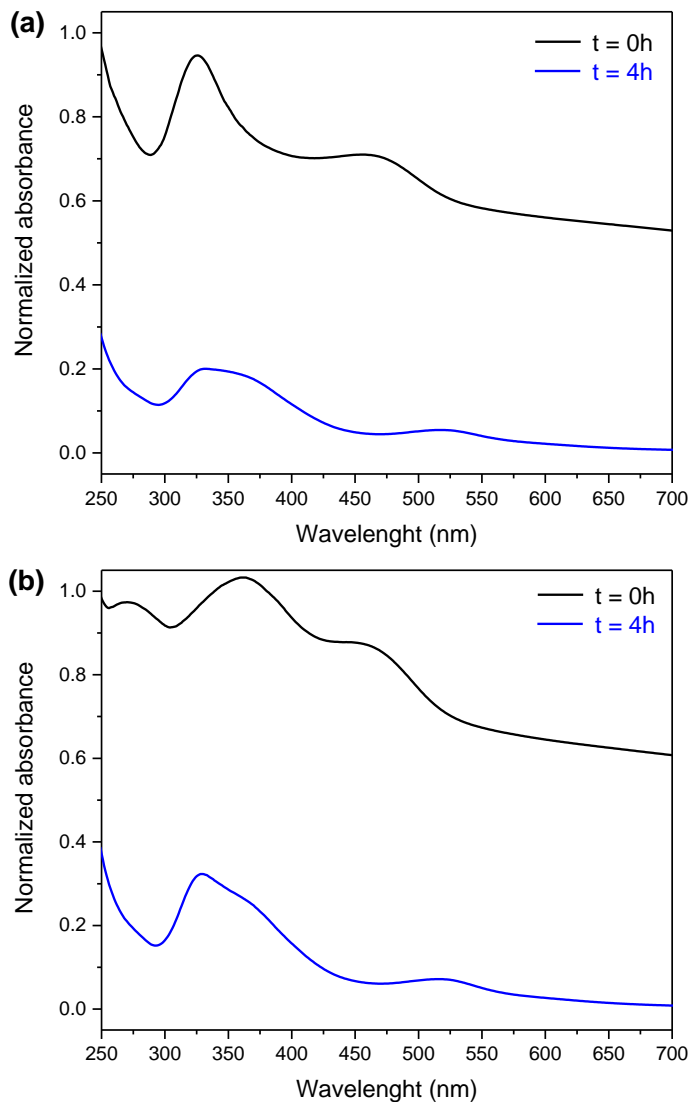


Figure S7. UV-Vis spectra of (a) FeFeOH and (b) NCOFeFe under analogous standard conditions (0.84 mM of homogeneous catalyst, 1 M of acetate buffer at pH 5.0 and ACN/H₂O with a 11.8 vol% organic phase) at t= 0 h and t= 4 h.

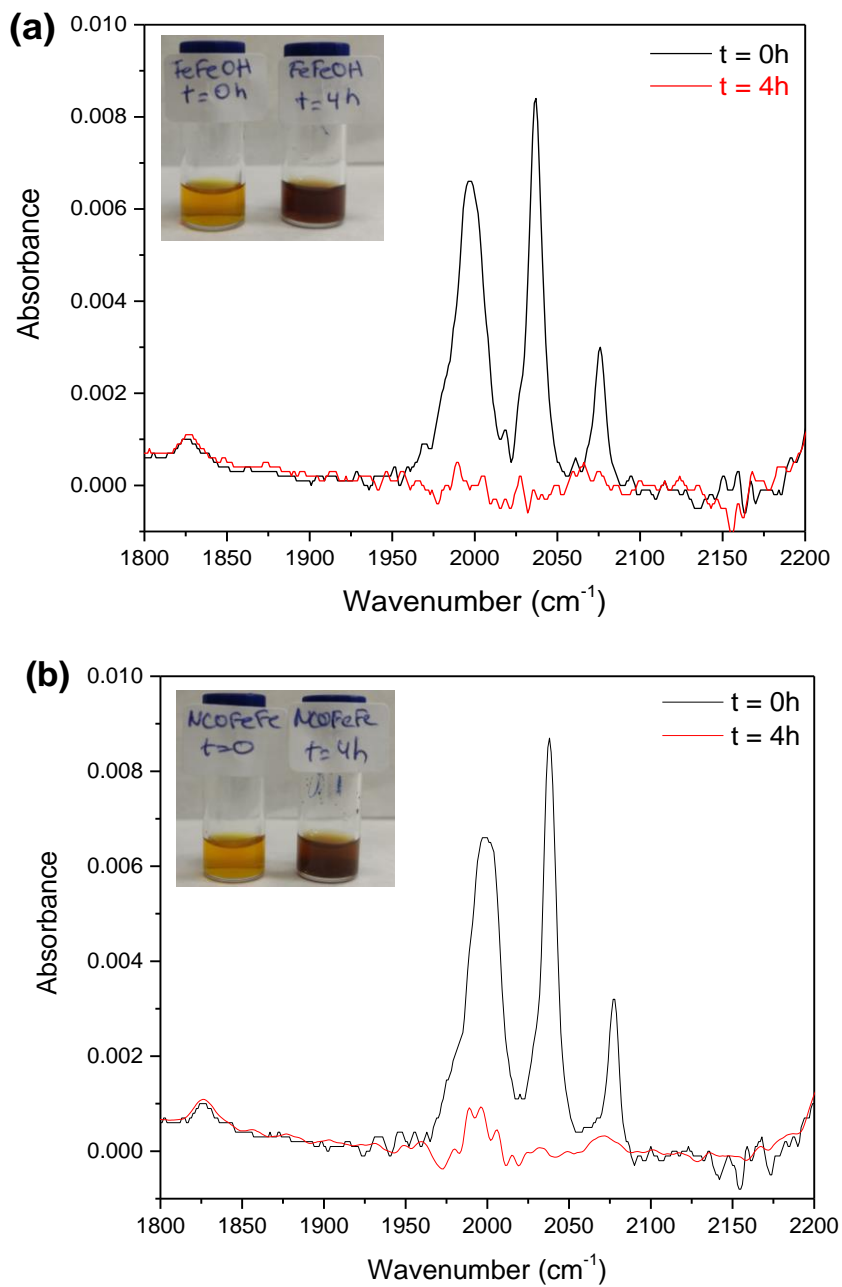


Figure S8. FTIR-ATR spectra of (a) 0.71 mM FeFeOH and (b) 0.71 mM NCOFeFe in ACN at $t = 0$ h and $t = 4$ h.

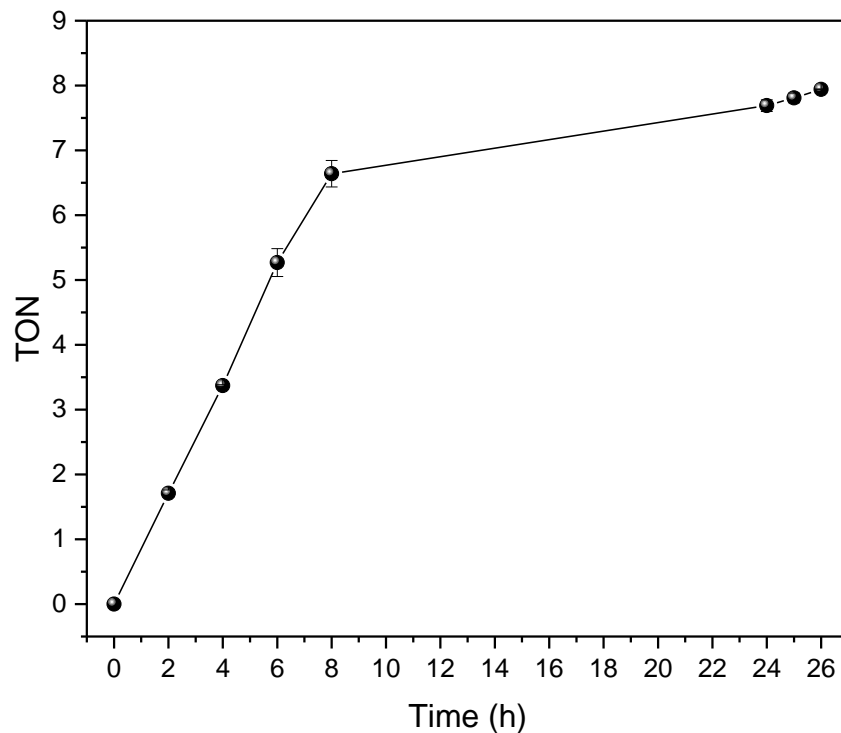
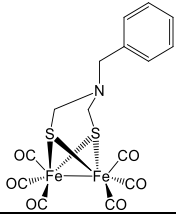
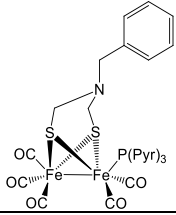
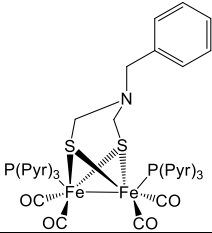
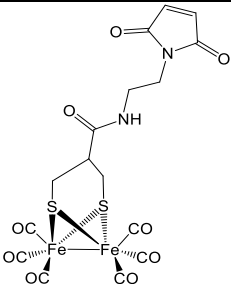
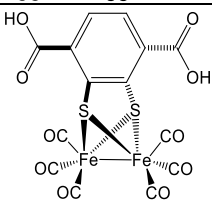
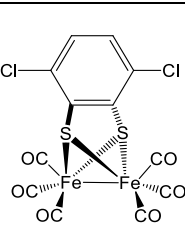
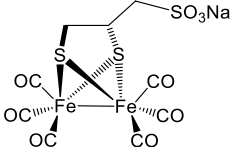
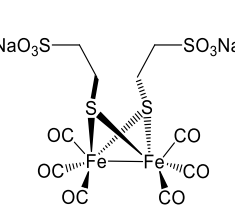
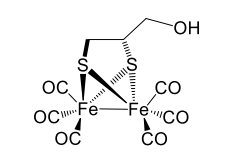


Figure S9. Photocatalytic hydrogen production under standard conditions (2 mg of EthanePMO@NCOFeFe, 0.5 mM of $\text{Ru}(\text{bpy})_3^{2+}$, 100 mM of ascorbic acid and 1 M of acetate buffer at pH 5.0) in heterogeneous phase (milli-Q water solution) after 26 h.

Table S1. Photocatalytic performance of diiron molecular catalysts in light-driven hydrogen production.

CATALYST	PS	EXPERIMENTAL CONDITIONS	LIGHT SOURCE	TIME (h)	TON	REFERENCE
	Ru(bpy) ₃ ²⁺	H ₂ O/MeCN (1:1), 1 mM catalyst, 0.1 mM PS, 100 mM H ₂ A, pH= 3.7	Xe lamp (500 W), λ>400 nm	3	0.78	1
	Ru(bpy) ₃ ²⁺	H ₂ O/MeCN (1:1), 1 mM catalyst, 0.1 mM PS, 100 mM H ₂ A, pH= 3.7	Xe lamp (500 W), λ>400 nm	3	4.3	1
	Ru(bpy) ₃ ²⁺	H ₂ O/MeCN (1:1), 1 mM catalyst, 0.1 mM PS, 100 mM ascorbic acid, pH= 3.7	Xe lamp (500 W), λ>400 nm	3	1.7	1
	Ru(bpy) ₃ ²⁺	H ₂ O/THF (1:0.04), 2.1 μM catalyst, 140 μM PS, 200 mM ascorbate, pH=4.5	Hg lamp, λ>400 nm	2	180	2
	Ru(bpy) ₃ ²⁺	DMF/H ₂ O (1:1), 14 μM catalyst, 140 μM PS, 100 mM H ₂ A, pH=5.5	Lamp not specified, λ=455-850 nm	2.5	200	3
	Ru(bpy) ₃ ²⁺	Water, 59 μM catalyst, 0.5 mM PS, 100 mM H ₂ A, 1 M acetate buffer, pH=5.0	LED (power not specified), λ>470 nm	2.5	1.7	4

 <p>The structure shows a ferrocene core with two iron atoms bridged by two sulfur atoms. Each iron atom is coordinated to two carbonyl (CO) groups. The sulfur atoms are part of a chain that ends in two sodium sulfonate (SO₃Na) groups.</p>	$\text{Ru}(\text{bpy})_3^{2+}$	Water, 0.1 mM catalyst, 0.4 mM PS, 100 mM H ₂ A, pH=4.0	Hg lamp, (500W), $\lambda > 400$ nm	4	88	5
 <p>The structure is similar to the first one, but the chain between the sulfur atoms is longer, and it features one sodium sulfonate (NaO₃S) group and one sodium sulfonate (SO₃Na) group.</p>	$\text{Ru}(\text{bpy})_3^{2+}$	Water, 1 μM catalyst, 0.1 mM PS, 200 mM H ₂ A, pH=4.0	LED (power not specified), $\lambda > 450$ nm	6	178	6
 <p>The structure is similar to the first one, but the chain between the sulfur atoms ends in a hydroxyl (OH) group.</p>	$\text{Ru}(\text{bpy})_3^{2+}$	Water (11.8 vol% ACN), 0.084 mM catalyst, 0.5 mM PS, 100 mM ascorbic acid, pH=5.0	Xe lamp (300 W), $\lambda > 420$ nm	4	69.5	This work

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5.3. Section 3: Graphene-based hybrid materials

5.3.1. A comparative study of particle size distribution of graphene nanosheets synthesized by an ultrasound-assisted method

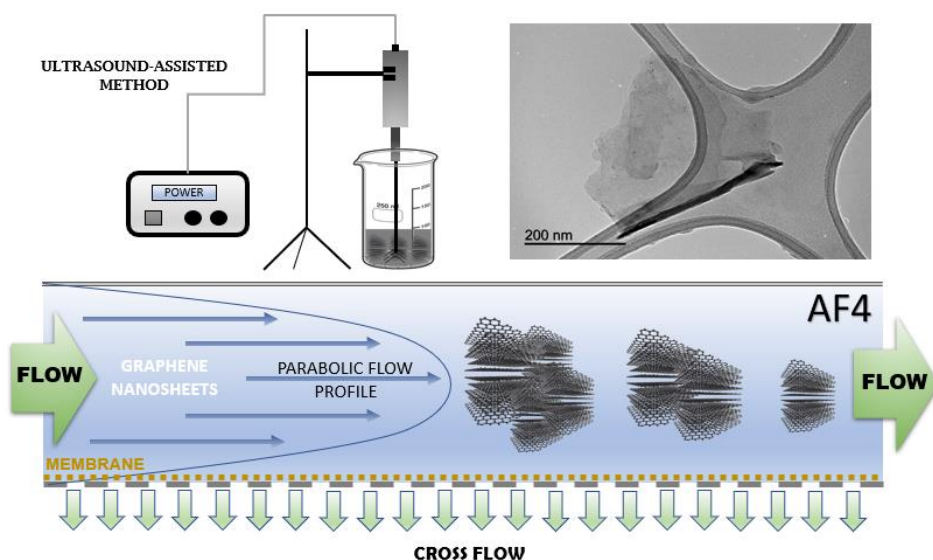
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Published in *Nanomaterials*

Nanomaterials, 2019, vol. 9, no 2, p. 152

DOI: <https://doi.org/10.3390/nano9020152>

Abstract

Graphene-based materials are highly interesting in virtue of their excellent chemical, physical and mechanical properties that make them extremely useful as privileged materials in different industrial applications. Sonochemical methods allow the production of low-defect graphene materials, which are preferred for certain uses. Graphene nanosheets (GNS) have been prepared by exfoliation of a commercial micrographite (MG) using an ultrasound probe. Both materials were characterized by common techniques such as X-ray diffraction (XRD), Transmission Electronic Microscopy (TEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). All of them revealed the formation of exfoliated graphene nanosheets with similar surface characteristics to the pristine graphite but with a decreased crystallite size and number of layers. An exhaustive study of the particle size distribution was carried out by different analytical techniques such as dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and asymmetric flow field flow fractionation (AF4). The results provided by these techniques have been compared. NTA and AF4 gave higher resolution than DLS. AF4 has shown to be a precise analytical technique for the separation of GNS of different sizes.

Keywords: Graphene Nanosheets; Exfoliation; Particle Size Distribution; Nanoparticle Tracking Analysis; Asymmetric Flow Field Flow Fractionation

5.3.1.1. Introduction

Particle size analysis is a key element because many properties of nanomaterials are size dependent [1]. This parameter is essential since the synthesis at a small scale must be monitored for subsequent bulk production and for the control of nanotechnological products in the market. The control of size during the synthesis of nanomaterials is decisive in various industrial sectors such as nanomedicine, nanofood, nanoenergy or nanocosmetics [2–6].

It is well known that graphene has excellent properties that provide a multitude of technological applications in different fields. It is formed by a pattern of hexagonal rings of carbon atoms constituting a huge flat molecule [7]. Some of its most important properties are its high thermal and electrical conductivity, its high elasticity, its hardness and strength and its flexibility, being more flexible than carbon fiber and equally lightweight [8].

Many methods for obtaining graphene have been reported. Graphene layers can be obtained by liquid-phase exfoliation of commercial graphite in different organic solvents using the ultrasonic technique. This method requires special experimental conditions at which very high pressures and temperatures are reached in very short periods of time [9]. The colloidal graphene generated has the same surface energy as the solvent used. In this way, the free energy is negative, and the structure is broken, giving rise to fragments of graphite interspersed with solvent molecules [10]. For the successful exfoliation of graphite, different organic solvents have been used, such as N-methyl pyrrolidone (NMP), dimethylformamide (DMF), pyridine and o-dichlorobenzene (ODBC) [11,12]. By means of the ultrasound method, a maximum of 15% of individual graphene sheets is obtained. The rest is a mixture of multilayer graphene or few-layer graphene. A very important parameter for obtaining few-layer graphene is to carry out a selective centrifugation [13]. By carrying out this operation it is possible to separate the non-exfoliated graphitic particles from the exfoliated graphene sheets. This method of synthesis has different advantages with respect to conventional graphene production methods: strong oxidizing agents are not required, the synthesis time is reduced and unfunctionalized and non-oxidized graphenes are obtained in one-step [14]. On the contrary, this process can have negative effects, since prolonged sonication times can facilitate the existence of defects in the surface of the graphene sheets and the reduction of the layer

size [15]. For instance, these problems have been observed when DMF is used as an exfoliating liquid phase [16]. For this reason, it is very important to control the sonication times during the exfoliation process of the graphite and, above all, to choose the solvent that generates the least problems [17].

o-Dichlorobenzene is an organic solvent that has excellent properties to be used as liquid phase for the process of graphite exfoliation. It is commonly applied as a reaction medium in fullerene chemistry and it is well known that it forms very stable dispersions due to its very efficient interactions with graphene via π - π stacking [18]. On the other hand, it has a high boiling point and a surface tension suitable for the correct exfoliation [12].

Graphene-based materials have been characterized by a variety of different techniques, such as X-ray diffraction, transmission electron microscopy and Raman spectroscopy, among others [19,20]. Although these techniques can provide some information about the size of these materials, dynamic light scattering (DLS) is particularly useful to determine particle size. Thus, the use of DLS to measure the size of graphene nanosheets and exfoliated graphene oxide has been reported as a simple and fast method of characterization [21]. This technique is based on the Brownian motion of the particles in suspension causing the scattering of light at different time-dependent fluctuations intensities. These fluctuations are directly related to the diffusion coefficient of the particles in the solvent, which provides in turn the particle size using the Stokes-Einstein relationship. However, it is well known that this technique is more reliable for spherical particles than for non-spherical particles [22]. Moreover, if a sample is polydisperse, as usually happens for graphene nanomaterials prepared by most methods, DLS will exhibit some limitations to measure particle size (vide infra) [23]. Furthermore, two techniques have emerged in the last years for the characterization of nanoparticles, i.e. nanoparticle tracking analysis (NTA) and asymmetric flow field-flow fractionation (AF4). To the best of our knowledge, none of them has been used for the characterization of graphene-based materials.

NTA is a relatively novel technique for the study of particle size distribution. Like DLS, NTA uses light scattering and the Brownian motion of liquid suspensions of particles to obtain the size distribution in a sample. This technique allows real-time visualization and recording of nanoparticles during the measurement by combining a charge-coupled device with laser light scattering microscopy [24]. In this way, the NTA

software tracks individual particles and, using a formula derived from the Stokes-Einstein equation, provides particle size values by calculating the particle hydrodynamic diameter. In addition, it gives other parameters such as particle concentration, whose range must be between 10^6 to 10^9 particles/mL, aggregation and fluorescence [25]. The concentration of particles present in the sample does not depend on the scattered light, so this technique allows an accurate and reproducible determination of the concentration of non-spherical particles as in the case of carbon nanotubes or colloids [26]. Based on these characteristics, NTA is frequently used to accurately obtain the size of protein aggregates and drug delivery nanoparticles [27].

AF4 is one of the most promising techniques for the characterization of nanoparticles due to the high precision and wide separation range it provides, as well as the great variety of nanomaterials that can be analyzed. Currently, this technique is in continuous progress and shows high versatility, because it has been used to characterize many types of nanomaterials such as nanodrugs, silica nanoparticles, nanocellulose, and nanoplastics, among others [28–31]. AF4 is a chromatographic technique consisting of a laminar flow of a carrier liquid combined with a transverse flow. The induced cross-flow field interacts with any molecule or particle in the channel and, in this way, size separation occurs [32]. This phenomenon gives rise to different elution times, which are inversely proportional to the diffusion coefficients of the particles in the sample, that is, to the radius of gyration. This technique is able to separate particles with sizes ranging from 2 nm to 1 μm [33]. Furthermore, it can be coupled with different types of detectors such as UV-Vis, multiangle light scattering (MALS) and / or dynamic light scattering (DLS) that would allow the complete characterization of different nanomaterials [34,35], and the determination of the molar mass distribution of macromolecules [36]. In addition, AF4 has been coupled online with ICP-MS for the selective detection of TiO_2 nanoparticles [37] and in combination with UV-vis spectroscopy and off-line HR-ICP-MS for the determination of Ag nanoparticles [38], rendering this technique very useful and versatile for analyzing different types of materials.

Herein, we report the synthesis of unfunctionalized, non-oxidized and isolated graphene nanosheets (GNS) applying the ultrasound-assisted method by liquid-phase exfoliation of a micrographite. The nanosheets obtained have been characterized using different techniques, particularly

related to the study of particle size. Thus, besides XRD, TEM and Raman spectroscopy, three techniques, specifically oriented to the determination of particle size, i.e. DLS, NTA and AF4, were investigated. The proper choice of the parent micrographite has been essential because it has provided GNS particles measurable by all these techniques. A comparative study of the results obtained with the different characterization techniques is reported.

5.3.1.2. Materials and Methods

5.3.1.2.1. Materials

Microcrystalline graphite powder (98 %) was purchased from Nanostructured & Amorphous Materials Inc. 1,2-Dichlorobenzene (ODCB, anhydrous, 99%), dichloromethane (anhydrous, $\geq 99.8\%$, contains 40-150 ppm amylene as stabilizer) and lanthanum hexaboride (powder, 10 μm , 99%) were obtained from Sigma Aldrich.

5.3.1.2.2. Methods

5.3.1.2.2.1. Synthesis of graphene nanosheets (GNS)

250 mg of microcrystalline graphite powder (MG) were stirred in 50 mL of o-dichlorobenzene (ODCB) for 30 min. Subsequently, the resulting dispersion was subjected to treatment with a pulsed ultrasound probe for 2 h using an Ultrasonic Homogenizer 4710 Series from Cole Parmer Instrument Co. (45 % amplitude, 60 % duty cycle). The power supplied by the equipment was 9.96 W, according to a calorimetric calibration method [39] (see SI and **Figure S1**). The suspension obtained was centrifuged at 1935 g (4000 rpm) for 30 min to remove the non-exfoliated micrographite. The remaining suspension was again centrifuged at 12096 g (10000 rpm) to isolate the graphene nanosheets. They were washed three times with dichloromethane by successive redispersions and centrifugations to remove the ODCB. A Sorvall Super T-21 Tabletop Superspeed Centrifuge was used to carry out all centrifugation processes. Dichloromethane was evaporated from the resulting graphene nanosheets dispersion at room temperature for 12 h and, finally, the powdered exfoliated GNS were dried under vacuum at 80 °C overnight.

5.3.1.2.2.2. X-ray diffraction analysis (XRD)

X-ray diffraction patterns of the micrographite and graphene nanosheets were performed using a Bruker D8 Discover with a monochromatic $\text{CuK}\alpha$ radiation source. The scanning conditions for structural analysis were an angular range of $15\text{--}80^\circ$ (2θ), a 0.040° step size and 1.05 s per step. Additional measurements of X-ray diffraction were carried out using a Bruker D8 Advance. The scanning condition for this analysis were an angular range of $5\text{--}40^\circ$ (2θ), a 0.002° step size and 9 s per step.

5.3.1.2.2.3. Transmission electron microscopy

Transmission electron microscopy (TEM) images were recorded on a Jeol JEM-1400 transmission electron microscope operated at an accelerating voltage of 120 kV. The instrument has a high-contrast objective-lens polepiece, enabling high-contrast TEM image observation at all magnifications and good image quality, as well as easy handling. In addition, it has an advanced vacuum system. The digital-camera configuration includes a CCD camera that enables focusing and image verification on the operation screen. The measurement CCD camera (MC), orthogonal to the alignment camera, has a resolution of 1344×1024 pixel (12 bits/pixel). The measurements have been made in a magnification range between $8,000 \times$ – $150,000 \times$ with an instrument resolution of 0.38 nm between points.

5.3.1.2.2.4. Raman spectroscopy

Raman spectra were acquired with a Renishaw Raman instrument (InVia Raman Microscope) equipped with a Leica microscope furnished with various lenses, monochromators and filters in addition to a CCD camera. A silicon standard sample was used as reference for calibration (520 cm^{-1}). Spectra were obtained by excitation with green laser light (532 nm) from 150 to 3500 cm^{-1} . A total of 32 scans per spectrum were acquired to improve the signal-to-noise ratio.

5.3.1.2.2.5. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed through a SPECS mod. PHOIBOS 150 MCD spectrometer using non-monochromatic $\text{Mg K}\alpha$ radiation and a multichannel detector. All spectra were fitted to Gauss–Lorentz curves to better identify the different

chemical environment of the elements in each material. The binding energy values were calibrated with the adventitious carbon C1s signal (284.8 eV).

5.3.1.2.2.6. *Dynamic light scattering (DLS)*

Particle sizes were measured in a Zetasizer ZSP (Malvern Instrument Ltd, Worcestershire, UK) at 25°C based on laser Doppler velocimetry and dynamic light scattering (DLS) techniques. Previously, the suspension was homogenized using an ultrasonication probe for a period of 5 min.

The refraction index values were set at 1.33 and 2.38 for the dispersant (deionized water) and the material (carbon), respectively. The analysis was carried out by triplicate and medium and standard deviation were calculated. To obtain the hydrodynamic radius (R_h) of the GNS particles, the hydrodynamic diameter (D_h) was calculated by using the Stokes-Einstein equation (1).

$$D_h = \frac{K_B T}{3\pi\eta_0 D_t} \quad (1)$$

where K_B is the Boltzmann constant, T the temperature in K degrees, η_0 the solvent viscosity, and D_t the translational diffusion coefficient.

The intensity size distribution or the Z-average diameter was obtained from the autocorrelation function using the “general purpose mode” for the materials.

5.3.1.2.2.7. *Nanoparticle tracking analysis (NTA)*

NTA measurements were performed in a NanoSight NS300 (NanoSight, Malvern), equipped with a sample chamber and a 488 nm laser.

For the NTA measurements, 1 mg of GNS was suspended in 1 mL of water. Before the analysis, the solution was homogenized for 3 min in an ultrasonic bath. The samples were injected into the chamber with sterile syringes. Many individual particles are tracked during their Brownian motion by the software, which uses the Stokes-Einstein equation (2) to provide sample information:

$$\overline{(x, y)^2} = \frac{2k_B T}{3R_h \pi \eta} \quad (2)$$

where k_B is the Boltzmann constant and $\overline{(x, y)^2}$ is the mean-squared speed of a particle with a hydrodynamic radius of R_h in a medium of defined viscosity and temperature. All measurements were performed at room temperature.

5.3.1.2.2.8. Asymmetric flow field flow fractionation (AF4)

An AF4 system (AF2000, Postnova Analytics, Landsberg am Lech, Germany) coupled online to a 21-angle MALS detector (PN3621, Postnova Analytics) and UV-vis diode array detector (PN3241 Postnova Analytics) was used. The MALS detectors were calibrated using bovine serum albumin monomer and detectors at different angles were normalized with respect to a 90° detector measuring a sodium poly(styrenesulfonate) (PSS) standard. The AF4 channel was trapezoidal-shaped, 350 μm thick (defined by a spacer), 29.8 cm long (inlet to outlet) and had a maximum width of 2 cm. Particle recoveries over AF4 were tested with several commonly used membranes. The analytical parameters and characteristics of our AF4 system are presented in **Table 1**. All injections were carried out with an autosampler in triplicate (PN5300, Postnova Analytics).

Table 1: Analytical parameters and characteristics of AF4.

AF4 parameters	AF2000 system
Membranes	CR, PAN, PVDF
Channel geometry	Trapezoidal
Spacer thickness	350 μm
Focusing time	4 min
Elution time	40 min
Detector flow	0.5 ml/min
Injection flow	0.2 ml/min
Cross flow	1 ml/min
UV-vis	254 nm

5.3.1.3. Results

5.3.1.3.1. X-ray diffraction (XRD)

The structural properties of micrographite (MG) and graphene nanosheets (GNS) samples were examined by XRD. **Figure 1** shows the XRD patterns, which revealed the characteristic peaks for these materials. Both samples exhibited a strong peak at ca. 26.5° (2θ), which corresponded to the (002) graphite reflection [40]. Also, a weak peak at 54.5° (2θ),

attributed to the (004) reflection, was present in the samples, especially in the micrographite. The absence of the graphite peak for graphene oxide (GO) at 11° (2θ) [41] confirmed that the graphene nanosheets preparation method did not cause partial oxidation of the starting graphite, as shown in the inserted image in **Figure 1**.

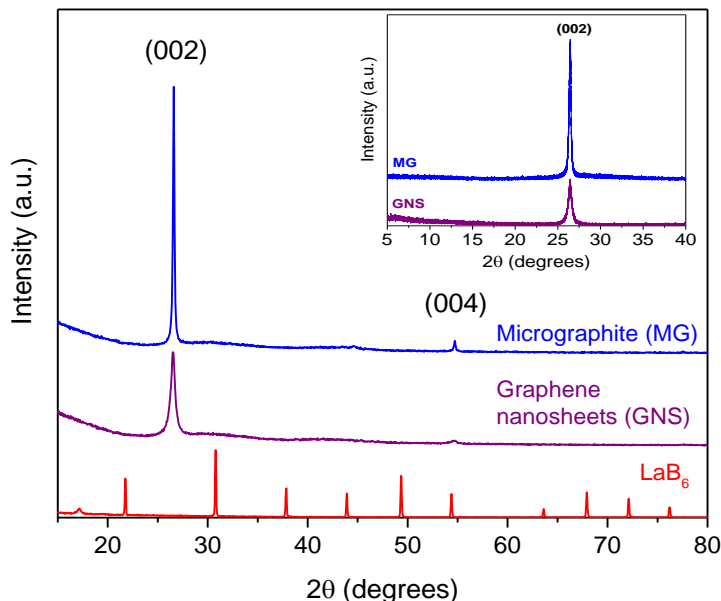


Figure 1. XRD patterns of micrographite (MG), graphene nanosheets (GNS) and LaB₆ samples. Inset: XRD patterns of MG and GNS recorded from 5 to 40° (2θ).

The higher relative intensity of the graphite signals indicated a higher crystallinity compared to the GNS. The full widths at half maximum of the (002) peak (FWHM) were studied to determine the crystallite size (LaB₆ was used as a pattern to determine the instrumental broadening). FWHM for GNS was higher than for MG (see **Table 2**). The crystallite size, L , was calculated through the Scherrer's equation (3):

$$L = \frac{k \lambda}{\beta \cos \theta} \quad (3)$$

where λ is the X-ray wavelength in nanometer (nm), β is the peak width of the diffraction peak profile at half maximum height in radians, θ is the scattering angle in radians, and k is a constant related to crystallite shape, taken as 0.9 for the (002) Bragg reflection.

The instrumental broadening effect on FWHM was subtracted out using Warren's method on the assumption of a Gaussian peak [42]:

$$\beta^2 = \beta_{\text{sample}}^2 - \beta_{\text{instrumental}}^2 \quad (4)$$

where β instrumental is referred to LaB₆ and equal to 0.130.

Table 2. Structural parameters of the studied materials derived from their XRD patterns.

Samples	Peak ° (2 θ)	d ₀₀₂ (Å)	FWHM	Crystallite size* (nm)
Micrographite	26.6	3.346	0.171	73.3
Graphene nanosheets	26.5	3.356	0.509	16.6

*Parameter calculated considering the instrumental broadening

Liquid-phase exfoliation by ultrasound-assisted synthesis for obtaining graphene nanosheets (GNS) produced smaller crystallite sizes. Also, the thickness of the crystallites along c axis decreased because the full width at half-maximum (FWHM) of the peak (002) was higher than that of the starting micrographite (MG) [42,43]. Thus, the action of ultrasonic waves generates a cavitation energy that caused an increase in the interlayer spacing (d₍₀₀₂₎) due to the exfoliation of the MG [44]. In this way, the GNS sample had a smaller crystallite size and a lower average stacking height of the layered structure, confirming an effective exfoliation of the graphite by the ultrasound probe treatment.

5.3.1.3.2. Transmission electronic microscopy (TEM)

The surface morphology of the original graphite and the synthesized graphene was examined by TEM images. Nanometric particles of graphite flakes are shown in **Figure 2 A-C**. Graphene nanosheets (GNS) were observed as transparent layers (see **Figure 2 D-F**). When graphene sheets were fold over themselves, cross-sectional and a few layers with nanometric size between 200-500 nm could be viewed. The folded graphene sheets that were placed parallel to the electron beam were observed as several dark lines. However, TEM images for graphite showed a dark spot due to the ordered stacking of a large number of layers. Also, it was verified that the size of the graphite particles were several times larger than GNS particles [40].

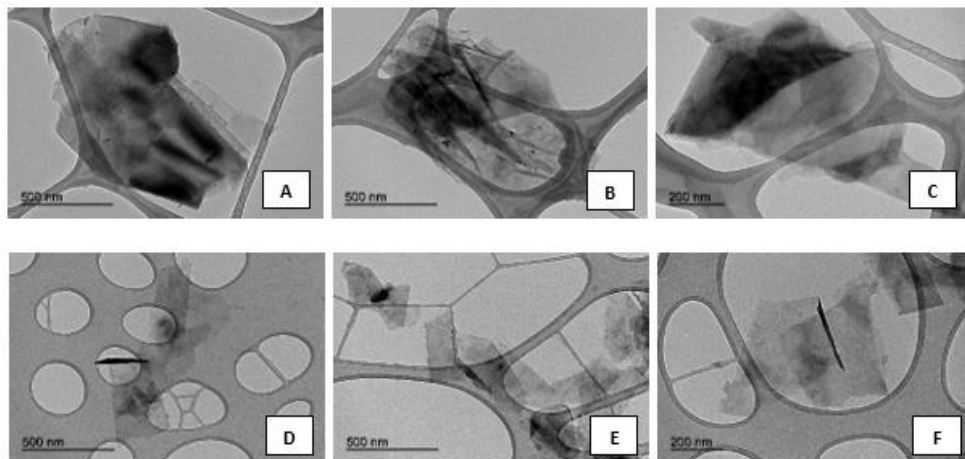


Figure 2. TEM images with different magnification for (A-C) micrographite and (D-F) graphene nanosheets samples.

5.3.1.3.3. Raman spectroscopy

Raman spectroscopy was performed to confirm the exfoliation of the micrographite by ultrasound irradiation. The typical bands of graphene materials were observed in the spectra (**Figure 3**). The G peak corresponds to the phonons of the energy level E_{2g} in the Brillouin zone. The intensity of the D band indicates the degree of disorder that the material possesses, which is related to several factors such as functionalization in the graphene macromolecular sp^2 ring or, in our case, the ultrasonic exfoliation in ODCB. In many studies, the ratio of I_D/I_G intensities is used to verify that the material has undergone a structural change during the synthesis process [45]. In addition, it has already been reported that this ratio is related to the flake size. Thus, an increase in the I_D/I_G ratio indicates a smaller sheet size because the ratio of edge defects is greater for smaller layers [46].

The reference micrographite (MG) had $I_D/I_G = 0.10$ while this ratio increased to 0.38 for the exfoliated graphene nanosheets (GNS). These values confirmed the exfoliation of the graphite in ODCB using the ultrasound probe, which caused a certain disorder in the material.

The calculation of the number of graphene layers is very relevant in this type of study. Many investigations relate the position of the G peak with the number of graphene layers. The G peak of the graphene nanosheets was at a Raman shift of 1582 cm^{-1} and so, applying the equation proposed by Wang et al [47], it can be deduced that this material consisted of

approximately 7 layers of graphene nanosheets. It was very remarkable the 2D peak, which is the overtone of the peak D. The position, the shape of the line and the intensity of the peak are related to the number of layers [48]. Normally, a single layer of graphene shows a band at 2679 cm^{-1} . It has been shown that in the case of multilayers graphene, the 2D peak would shift toward higher Raman shift and becomes broader [49].

In the case of GNS, the 2D band was centered at 2716 cm^{-1} , similarly to MG, although there was a clear difference in peak intensity between them. It is common to calculate the ratio of peak intensity I_{2D}/I_G . An approximate value of 2 identifies a single layer of graphene [50]. The original micrographite showed an intensity ratio of 0.38 while the graphene nanosheets obtained after the ultrasonication process had a higher ratio of 0.55, thus again confirming the exfoliation of graphite.

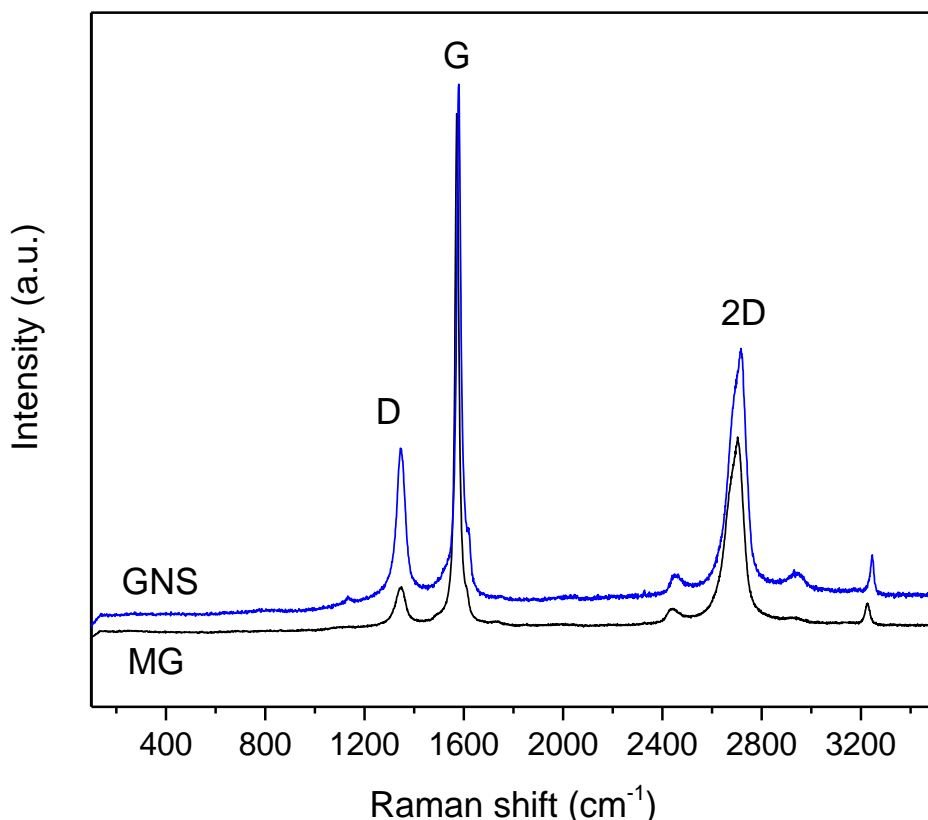


Figure 3. Raman spectra of micrographite (MG) and graphene nanosheets (GNS) samples.

5.3.1.3.4. X-ray photoelectron spectroscopy (XPS)

In order to study the composition of micrographite (MG) and graphene nanosheets (GNS), XPS spectra of these samples were measured. **Figure 4a** shows the XPS survey for the MG and GNS samples. Both materials were composed of C and O. The presence of Al is due to the holder where samples were placed. The oxygen content in the original graphite is in accordance with the purity of the sample and the presence of noncovalently bonded adsorbed oxygen [51]. The C/O ratio for GNS and MG samples, which is inserted in this figure, confirmed that the GNS material underwent a very slight oxidation upon exfoliation even though the difference between the MG and GNS ratios was almost negligible and insignificant compared to a common graphene oxide (GO) [52].

The X-ray photoelectron spectra in the C1s region of MG (**Figure 4b**) and GNS (**Figure 4c**) were fitted by overlapped peaks attributed to C-C bonds (284.8 eV), C-O bonds in hydroxy (286.1 eV), epoxy (287.7 eV), carbonyl (289.1 eV), and carboxyl (290.6 eV) groups, and the $\pi \rightarrow \pi^*$ transition (shake-up satellite peak at 292.3 eV) [53]. Therefore, no obvious changes were observed on the chemical structure of pristine MG and GNS obtained by the ultrasound-assisted method according to the C 1s spectra. Therefore, it is confirmed that this method of synthesis allows obtaining GNS directly from MG thus avoiding the synthesis of graphitic oxide (GO).

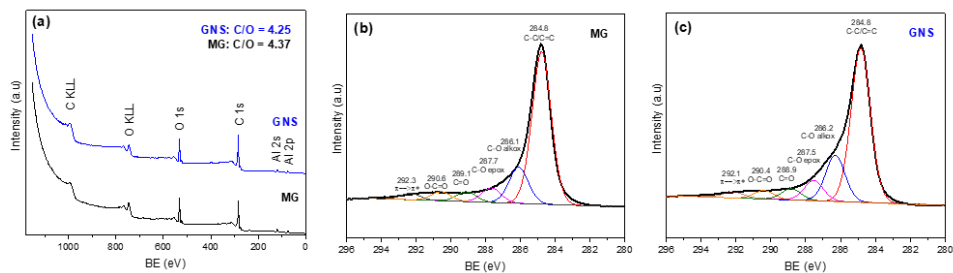


Figure 4. a) XPS survey for MG and GNS and XPS spectra for the C 1s photoemission peak of b) micrographite (MG) and c) graphene nanosheets (GNS).

The contribution of each component is summarized in **Table 3**. The values obtained for both samples are very similar, concluding that this method of exfoliation of the micrographite by the ultrasound treatment causes a delamination of the pristine graphite avoiding oxidation processes. These results are in agreement with those reported for graphene nanosheets

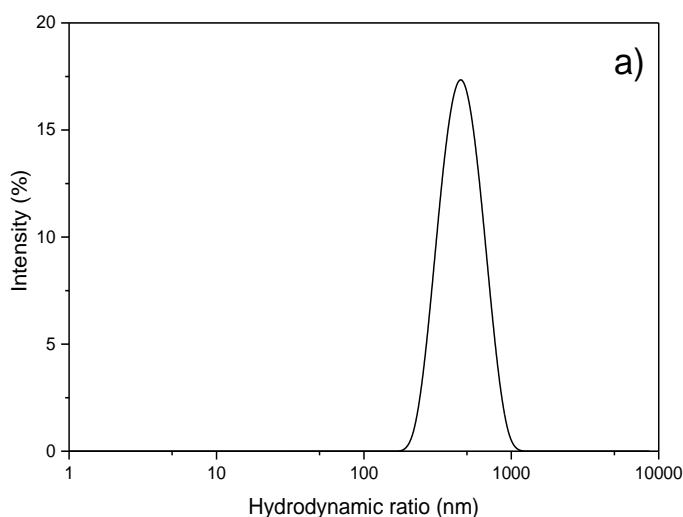
prepared via ultrasonic exfoliation of graphite powder in N-methyl-2-pyrrolidone [54].

Table 3. Contribution of the six components used in fitting of the C 1s photoemission peak (in %)

Samples	C-C/C=C	C-O alkox	C-O epox	C=O	O-C=O	$\pi \rightarrow \pi^*$
(a) MG	65.7	16.9	6.4	4.3	3.9	2.8
(b) GNS	64.2	18.2	8.1	4.1	3.5	1.9

5.3.1.3.5. Particle size distribution by DLS

The size distribution and intensity correlation function normalized between one and zero of the GNS using dynamic light scattering (DLS) are shown in **Figure 5**. The advantage of applying this technique is its versatility in terms of fast, easy, reproducible and non-destructive results. DLS provides the hydrodynamic radius (R_h), which is defined as the radius of an equivalent hard sphere diffusing at the same rate as the particle under observation, and so it is indicative of the apparent size adopted by the GNS in the aqueous dispersion. GNS exhibited a gaussian peak located at 450 ± 14 nm. The measurement carried out for the MG material revealed a particle size outside the quantification limits of this technique ($> 1 \mu\text{m}$).



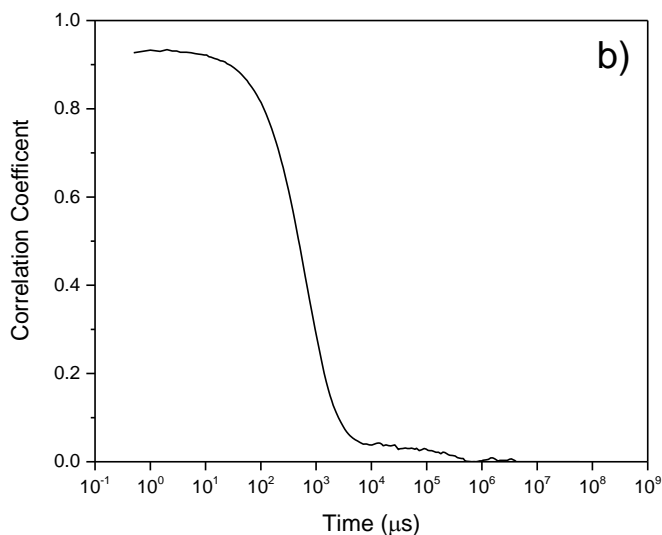


Figure 5. a) DLS size distribution curve of graphene nanosheets (GNS) and b) normalized intensity correlation function of the scattered light intensity of graphene nanosheets (GNS).

DLS also provides the polydispersity index (PDI), which indicates the width of the particle size distribution, being calculated as (peak width/peak height)². A value of PDI <0.1 indicates that the sample is monodisperse. Instead, if PDI is between 0.1 <PDI <0.2, the sample would have a narrow particle size distribution. In the case of GNS, PDI was 0.36, value between 0.2 <PDI <0.5, which indicates that the sample has a wide particle size distribution according to the results reported by J. Lohrke et al [55].

5.3.1.3.6. Particle size distribution by NTA

In order to further define the size of the graphene nanosheets, nanoparticle tracking analysis (NTA) was used (**Figure 6**). This technique provides individual particle sizing, intensity distribution and approximate concentrations (**Figure S2**). So, different particle sizes ranging from 40 to 400 nm were observed. The average size of three measurements gave a value of 151.8 ± 12.7 nm and mean concentration of $1.02 \cdot 10^9 \pm 6.48 \cdot 10^7$ particles/g. However, most particles had sizes between ca. 30-200 nm, although the concentration of particles around 300 nm was also significant. The number of larger particles (>350 nm) was much lower. A comparison

between DLS and NTA reveals that DLS could overestimate the particle sizes of the sample. Both techniques provide a hydrodynamic radius (R_h) value, but larger particles scatter stronger and are preferably detected by DLS than the smaller particles since the scattering intensity effect depends on size rather than on the number of particles with similar diameter. DLS is a fast, simple and non-destructive technique, but it presents this inherent feature when analyzing samples that present some polydispersity [56]. In these cases, it shows distributions shifted to the largest particle sizes. NTA, on the other hand, allows to distinguish with a greater precision the distribution of sizes (10-2000 nm) because it is based on the tracking of individual particles (**Figure S3**) [27].

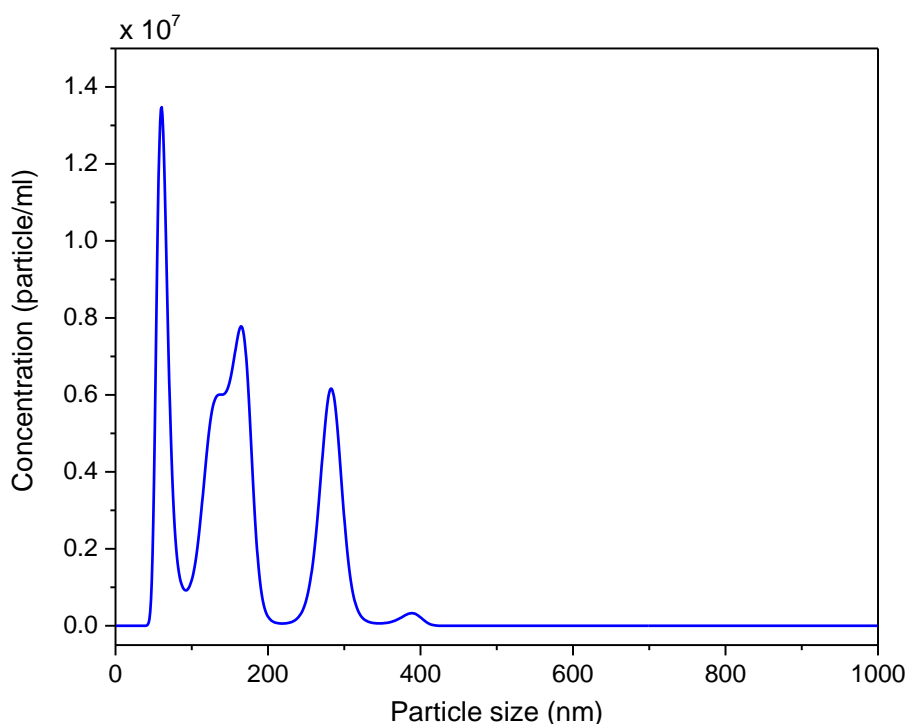


Figure 6. NTA size distribution curve of graphene nanosheets (GNS).

5.3.1.3.7. Particle size distribution by AF4

Firstly, the influence of the membrane composition on retention properties and recovery from the AF4 channel was studied. Polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN) and regenerated cellulose (RC) were used. **Figure 7** shows the AF4 fractograms using different membranes and the frequently used 0.2% Novachem (Postnova Analytics) as carrier.

Novachem is an aqueous surfactant mixture that stabilizes nanoparticles in solution.

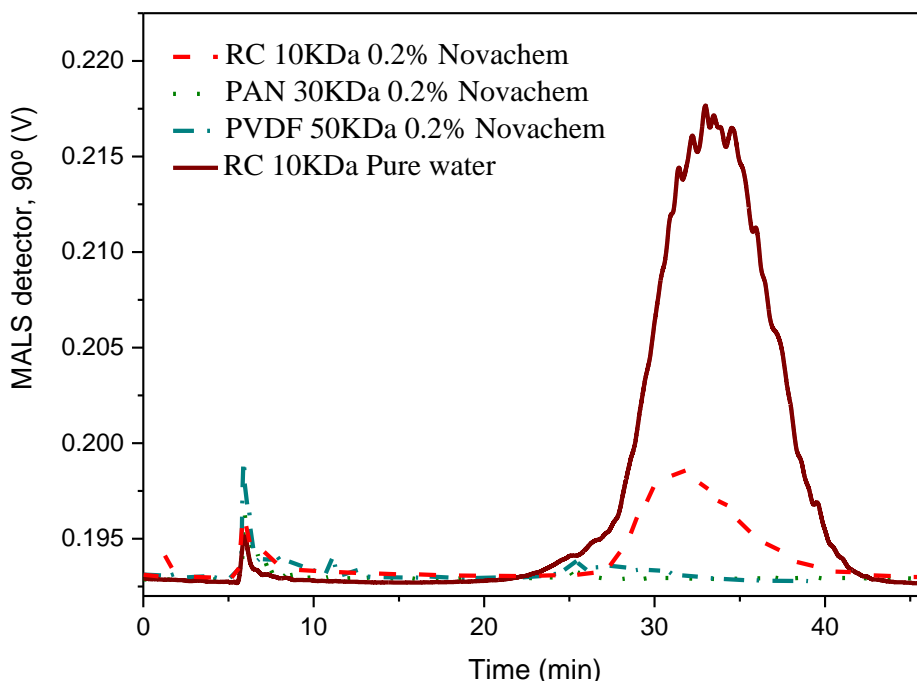


Figure 7. AF4 fractograms of GNS using RC, PAN and PVDF as membranes and Novachem and water as carriers.

The recovery from AF4 runs was determined as follows:

$$R (\%) = \frac{S}{S_0} \cdot 100 \quad (4)$$

where S and S_0 are the peak areas without void peak of the detector signal (UV, $\lambda = 254$ nm/MALS 90°), obtained with and without cross-flow, respectively. The MALS detector allows the direct measurement of the radius of gyration in the 1-1000 nm particle size range [57].

The fractograms (90° light scattering detector) showed a low recovery using PAN and PVDF (less than 30%) due to the retention of graphene nanosheets in these membranes. It was easily visualized because they became black. This fact had to be due to the interaction of the graphene sheets with these polymeric membranes. However, the fractogram exhibited a broad peak centered at around 33 min using a RC with a recovery of 30%, thus suggesting a weaker interaction with this membrane.

To increase the recovery, pure water was essayed as carrier. **Figure 7** shows an AF4 fractogram of GNS using a RC membrane, which resulted in a recovery of 95%. These results indicated that there was no interaction between the membrane and the sample, and that water was the appropriate carrier to separate GNS by AF4.

The size distribution derived from the MALS detector showed the presence of different populations of particles (**Figure 8**). The most satisfactory fitting was achieved with the random coil model. This model is usually chosen for this particle range with all the different angles of the MALS detector providing robustness to the method (**Figure S4**). This detector provides the radius of gyration (R_g), which is defined as the mass weighted average distance from the core of a particle to each mass element in the particle. R_g is more dependent on the structure of the particle than the value of R_h . R_g increases with increasing the elution volume.

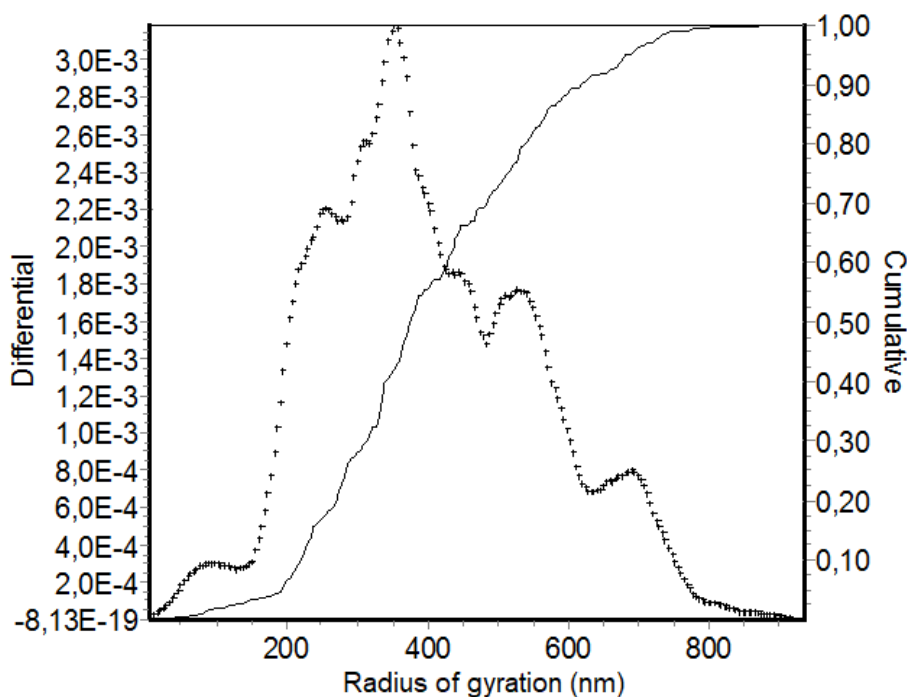


Figure 8. AF4 size distribution of GNS with a RC membrane using water as carrier.

Figure 8 shows the size distribution (radius of gyration in nm) as a function of the differential and cumulative distribution of the sample. The cumulative distribution indicates the fraction of a sample that has a mass in

a certain range. Based on this, it is possible to determine GNS sample fractions simply by observing the height of the step. This parameter is provided by the differential distribution, which is calculated taking the differential of the cumulative distribution. In this way, it visually provides the weight fraction of the sample within a certain mass range, thus giving information on the resolution of the fractionation system and the analysis. The main peak of the fractogram was centered at around 360 ± 11 nm. As can be observed, this technique is able to discriminate populations of particles with similar sizes, thus allowing a better characterization of the graphene nanosheets.

MALS detector coupled to AF4 can provide relevant information about the mechanism of aggregation and nanoparticle structure. This information is included in the fractal dimension structural parameter (D_f). D_f gives a detailed information of the shape of the materials, thus allowing to understand the distribution of particles in aqueous media. A sphere has a D_f of 3, whereas D_f is 2 for a planar structure and 1 for a rigid rod [58,59]. In the case of GNS, the calculated value was approximately 2 (1.85), which corresponded to 2-D objects with plain surface (**Figure S5**), thus confirming the regular layer structure observed by TEM.

Also, additional information on the particle shape can be obtained by calculating the shape factor, $p = R_g/R_h$, where R_g is the average radius of gyration facilitated by AF4 (360 nm) and R_h is the Z-average hydrodynamic radius provided by DLS (450 nm). The theoretical value of p for a hard sphere is 0.778 and for a stiff rod of approximately 2 [60]. The shape factor increases as the particle deviates from an ideal homogeneous spherical shape to a prolate ($p > 1$) or oblate ($0.775 < p < 1$) ellipsoid [61,62]. The shape factor for graphene nanosheets (GNS) obtained by exfoliation of micrographite (MG) was 0.80, thus indicating that the GNS particles have an oblate ellipsoid shape. The ability of AF4 to separate and fractionate GNS particles can be used to minimize the polydispersity of graphene preparations and so to obtain more accurate data on size and shape of these materials in future investigations.

In summary, AF4 and NTA give much richer information on particle size than DLS when dealing with a polydisperse material as graphene nanosheets. AF4 can be considered a promising technique for the separation and characterization of a variety of graphene structures, including not only graphene nanosheets, as described in this work, but also graphene oxide, graphene quantum dots and other carbon nanostructures.

Unlike DLS and NTA, AF4 is a separation technique and can be coupled to a great variety of detectors, thus gathering rich information from the sample. It separates particles in the range from 1 nm to 1-2 μm , although other field flow fractionation techniques could expand this range up to particle sizes higher than 100 μm . Interestingly, the existence of semipreparative channels would allow the separation and collection of milligram quantities of these graphene structures. In addition, NTA can provide the concentration of GNS nanoparticles. Nevertheless, stability concerns of aqueous dispersions of large graphene particles, a more limited range of particle size determination and the current limited availability in many laboratories are among the disadvantages of NTA and AF4 relative to DLS.

5.3.1.4. Conclusions

The ultrasound-assisted exfoliation of micrographite to graphene nanosheets (GNS) was confirmed by different techniques, such as XRD, TEM (sheets size between 200-500 nm) and Raman spectroscopy. The particle size distribution of GNS was firstly determined by DLS (ca. 450 nm), which provided the hydrodynamic radius and polydispersity of GNS. Subsequently, two different techniques, i.e., NTA and AF4, were applied here for the first time to graphene. NTA provided an average size of ca. 150 nm and higher resolution than DLS as well as approximate concentrations. In addition, it proved that DLS gave an average particle size whose intensity was biased towards the larger graphene particles. AF4 was able to separate various populations of GNS with different radius of gyration (centered at approx. 360 nm) and in addition it provided information concerning the structure and shape of the particles. Clearly, the application of NTA and AF4 besides DLS allows gathering much rich information on graphene particles.

The above-mentioned advantages for NTA and AF4 reveal their usefulness for the determination of the actual polydispersity in graphene preparations, evaluation of their synthetic procedures and size determination and fractionation in aqueous media for studies related to biological applications, sensing and toxicity.

Supplementary Materials

The following are available online at <http://www.mdpi.com/2079-4991/9/2/152/s1>, **Figure S1**. Calorimetric curve and linear fitting for the

operational calibration of the Ultrasonic equipment used for the GNS synthesis. **Figure S2**: NTA graph that represents GNS particle size and intensity, **Figure S3**: Nanoparticle tracking analysis images of GNS, **Figure S4**: Random Coil data fitting method, **Figure S5**: Analysis of the fractal factor dimension to identify the GNS particle shape where M is molecular weight and r is the radius of gyration.

Author Contributions

Conceptualization, A.C. and F.J.R.-S.; investigation, J.A.-G., A.B. and R.O.; writing—original draft preparation, J.A.-G. and A.B.; writing—review and editing, A.C., D.E. and F.J.R.-S.; supervision, C.J.-S. and J.M.

Acknowledgments

The authors wish to acknowledge the financial support from Ramon Areces Foundation, Spanish Ministry of Economy and Competitiveness (Project MAT2013-44463-R, MAT2017-87541-R), Spanish Ministry of Education, Culture and Sport for a FPU teaching and research fellowship (FPU17/03981), Andalusian Regional Government (FQM-346 and FQM-175 groups), Feder Funds, the support of Evelin Moldenhauer from Postnova Analytics GmbH and the technical staff from the Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUIQFN).

Conflicts of Interest

The authors declare no conflict of interest.

5.3.1.5. References

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Appendix IV: Supplementary Information

A calorimetric method was applied for the calibration of the Ultrasonic Homogenizer 4710 Series from the Cole Parmer Instrument Co., following the method described by Taurozzi et al. [1]. The experimental procedure to carry out the calibration was:

- Fill a 100 mL beaker with 50 mL of o-dichlorobenzene (ODCB), determining the mass of this solvent (65.11 g).
- The ultrasound probe (Ultrasonic Homogenizer 4710 Series from Cole Parmer Instrument Co.) is introduced under the surface of the solvent approximately 2.5 cm. Then, a thermometer is introduced approximately 1 cm below the tip of the ultrasonic probe.
- The conditions of the ultrasound equipment are selected by setting 40% amplitude, 60% duty cycle and pulsed mode of operation.
- Temperature and time data are recorded in order to carry out a linear fitting by least-squares regression.

Following the next equation: $P = \frac{dT}{dt} MC_p$

$C_{p, \text{ODCB}} = 170.68 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 1.219 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$; $dT/dt = 0.12545 \text{ K/s}$

The resulting power value was $P = 9.96 \text{ W}$.

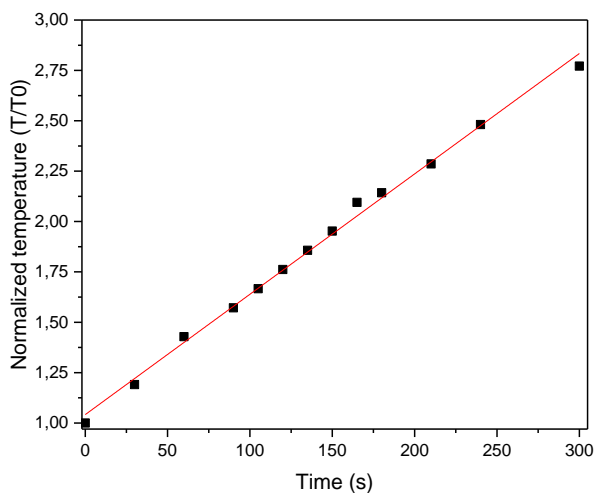


Figure S1. Calorimetric curve and linear fitting for the operational calibration of the Ultrasonic equipment used for the GNS synthesis.

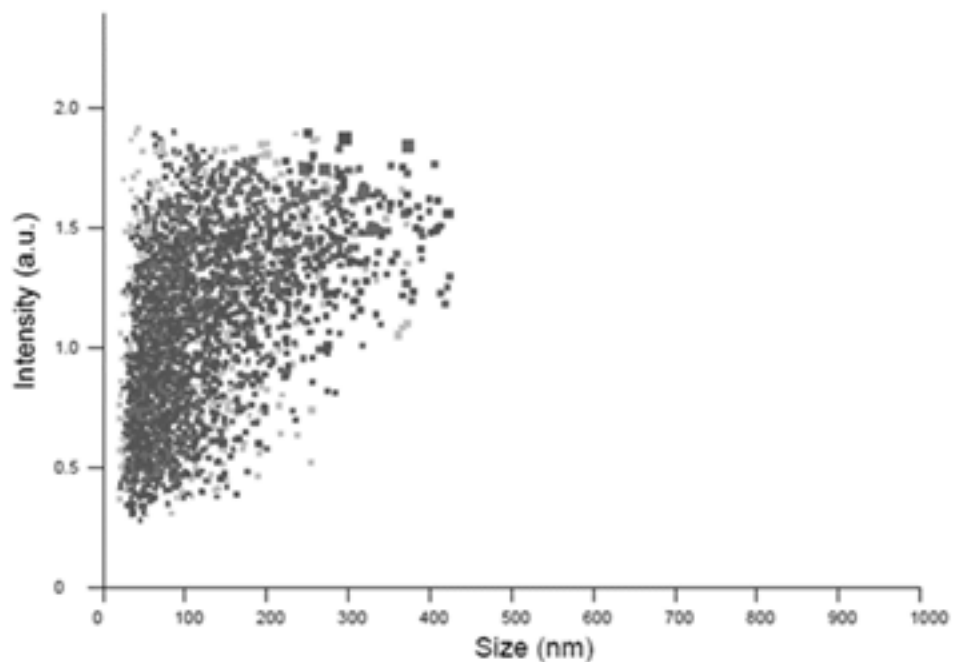


Figure S2. NTA graph that represents GNS particle size and intensity.

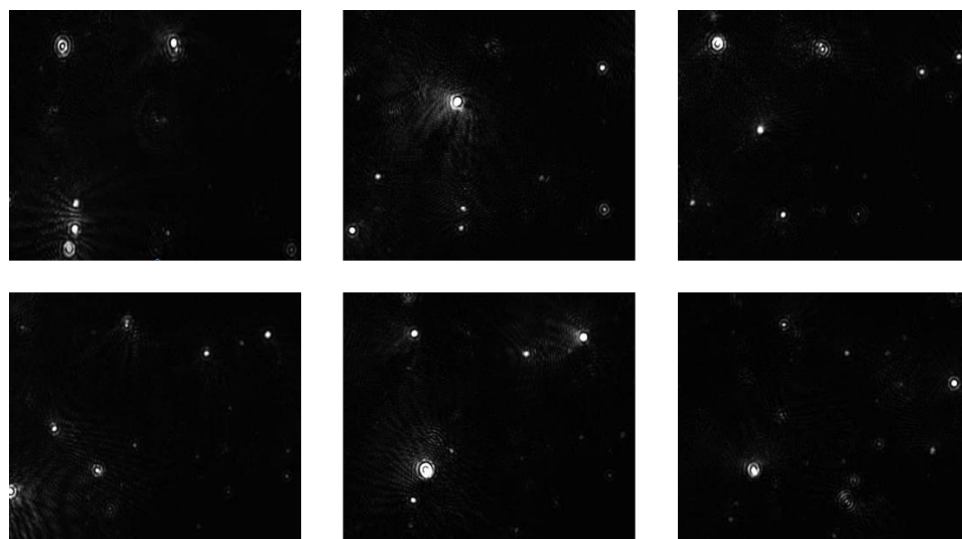


Figure S3. Nanoparticle tracking analysis images of GNS.

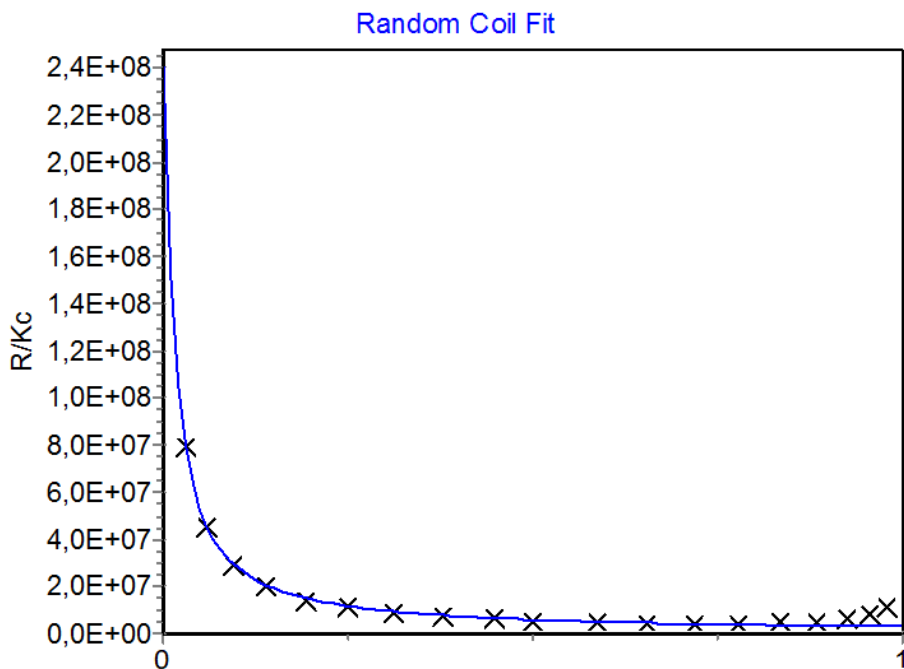


Figure S4. Random Coil data fitting method.

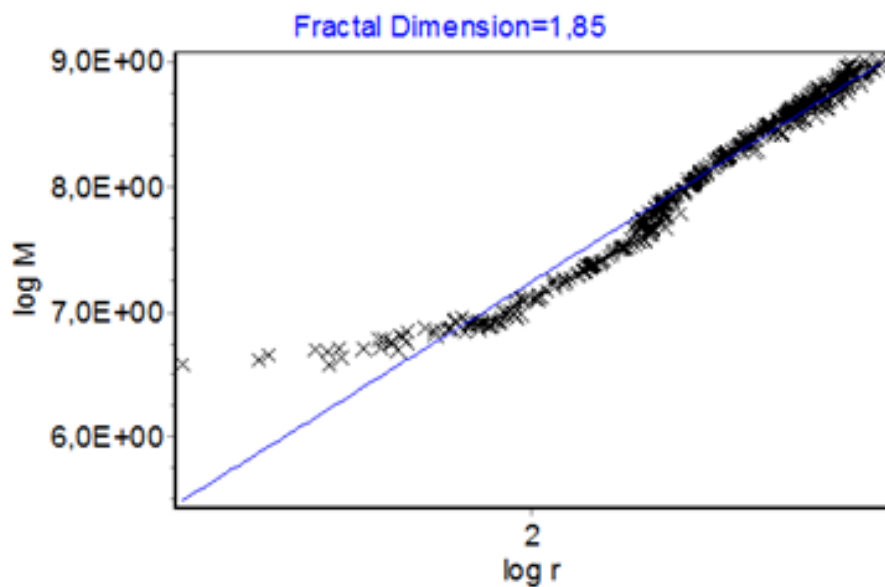


Figure S5. Analysis of the fractal factor dimension to identify the GNS particle shape where M is molecular weight and r is the radius of gyration.

References of the Supplementary Information

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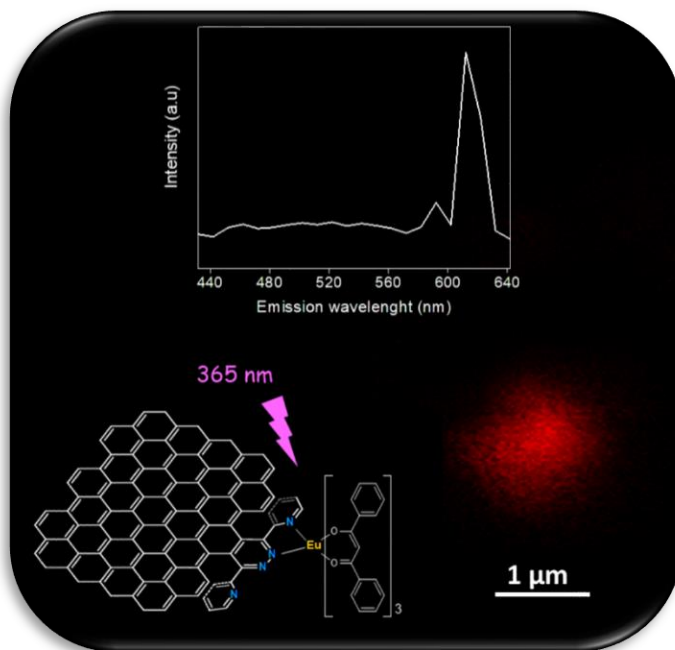
5.3.2. Luminescent graphene-based materials via europium complexation on dipyridylpyridazine-functionalized graphene sheets

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Dedicated to Prof. Jean-Marie Lehn on the occasion of his 80th birthday



Published in *Chemistry–A European Journal*

Chemistry–A European Journal, 2019, vol. 25, no 27, p. 6823-6830

DOI: <https://doi.org/10.1002/chem.201900512>

Abstract

Graphene-based materials exhibit outstanding physical properties and so are potentially applicable in a great variety of fields. Unlike their corresponding oxides, graphite and graphene are not prone to functionalization. Diels-Alder reactions are among the scarce reactions that they can undergo without disrupting their conjugated sp^2 systems. Herein, the reaction between graphite and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine under different conditions affords several graphene-based materials consisting of dipyridylpyridazine functionalized few layer graphene, multilayer graphene and graphite whose sheets act as ligands for the grafting of a europium complex. These three materials show strong red emission under 365 nm UV radiation. Their emitting particles can be visualized by confocal microscopy. The rich coordination chemistry of dipyridylpyridazine ligands envisages novel properties for similarly functionalized graphene-based materials grafted with other metal complexes.

Keywords: Cycloaddition, Graphene, Lanthanides, Luminescence, N ligands

5.3.2.1. Introduction

Graphene-based materials will have an outstanding technological impact in the future in virtue of their availability and excellent mechanical, thermal, electrical and electronic properties. The possibility to impart them with photonic properties is challenging and will be of a high interest. Emitting nanomaterials have potential applications in many areas, including sensing, bioimaging and photocatalysis, among others.^[1] However, graphene is a zero band gap semiconductor and so practically it does not exhibit any luminescence.^[2] At present there are two general strategies to produce luminescent graphene-based materials.^[3] The first one involves the existence of sp^2 isolated islands without π connections, as occurs in some reduced graphene oxides. The second one originates from the presence of defects, as occurs in carbon quantum dots. These nanomaterials exhibit emissions that are concentrated in the blue and green regions. Previous strategies are basically based on the introduction of defects in the graphene sheets and so unavoidably will lead to materials with depleted properties.

3,6-Di(2-pyridyl)pyridazine units have received great attention as ligands for coordination and supramolecular chemistry.^[4] These ligands can be synthesized by an inverse electron demand Diels–Alder reaction between the corresponding 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (as diene) and alkynes or alkenes (as dienophiles).^[5] Hybrid materials have also been functionalized through hetero Diels-Alder reactions. Thus, in recent years, the emission properties of different organosilicas via their functionalization with lanthanide complexes via surface dipyridylpyridazine ligands have been explored. These surface adducts were generated by Diels-Alder reaction between C=C double bonds in the organosilica (dienophile) and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (diene). In particular, these surface adducts were proven to be suitable sensitizing ligands for europium ions,^[6] provided hybrid near-infrared (NIR) emitting materials upon complexation with NIR emitting lanthanide ions (Nd^{3+} , Er^{3+} , Yb^{3+})^[7] and a luminescent optical thermometer when grafted with Eu^{3+}/Tb^{3+} ions.^[8]

Nitrogen-doped graphenes can be obtained by two general strategies, i.e. direct synthesis and posttreatment. Regardless of the doping procedure, different nitrogen types at different locations are generated and so specific sites for metal coordination are ill-defined.^[9] Haddon et al.^[10,11] have reported that both graphite and graphene can act as dienes and dienophiles in the Diels-Alder reaction. Particularly, their behavior as

dienophiles was investigated using 9-methylanthracene, 9,10-dimethylanthracene and 2,3-dimethoxy-1,3-butadiene, all of them electron-rich dienes. A later computational study revealed that these cycloaddition reactions did not take place in the inner bonds of graphene but in its edges.^[12] Recently, Schirmacher et al.^[13] have demonstrated the effectiveness of the Diels-Alder reaction with a carbonaceous matrix material and a tetrazine-based compound functionalizing single-walled carbon nanotubes with 3,6-dichlorotetrazine conjugated to Au nanoparticles. Similarly, they reported later the Diels-Alder reaction between substituted chlorotetrazines and HOPG under mild conditions.^[14]

Considering that dipyridylpyridazine derivatives are excellent ligands for the coordination of different metals and the exciting applications of Ln grafted materials, herein we have prepared dipyridylpyridazine (dppz) graphene-based materials, which subsequently have been used for the coordination of europium complexes as examples of visible emitting lanthanide ions.

5.3.2.2. Experimental Section

5.3.2.2.1. Materials

Microcrystalline graphite (MG) powder (98 %) was purchased from Nanostructured & amorphous materials Inc. 1,2-Dichlorobenzene (ODCB, anhydrous, 99%), dichloromethane (anhydrous, $\geq 99.8\%$, contains 40-150 ppm amylene as stabilizer), chloroform (anhydrous, $\geq 99\%$, contains 0.5-1.0% ethanol as stabilizer), 2-cyanopyridine (99%), hydrazine hydrate (reagent grade, N_2H_4 50-60 %), acetic acid (ReagentPlus, $\geq 99.99\%$), p-xylene (anhydrous, $\geq 99\%$), sodium nitrite (ACS reagent, $\geq 97.0\%$) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 98%) were obtained from Sigma Aldrich. 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine (dptz) and phenyl-3,6-di(2-pyridyl)pyridazine were synthesized by reported procedures.^[7,21]

5.3.2.2.2. Synthesis of dppz-FLG

250 mg of microcrystalline graphite powder (MG) were added to a solution of 100 mg dptz in 50 mL of ODCB. The mixture was homogenized by stirring for 30 min. Then, the resulting dispersion was sonicated for 2 h (pulsed mode at 40% amplitude in an Ultrasonic Homogenizer 4710 Series from Cole Parmer Instrument Co.). The suspension obtained was

centrifuged three times at 4000 rpm for 30 min to remove non-exfoliated graphite. The dispersion in ODCB was centrifuged at 10000 rpm for 30 min and the solid was washed five times with dichloromethane by successive redispersions and centrifugations. The resulting solid was dried under vacuum at 120 °C overnight. A dehydrogenation step was carried out with DDQ with a weight ratio solid:DDQ of 4:1 for 24 h using CHCl₃ as solvent. The dispersion was washed five times with dichloromethane by successive redispersions and centrifugations to eliminate excess of DDQ. The resulting solid, named dppz-FLG, was dried under vacuum at 120 °C overnight.

5.3.2.2.3. *Synthesis of dppz-MLG*

100 mg of microcrystalline graphite powder (MG) and 100 mg of dptz were introduced into the jar of a ball mill (Retsch PM100). The mixture was stirred for 24 h at 600 rpm with reversal of rotation every 30 min. The solid obtained was washed three times with dichloromethane: two with 25 mL at room temperature and one with 25 mL at 80 °C. After, the solid was dried at 120 °C under vacuum. A dehydrogenation step was carried out with DDQ with a weight ratio solid:DDQ 4:1 for 24 h using CHCl₃ as solvent. The dispersion was washed five times with dichloromethane by successive redispersions and centrifugations to eliminate excess of DDQ. The resulting solid, named dppz-MLG, was dried under vacuum at 120 °C overnight.

5.3.2.2.4. *Synthesis of dppz-MG*

A suspension of 100 mg of microcrystalline graphite powder (MG) and 100 mg of dptz in 10 mL of p-xylene was stirred for one week at 130 °C under a N₂ atmosphere. The solid was isolated by centrifugation at 4000 rpm. Subsequently, it was washed three times with dichloromethane: two with 25 mL at room temperature and one with 10 mL at 40 °C. Then, the solid was dried at 120 °C under vacuum. A dehydrogenation step was carried out with DDQ with a weight ratio solid:DDQ 4:1 for 24 h using CHCl₃ as solvent. The solid was washed five times with dichloromethane by successive redispersions and centrifugations to eliminate excess of DDQ. The resulting solid, named dppz-MG, was dried under vacuum at 120 °C overnight. *Synthesis of europium grafted dppz-FLG (Eu(dbm)₃@dppz-FLG; dbm = 1,3-Diphenyl, 1,3-propanedione)*

For the preparation of $\text{Eu}(\text{dbm})_3@ \text{dppz-FLG}$ a certain amount of presynthesized $\text{Eu}(\text{dbm})_3$ complex (prepared according to previously reported procedure)^[33] was dissolved in methanol in a Pyrex tube. Next, dppz-FLG in solid form was added to the lanthanide complex solution. This mixture was treated in an ultrasound bath for 30 min and left to soak at room temperature for the following 24 h. After this time, it was treated with ultrasound irradiation again for 30 min and next heated on a heating block for 24 h at 85 °C. After cooling down to room temperature the solid was collected on a glass filter, washed several times with methanol and left to dry in an oven at 50 °C.

5.3.2.2.6. Synthesis of europium grafted dppz-MLG

($\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$; dbm = 1,3-Diphenyl, 1,3-propanedione)

The synthesis of the $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$ materials was performed in a similar way as that described in 2.2.4. except dppz-MLG was used instead of dppz-FLG.

5.3.2.2.7. Synthesis of europium grafted dppz-MG ($\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$; dbm = 1,3-Diphenyl, 1,3-propanedione)

The synthesis of the $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$ materials was performed in a similar way as that described in 2.2.4. except dppz-MG was used instead of dppz-FLG.

5.3.2.2.8. Characterization of graphene-based materials

The nitrogen content was determined by elemental analysis in an Eurovector EA 3000. Transmission electron microscopy (TEM) images were recorded on a Jeol JEM-1400 transmission electron microscope operated at an accelerating voltage of 120 kV. The measurements have been made in a magnification range between 8,000x – 150,000x with an instrument resolution of 0.38 nm between points. Raman spectra were measured with a Renishaw Raman instrument (InVia Raman Microscope) by excitation with green laser light (532 nm). A total of 25 scans per spectrum were acquired to improve the signal-to-noise ratio. Raman spectroscopy was used to estimate the number of sheets in the graphitic materials (see SI) and to corroborate the coordination of the Eu complex with the nitrogen atoms present in the dppz-graphene/graphite matrix. XPS spectra were recorded on a SPECS mod. PHOIBOS 150 MCD

spectrometer using monochromatic Mg $K\alpha$ radiation and a multichannel detector. All spectra were fitted to Gauss–Lorentz curves. Eu(III) loadings in $\text{Eu}(\text{dbm})_3@$ dppz-graphene-based materials were determined by ICP-MS analysis in an ICP Mass Spectrometer model NexION™ 350X, PerkinElmer Inc. 1 mg of $\text{Eu}(\text{dbm})_3@$ dppz-graphene-based materials was dissolved in a mixture of 200 μL of 69% HNO_3 (Merck, Suprapur), 50 μL of $\geq 30\%$ H_2O_2 (Fluka, TraceSELECT@Ultra), 20 μl of 40% HF (Merck, Suprapur) and Milli-Q ultrapure water up to a total volume of 5 mL using an Ultrawave Single Reaction Chamber Microwave Digestion System, Milestone Inc. at 1500 W and temperature up to 220 °C. Confocal measurements were carried out in a ZEISS LSM 800 confocal microscope with oil immersion objective and equipped with 405 nm diode laser, MBS-405 nm filter and a gallium arsenide phosphide photomultiplier tube (GaAsP PMTs) as detector. One drop of an aqueous dispersion of the materials (1 mg of solid:3 mL of water) was placed on a microscope slide and subsequently protected with a cover slip. The edges of the protective glass were sealed with silicone. The lambda stack mode was selected to determine the emission spectrum of the fluorophore. NTA measurements were performed in a NanoSight NS300 (NanoSight, Malvern), equipped with a violet 405 nm laser and a 430 nm long pass filter. The minimum size limit of this technique is 10-40 nm.

Luminescence measurements were performed on an Edinburgh Instruments FLSP920 UV-vis-NIR spectrometer setup. A 450 W xenon lamp was used as the steady-state excitation source. Time-resolved measurements were recorded using a 60 W pulsed Xe lamp operating at a frequency of 100 Hz (for visible emitting lanthanides). The very short decay times of the ungrafted dipyrildylpyridazine graphene-based materials were measured using a Supercontinuum white light laser for TCSPC (Time Correlated Single Photon Counting). A Hamamatsu R928P photomultiplier tube was used to detect the emission signals in the near UV to visible range. All luminescence measurements were recorded at room temperature. Crystals were put between quartz plates (Starna cuvettes for powder samples, type 20/C/Q/0.2). For all the compounds the luminescence decay curves were measured when excited into the broad ligand band (at different wavelengths) and monitored at the strongest europium transition. All the decay curves could be well fitted using either a single exponential function or biexponential function:

$$I = A \exp\left(-\frac{t}{\tau}\right)$$

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

Where I represent the luminescence intensity and A , A_1 and A_2 are constants, t is time and τ , τ_1 and τ_2 are the luminescence lifetimes. All steady state and decay time measurements were performed with slit sizes of 1 nm (both excitation and emission) and a step size of 1 nm. The absolute overall quantum yields of the materials were measured by using an integrated sphere with a BENFLEC coating provided by Edinburgh Instruments as follows:

$$\eta = \frac{\int L_{\text{emission}}}{\int E_{\text{blank}} - \int E_{\text{sample}}}$$

where L_{emission} is the integrated value of the emission spectrum, and E_{blank} and E_{sample} are the integrated values of the “excitation” band of the blank and the excitation band of the sample (since the sample absorbs part of the light, this value will be smaller than E_{blank}), respectively.

5.3.2.3. Results and Discussion

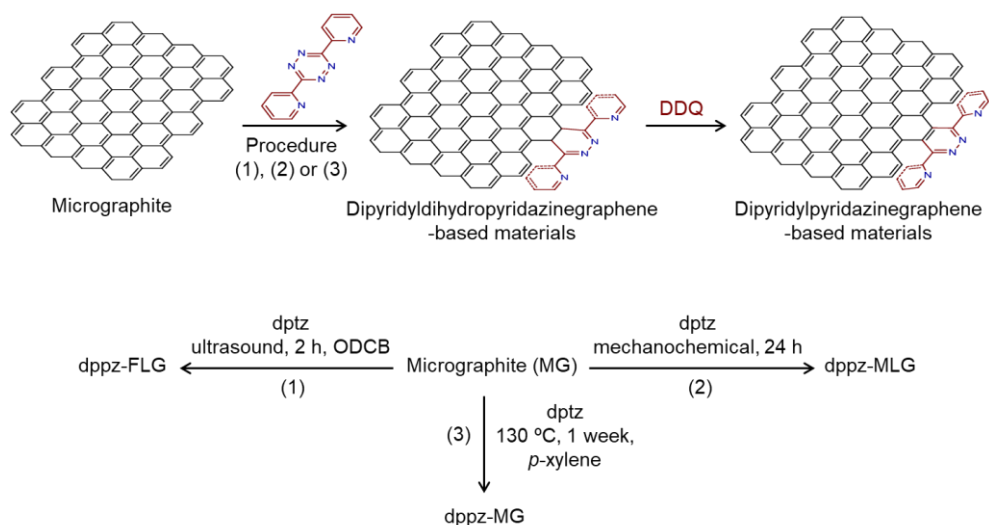
5.3.2.3.1. Synthesis and characterization of dipyrldylpyridazine graphene-based materials

A screening of the Diels-Alder reaction between graphene-based materials and 3,6-di(2-pyridyl)tetrazine was carried out under a variety of conditions (**Tables S1-S3**). The degree of functionalization, measured as the N content, varied with the substrate, activation of the reaction and time. Broadly, the reactivity of the graphene-derived materials decreased in the following order: graphene nanosheets > micrographite > graphite > multiwalled carbon nanotubes. These results agree with the preferential functionalization of the double bonds located at the edges of the graphene sheets, as proposed by Houk et al.^[12] Accordingly, a microcrystalline graphite powder was selected as starting material.

Three materials were synthesized by three different reaction procedures (see Experimental section): one-pot ultrasound-assisted exfoliation and functionalization (dppz-FLG); dry mechanochemical

reaction (dppz-MLG); and refluxing (dppz-MG). When a tetrazine is used as an electron-deficient diene, the Diels-Alder cycloaddition is subsequently followed by a retro-Diels-Alder reaction with N_2 release, giving rise to a dihydropyridazine adduct (**Scheme 1**). This adduct can be dehydrogenated to the corresponding pyridazine with different oxidizing agents. In this work, DDQ was used after the Diels-Alder reactions. As many of these reagents can also participate in oxidative cyclodehydrogenation reactions,^[15] the dppz units could be bound to the graphene sheet in different ways, which otherwise are indistinguishable.

Scheme 1. Hetero Diels-Alder reaction between graphene sheets and 3,6-di(2-pyridyl)tetrazine.



Elemental analysis of the three samples gave N contents of 3.5, 4.1 and 1.6 wt% for dppz-FLG, dppz-MLG and dppz-MG, respectively. Raman spectroscopy confirmed the functionalization of graphene sheets in the three materials (**Figure 1**). The intensity ratio of the D and G bands (I_D / I_G) has been related to the degree of disorder corresponding to the effective functionalization in the Diels-Alder reaction.^[10] In all cases, the I_D / I_G ratio increased for the functionalized materials, from 0.10 for the parent micrographite to ca. 1.0 for the dppz-MLG sample. Raman spectroscopy is also a useful technique to determine the number of sheets in graphene-based materials. Two procedures were selected and applied to unfunctionalized and dppz-functionalized materials (see SI). Equation S1 provided 7 and 15 layers for FLG and MLG materials, whereas equation 2 gave 9 and 11

layers, respectively.^[16,17] Concerning the functionalized materials, dppz-FLG and dppz-MLG presented a number of 5 and 12 layers according to equation 1 and 10 and 13 according to equation S3. As a consequence, the material obtained by the ultrasound method can be considered as a few layer graphene whereas that synthesized by a mechanochemical procedure can be classified as a multilayer graphene.^[18] The mechanochemical exfoliation of graphite has been reported previously. For example, ball-milling of graphite with melamine has been used for the production of few-layer graphenes.^[19]

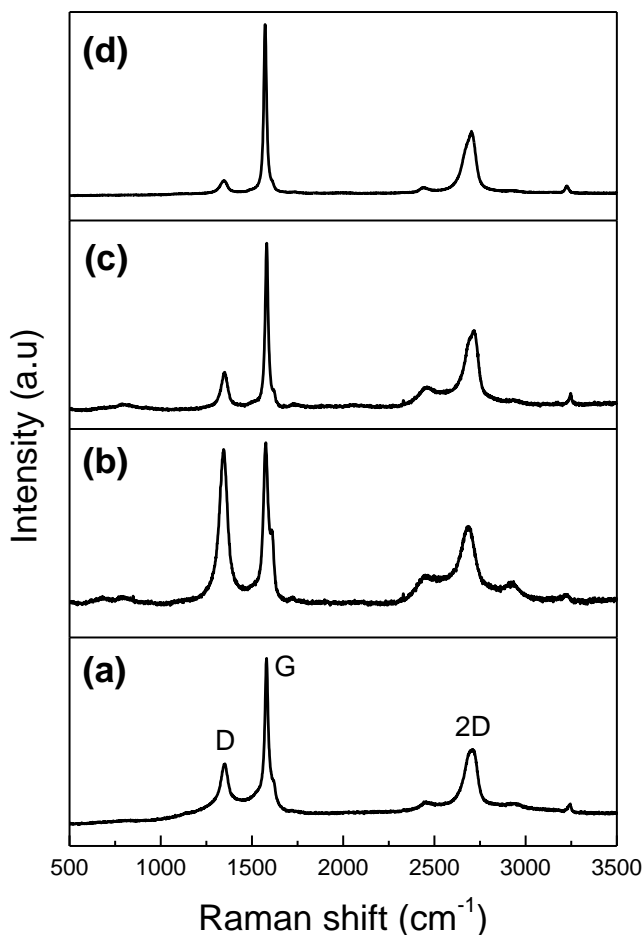


Figure 1. Raman spectra of materials (a) dppz-FLG, (b) dppz-MLG, (c) dppz-MG and (d) the parent MG.

The parent graphite and the functionalized materials were examined by TEM images. The original graphite showed a multilayered structure composed of numerous individual graphene sheets (**Figure 2-a**). A similar structure was observed for the material functionalized by a refluxing

procedure dppz-MG (**Figure 2-d**). Unlike, TEM images of dppz-FLG and dppz-MLG materials (**Figure 2-b** and **2-c**) revealed the presence of transparent thin sheets resulting from stacking of exfoliated layers, less in the former than in the latter material.

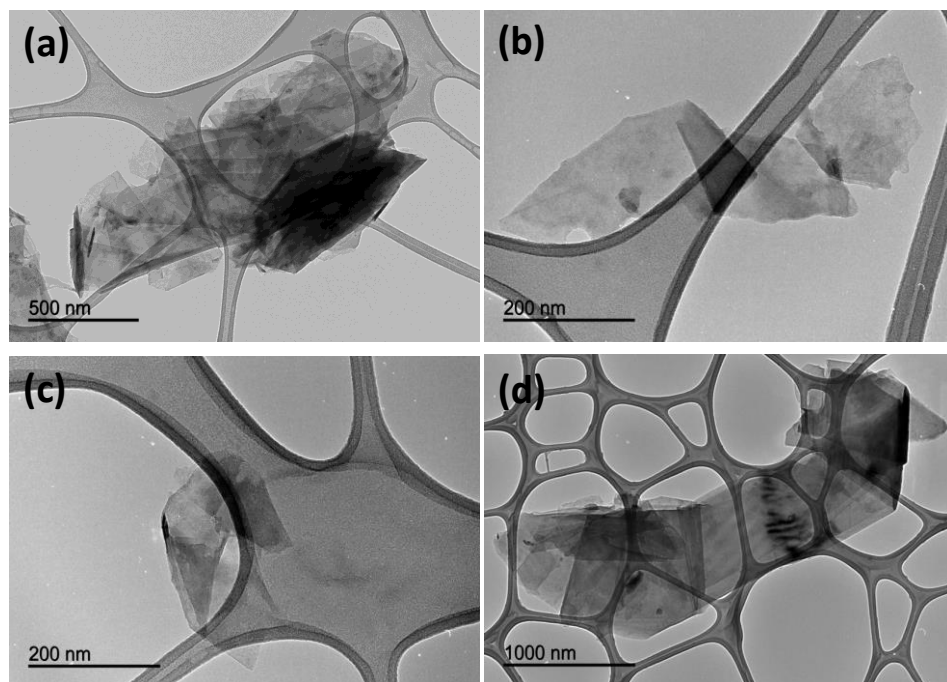


Figure 2. TEM images of the three functionalized materials (a) parent MG, (b) dppz-FLG, (c) dppz-MLG and (d) dppz-MG.

The functionalization of these materials was also confirmed by performing X-ray photoelectron spectroscopy (**Figure 3**). The charging effect has been corrected by taking the adventitious carbon to 284.8 eV as a reference. The N1s signal of 3,6-di(2-pyridyl)-1,2,4,5-tetrazine has been decomposed into two main components centered at 398.7 eV and 400.2 eV, corresponding to N in the pyridine and the tetrazine rings, respectively.^[20] In order to ascertain the changes in the N1s signal upon formation of the adduct, a model compound, i.e. phenyl-3,6-di(2-pyridyl)pyridazine, was synthesized by Diels-Alder reaction between 3,6-di(2-pyridyl)-1,2,4,5-tetrazine and phenyl acetylene.^[21] This compound only gave a N1s component at 399.2 eV, thus indicating that nitrogen in the pyridine and the pyridazine rings have the same signal, in agreement with Miomandre et al.^[22] However, these authors suggested that the signal at higher binding

energy separated by 1.4 eV was due to the N in the dihydropyridazine ring obtained by the Diels-Alder reaction between the tetrazine ring and the inner double bonds in the graphene sheets, which cannot be oxidized. Nevertheless, according to our results, the presence of two N1s signals separated by ca. 1.4 eV would be indicative of the presence of a tetrazine ring.

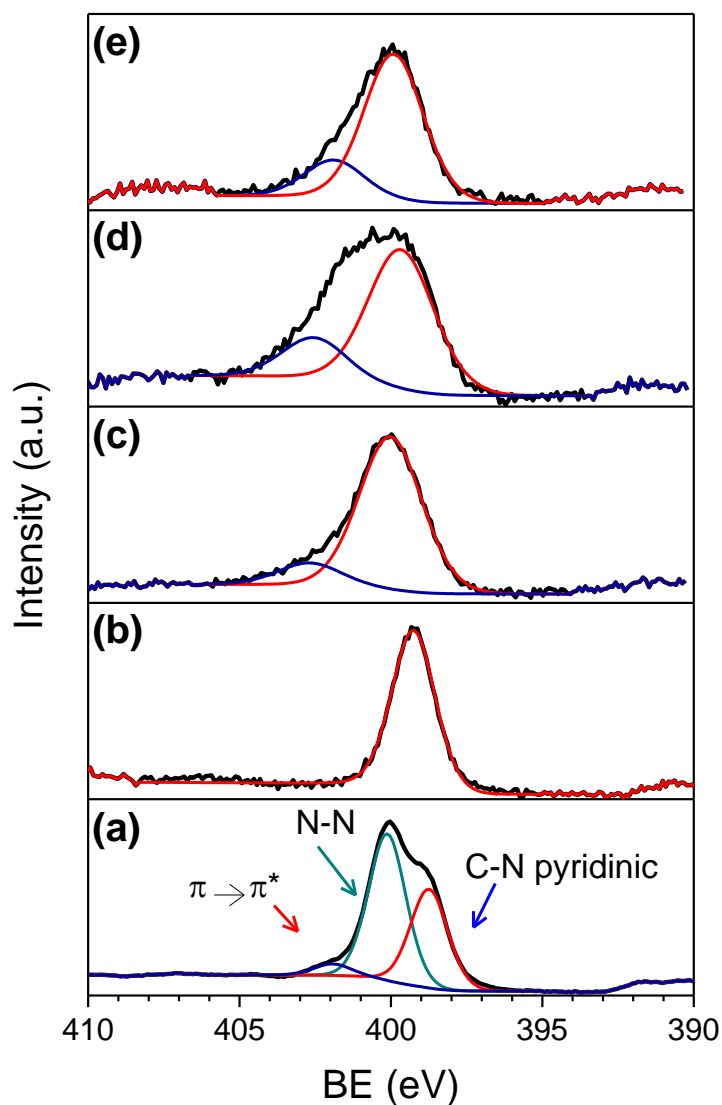


Figure 3. XPS spectra for the N1s photoemission peak of a) 3,6-di(2-pyridyl)-1,2,4,5-tetrazine, b) phenyl-3,6-di(2-pyridyl)pyridazine, c) dppz-FLG, d) dppz-MLG and e) dppz-MG.

XPS spectra of the three functionalized materials, i.e. dppz-FLG, dppz-MLG and dppz-MG, exhibited a N1s signal close to 400 eV, thus confirming the incorporation of nitrogen in the three samples. The small shift toward higher binding energy with respect to the model pyridazine can be explained by the uncertainty of giving the same reference binding energy to the sp^2 carbon atoms in both graphene derivatives and heterocyclic compounds, the latter being affected by the presence of electronegative N atoms.

In any case, this signal only contained one contribution and so it can be attributed to the formation of the dipyridylpyridazine adducts on the edges of the graphene sheets.

Additionally, all materials showed a band between 402-404.2 eV associated with the so-called π - π^* transitions, characteristics of aromatic structures or unsaturated bonds.^[23,24]

C1s XPS spectra of the three materials (**Figure S1**) revealed a slight oxidation of the graphene sheets in dppz-MLG, unlike dppz-FLG and dppz-MG. A comparison with the non-functionalized materials obtained by analogous procedures indicated that the oxidation occurred during the mechanochemical treatment. By contrast, dppz-FLG and dppz-MG exhibited a similar oxidation level to the parent graphite.

5.3.2.3.2. Room temperature photoluminescence properties of dppz-FLG, dppz-MLG and dppz-MG

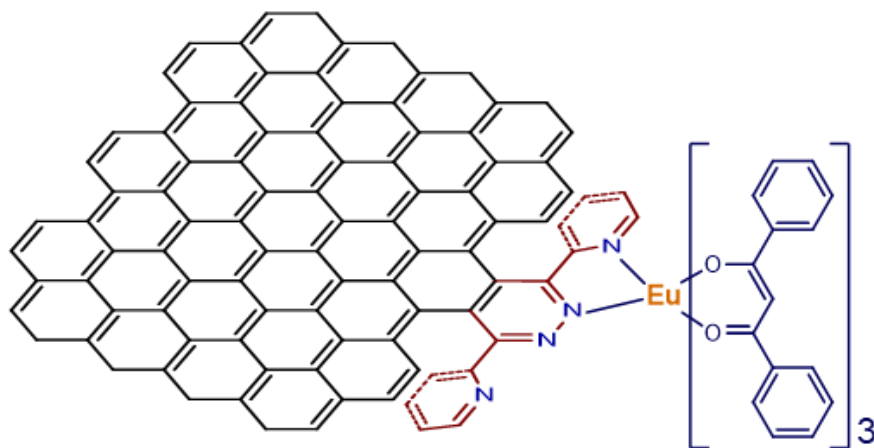
The excitation and emission spectra as well as luminescence decay times of the as prepared graphene-based materials were recorded and studied in detail. For the dppz-FLG material a broad band in the excitation spectrum was observed in the 250 – 350 nm range (**Figure S2**) When excited into the maximum of this band (280 nm), emission between 400 – 600 nm was observed with a maximum around 510 nm, showing emission in the green region (**Figure S3**). The luminescence decay profile of this sample could be well fitted using a monoexponential fit and yielded a decay time of 1.25 ns (**Figure S4**). For the dppz-MLG sample the excitation spectrum exhibited a broad band between 250 – 450 nm with a maximum at 375 nm (**Figure S5**). When excited at 375 nm an emission band with a maximum at 445 nm was observed, resulting in blue emission (**Figure S6**). The decay time for dppz-MLG could only be well fitted using a biexponential decay curve and yielded $\tau_1 = 1.51$ ns and $\tau_2 = 6.53$ ns (**Figure S7**). For the dppz-MG material the excitation and emission spectra were in a very similar range as that

described for dppz-MLG (**Figure S8 and S9**). The decay time was recorded to be $\tau_1 = 1.55$ ns and $\tau_2 = 6.26$ ns (**Figure S10**) proving the dppz-MLG and dppz-MG materials to be very similar in their photoluminescence properties. All these values are similar to those reported in the literature for graphene oxides and reduced graphene oxides.^[25]

5.3.2.3.3. Europium dipyriddyridazine graphene complexes as visible emitters

Dipyriddyridazinegraphene-based materials were used as ligands for the grafting of europium complexes (**Scheme 2**). All the graphene-based materials were grafted with the $\text{Eu}(\text{dbm})_3$ complex forming $\text{Eu}(\text{dbm})_3@$ dppz-FLG, $\text{Eu}(\text{dbm})_3@$ dppz-MLG and $\text{Eu}(\text{dbm})_3@$ dppz-MG materials. ICP-MS analysis revealed Eu contents of 1.6, 1.2 and 1.4 mmol g^{-1} for $\text{Eu}(\text{dbm})_3@$ dppz-FLG, $\text{Eu}(\text{dbm})_3@$ dppz-MLG and $\text{Eu}(\text{dbm})_3@$ dppz-MG, respectively. The $\text{Eu}(\text{dbm})_3$ complex was used instead of a europium salt to ensure no (or a very low amount) water molecules in the first coordination sphere of the Eu^{3+} ions. Additionally, the dbm ligand also works as a second antenna for the absorption of light making more efficient photoluminescence materials.

Scheme 2. Bis(dibenzoylmethane) europium complexes of dipyriddyridazine graphene-based materials.



The coordination of $\text{Eu}(\text{dbm})_3$ to dipyriddyridazinegraphene-based materials was confirmed by Raman spectroscopy (**Figure 4**). The signal of Eu-O bond ($\nu \text{Eu-O} = 405.1 \text{ cm}^{-1}$) was present in the $\text{Eu}(\text{dbm})_3$ complex as well as in the three grafted materials, i.e. $\text{Eu}(\text{dbm})_3@$ dppz-

FLG, $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$ and $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$. The binding of Eu ions to the N atoms in dipyriddyipyridazinegraphene sheets was corroborated by the presence of a peak at 451.3 cm^{-1} .^[26] The Eu-N bond was not observable in the case of the $\text{Eu}(\text{dbm})_3$ complex. The parent MG showed no peaks in this Raman shift range.

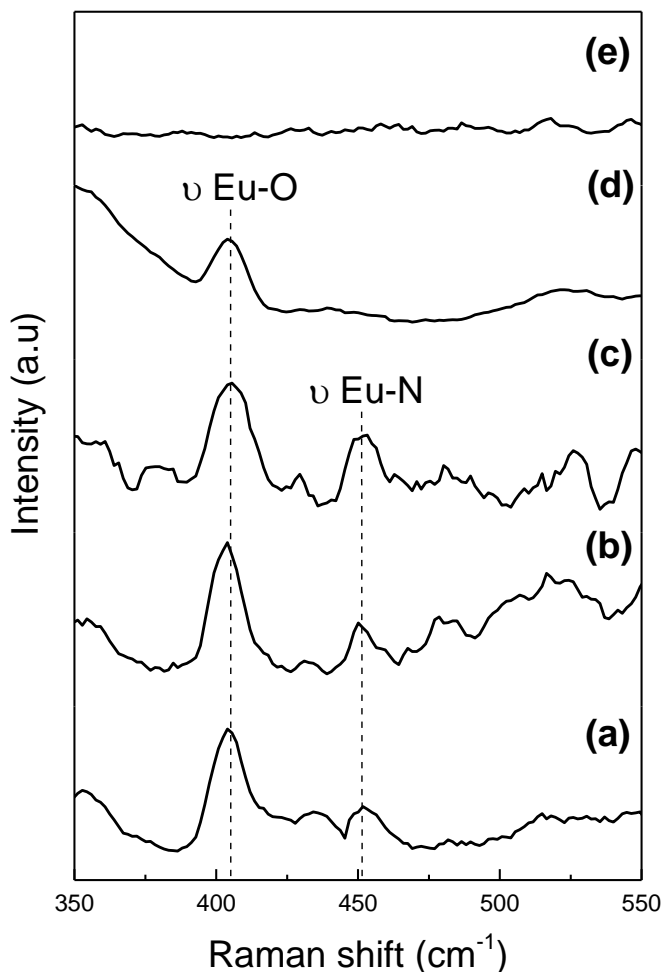


Figure 4. Raman spectra of materials (a) $\text{Eu}(\text{dbm})_3@ \text{dppz-FLG}$, (b) $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$, (c) $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$, (d) $\text{Eu}(\text{dbm})_3$ and (e) the parent MG.

The room temperature photoluminescence properties of the three materials were studied in detail – excitation and emission spectra, luminescence decay times and quantum yields. The combined excitation-emission spectrum of the pre-synthesized $\text{Eu}(\text{dbm})_3(\text{H}_2\text{O})_2$ complex has

been presented in **Figure S11**. The maximum of the excitation band was located around 400 nm and the characteristic $^5D_0 \rightarrow ^7F_{0-4}$ transitions were observed in the emission spectrum. The decay time was calculated to be 0.338 ms (**Figure S12**). The recorded excitation and emission spectra of the $\text{Eu}(\text{dbm})_3@ \text{dppz-FLG}$, $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$ and $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$ materials displayed quite similar photoluminescence properties. In the excitation spectra a broad band originating from the ligands can be observed between 250 – 425 nm, with a maximum around 390 nm. The samples could be excited at different wavelengths (320 nm, 350 nm and 390 nm) to yield the characteristic Eu^{3+} transition peaks: $^5D_0 \rightarrow ^7F_0$ (577 nm), $^5D_0 \rightarrow ^7F_1$ (591 nm), $^5D_0 \rightarrow ^7F_2$ (611 nm), $^5D_0 \rightarrow ^7F_3$ (651 nm) and $^5D_0 \rightarrow ^7F_4$ (701 nm). The combined excitation-emission spectra for the $\text{Eu}(\text{dbm})_3@ \text{dppz-FLG}$ material has been presented in **Figure 5**. The spectra for the $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$ and $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$ materials have been presented in **Figure S13** and **S14**. The luminescence decay times (excited into the maximum of the broad band) could only be well fitted using a biexponential equation, which suggests the presence of two different coordination environments of the Eu^{3+} ions in these materials. This could be a result of different binding modes to the dppz ligand or a different amount of dbm ligands and/or water molecules in the coordination environment. The decay times of the $\text{Eu}(\text{dbm})_3@ \text{dppz-FLG}$, $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$ and $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$ materials have been overviewed in **Table 1** and the decay profiles have been presented in **Figure S15-S23**.

Despite the low QY values (presented in **Table 1**) the three materials showed strong red emission under 365 nm UV radiation with a laboratory UV lamp. Interestingly, these QY values are in the order of magnitude of those reported for most carbon quantum dots.^[3]

Some graphene-based materials have been visualized by direct fluorescence microscopy. In particular, GO nanosheets can be used as fluorescence labels but micron sized GO and reduced GO are unobservable in practice.^[27] The strong fluorescence quenching of different dyes, such as fluorescein, by graphene-based materials has been used to visualize them by common fluorescence microscopy.^[28]

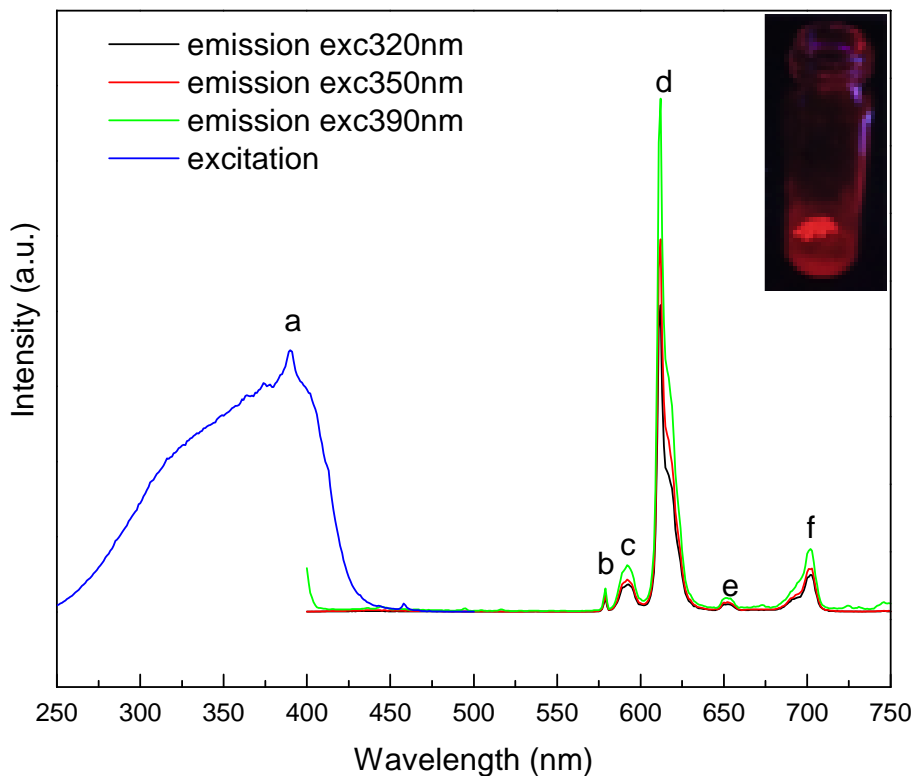


Figure 5. RT combined excitation-emission spectra for $\text{Eu}(\text{dbm})_3@ \text{dppz}$ -FLG material. The excitation spectrum was observed at 611 nm. The labeled peaks are assigned to the following transitions: a (399.0 nm) – $\pi \rightarrow \pi^*$, b (579.0 nm) – ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$, c (591.0 nm) – ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, d (612.0 nm) – ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, e (651.0 nm) – ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$, f (702.0 nm) – ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$. The insert shows a photo of the sample under a laboratory UV lamp (365 nm excitation).

Table 1. Luminescence decay times and quantum yields of the europium dipyriddyldipridazine graphene complexes

Material	τ_1 (ms)	τ_2 (ms)	R^2	QY (%)
$\text{Eu}(\text{dbm})_3@ \text{dppz}$ -FLG	0.209	0.065	0.999	2.8
$\text{Eu}(\text{dbm})_3@ \text{dppz}$ -MLG	0.221	0.072	0.999	3.6
$\text{Eu}(\text{dbm})_3@ \text{dppz}$ -MG	0.237	0.081	0.999	3.2

The fluorescence imaging of graphitic materials by labeling is challenging since the attached fluorophore will likely be quenched. In virtue of their interesting optical properties, the red emission of the Eu^{3+} complexes have been used to visualize these graphene-based materials by confocal microscopy. Material $\text{Eu}(\text{dbm})_3@$ dppz-FLG was observed both under dry conditions and dispersed in water (**Figure 6**). In both cases, particles with sizes between 300 and 600 nm were observable. Sample $\text{Eu}(\text{dbm})_3@$ dppz-MLG exhibited larger particles.

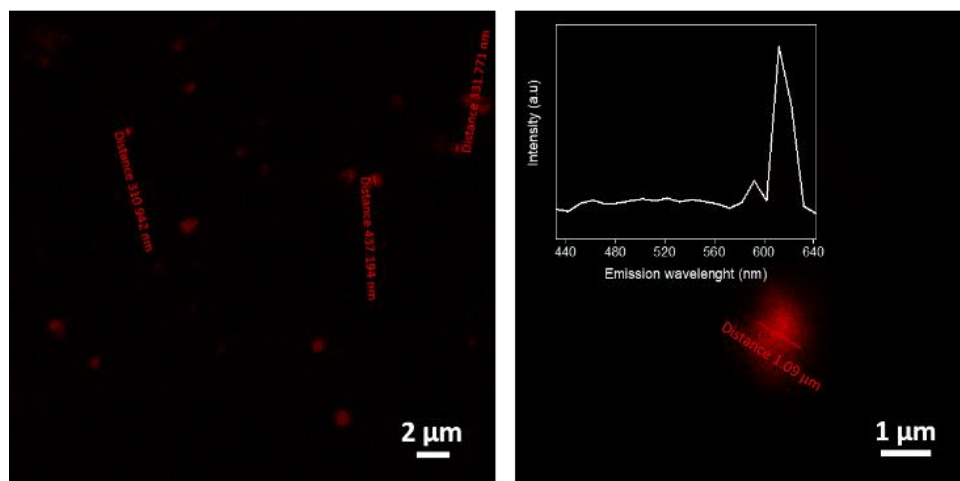


Figure 6. Images obtained by confocal microscopy of $\text{Eu}(\text{dbm})_3@$ dppz-FLG (left) and $\text{Eu}(\text{dbm})_3@$ dppz-MLG (right). The insert shown in the figure on the right represents the emission spectrum of a graphene particle determined by spectral image lambda stack from 427 to 668 nm with a resolution of 10 nm.

A spectral image lambda stack was gathered by the microscope for sample $\text{Eu}(\text{dbm})_3@$ dppz-MLG (**Figure 6**, inset). It provided a unique emission fingerprint that can be assigned to the graphene particle, thus revealing the sole contribution of this fluorophore to the sample emission.

In addition, material $\text{Eu}(\text{dbm})_3@$ dppz-FLG, which gives a stable dispersion in water, was subjected to tracking analysis (**Figure 7**). This technique allows to visualize and determine the size and concentration of nanoparticles.^[29]

A comparison of the scatter and fluorescence modes clearly indicated the formation of Eu^{3+} complexes in the graphene sheets since particles in the same range of sizes were observed in both cases, even though the fluorescence mode gave a higher resolution in the low size range, which can

be caused by the differences in camera focus and capture and the non-spherical geometry of the particles. Interestingly, NTA would permit the selective visualization of graphene-based materials in complex media, which is essential for the study of the interaction of these nanomaterials with biological systems.

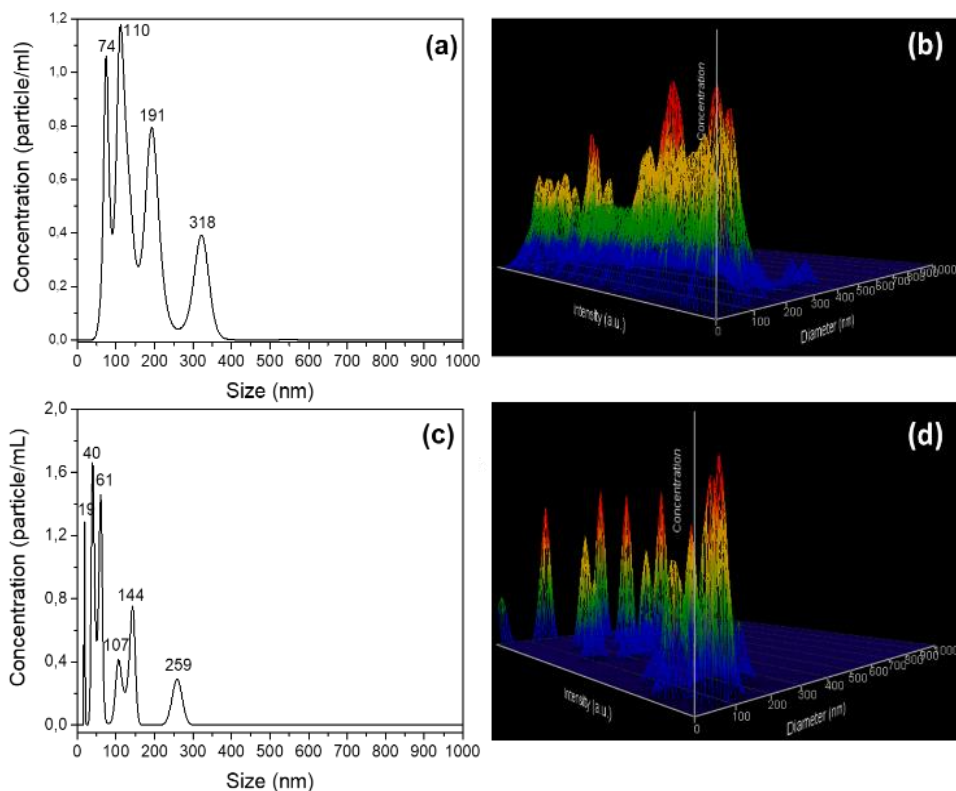


Figure 7. NTA analysis for Eu(dbm)₃@dppz-FLG in scatter mode ((a) and (b)) and fluorescence mode with excitation at 405 nm and a long pass filter at 430 nm ((c) and (d)).

5.3.2.4. Conclusions

The hetero Diels-Alder reaction between 3,6-di(2-pyridyl)-1,2,4,5-tetrazine and graphene-based materials provides well-defined coordination sites for metal complexation on graphene sheets. Starting from the same graphite, three different procedures with alternative activation energy, i.e. ultrasounds, ball-milling and heating, resulted in dipyridylpyridazine derived few layer graphene, multilayer graphene and graphite. All of them have been proven to be useful ligands for complexation of europium. The emission properties of these materials have been studied before and after

grafting with $\text{Eu}(\text{dbm})_3$ complexes. It was observed that when exciting at a wide range of excitation wavelengths strong red emission of the Eu^{3+} could be observed. Grafting of the Eu^{3+} complex to graphene sheets has been unequivocally proven by Raman spectroscopy, nanoparticle tracking analysis and confocal microscopy, where emitting particles were clearly observable. Thus, this methodology allows to label graphene-based materials for bioimaging irrespective of their particle size.

In virtue of the interesting properties of lanthanide complexes, such as those for optics^[30] and magnetism,^[31] its combination with the outstanding graphene properties envisages the design and synthesis of new graphene-based materials with integrated properties for new applications.

In addition, the extension of this methodology to other graphene metal complexes can give materials with potential applications in organometallic chemistry, catalysis, biomedicine, imaging and sensing, among others.^[32]

Acknowledgements

The authors wish to acknowledge the financial support from Ramon Areces Foundation (Spain), Andalusian Regional Government (FQM-346 group), Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981), Feder Funds and the technical staff from the Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUIQFN) and Servicio Central de Apoyo a la Investigación (SCAI). A.M.K. acknowledges Ghent University for funding and thanks Prof. Rik Van Deun for access to the Edinburgh Instruments Spectrofluorometer in his lab.

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Appendix V: Supplementary Information**METHODS****Raman spectroscopy**

The calculation of the number of sheets of all the graphitic materials was carried out according to two equations reported in the literature:

- 1) The equation S1 proposed by Wang et al.¹ includes the phonon energy dispersion adjusted based on the interatomic force constants. The n parameter represents the number of graphene layers that is calculated in relation to the graphene G peak and starting graphite G peak (1580.8 cm^{-1}) of the Raman spectrum:

$$\text{peak position } G \text{ (cm}^{-1}\text{)} = 1580,8 + 11/(1 + n^{1.6}) \quad (\text{S1})$$

This calculation is very reliable and precise for the determination of the number of layers of graphene materials, since it considers many parameters of force constants for the modulation of the G peak by changes in the graphene structure and the evolution of phonon dispersion from graphene to starting graphite.

- 2) In this article, J.N. Coleman et al.² propose the calculation of the number of sheets of graphene by taking into account the shape and intensity of the 2D peak. They suggest that the 2D band is composed of two subpeaks, the $2D_G$ with the highest energy (2725 cm^{-1}) located at 30 cm^{-1} above that with the lowest energy $2D_{G'}$. Applying the following quantitative relation of the 2D band of the graphene material synthesized ($2D_{ene}$) with respect to the 2D band of the starting graphite ($2D_{ite}$) the parameter M is obtained (equation S2):

$$M = \frac{I_{G,ene}/I_{G,ene}}{I_{G,ite}/I_{G,ite}} \quad (\text{S2})$$

Then, the thickness of graphene sheets (n) is calculated by equation S3:

$$n = 10^{0.84M+0.45M^2} \quad (\text{S3})$$

Nanoparticle tracking analysis (NTA)

NTA measurements were performed in a NanoSight NS300 (NanoSight, Malvern), equipped with a sample chamber and a violet 405 nm laser. In order to observing the labeled fluorescent particles, a standard filter supplied with fluorescence of 430 nm was placed. For the NTA measurements, 1 mg of solid was resuspended in 3 mL of water. Before the analysis, the solution was homogenized for 15 minutes in an ultrasonic bath. The samples were injected into the chamber with sterile syringes. A concentration rate between $10^7 - 10^8$ particles per milliliter were tracked during their Brownian motion by the software, which uses the Stokes-Einstein equation to provide sample information:

$$\overline{(x, y)^2} = \frac{2k_B T}{3r_h \pi \eta} \quad (\text{S4})$$

where k_B is the Boltzmann constant and $\overline{(x, y)^2}$ is the mean-squared speed of a particle with a hydrodynamic radius of r_h in a medium of defined viscosity and temperature. All measurements were performed at room temperature. Moreover, it was possible to obtain the particle size distribution and concentration in particle per milliliter.³

RESULTS AND DISCUSSION**Table S1.** Influence of reaction conditions and activation in the Diels-Alder reaction between graphite powder (extra pure, Merck ref. 4206) and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine.

Reaction procedure	N content (wt%)
130 °C, <i>p</i> -xylene, 24 h	0.2
130 °C, <i>p</i> -xylene, 1 week	0.6
Microwave, 130 °C, H ₂ O, 3 h, 350 W	0.4
Autoclave, 200 °C, <i>o</i> -Dichlorobenzene, 1 week	0.5
Planetary ball-mill, <i>p</i> -xylene, 3 h	0.3
Planetary ball-mill, dry conditions, 3 h	1.0
Planetary ball-mill, dry conditions, 24 h	3.3

Table S2. Influence of the type of graphene-based material in the Diels-Alder reaction with 3,6-di(2-pyridyl)-1,2,4,5-tetrazine at 130 °C in *p*-xylene for 1 week.

Graphene-based material	N content (wt%)
Multiwalled carbon nanotubes (6-9 nm, 5 μ m long) from Aldrich ref. 724769	0.3
Graphite powder (extra pure, Merck ref. 4206)	0.6
Graphite powder, 98%, max < 100 nm, from Nanostructured & Amorphous materials Inc.	1.6
Exfoliated synthetic graphite powder < 20 μ m from Aldrich ref. 282863	2.6

Table S3. One-pot ultrasound-assisted exfoliation and functionalization in *o*-dichlorobenzene for 2 h (pulsed mode at 40% amplitude in an Ultrasonic Homogenizer 4710 Series from Cole Parmer Instrument Co.).

Starting graphite	N content (wt%)
Synthetic graphite powder < 20 μ m from Aldrich ref. 282863	1.3
Graphite powder, 98%, max < 100 nm, from Nanostructured & Amorphous materials Inc.	3.5

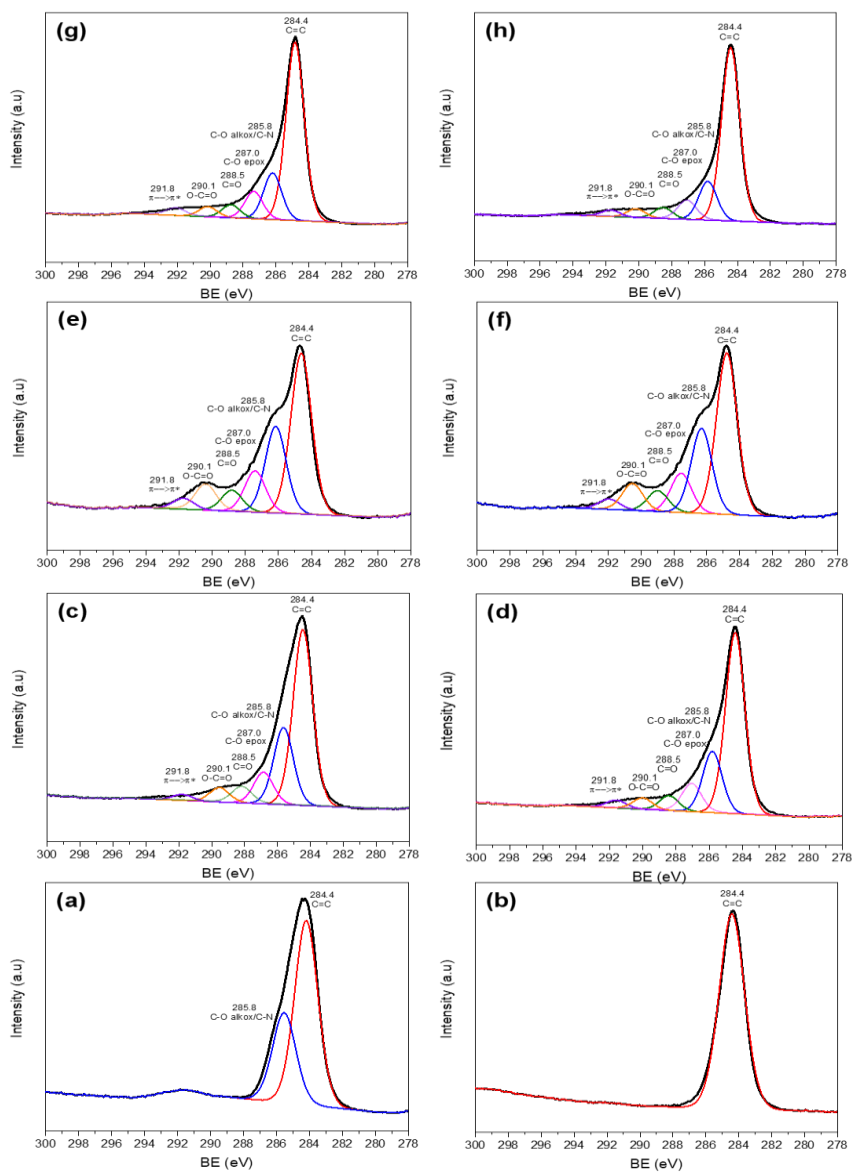


Figure S1. XPS spectra for the C1s photoemission peak of a) 3,6-di(2-pyridyl)-1,2,4,5-tetrazine, b) phenyl-3,6-di(2-pyridyl)pyridazine, c) FLG, d) dppz-FLG, e) MLG, f) dppz-MLG, g) MG and h) dppz-MG.

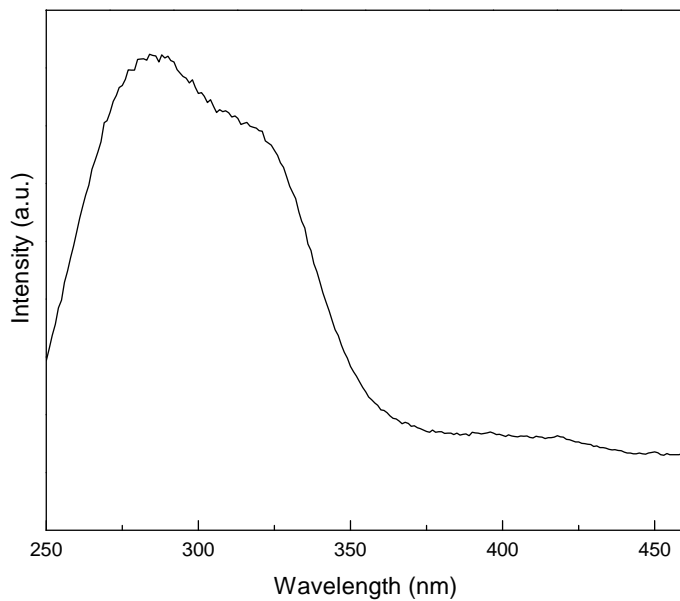


Figure S2. Excitation spectra of dppz-FLG (monitored at 511.0 nm).

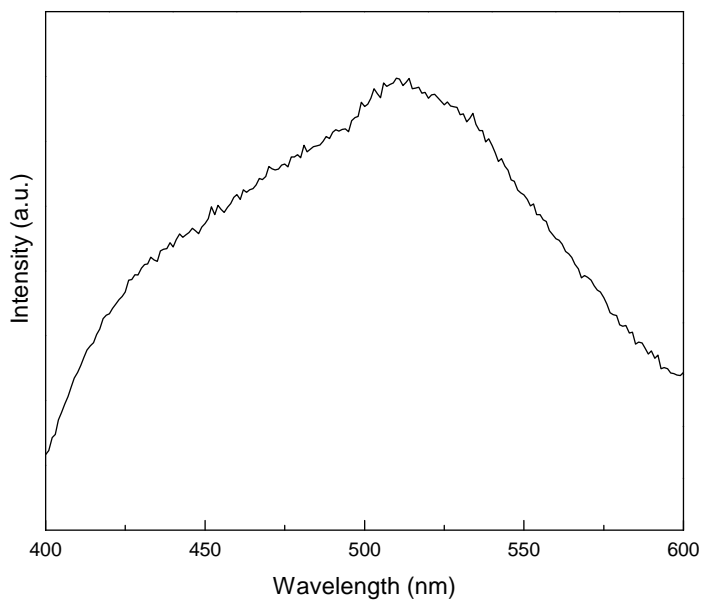


Figure S3. Emission spectra of dppz-FLG (excited at 285.0 nm).

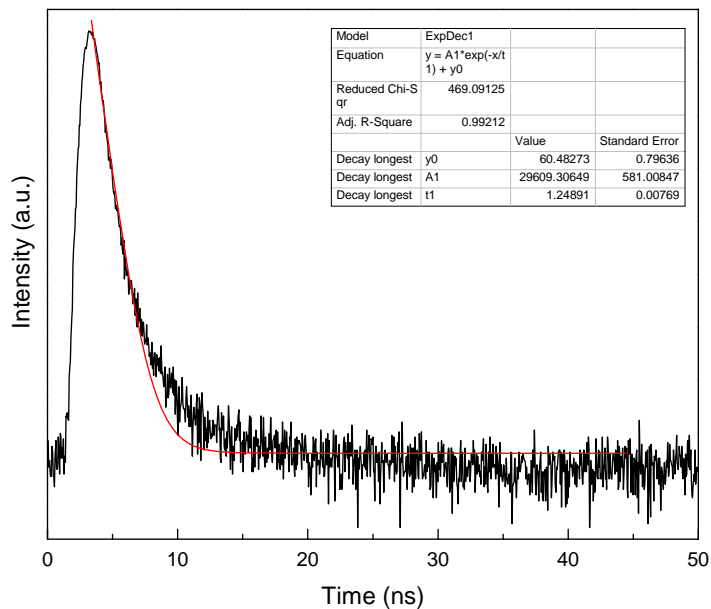


Figure S4. Luminescence decay time for dppz-FLG (excited at 285.0 nm and monitored at 511.0 nm).

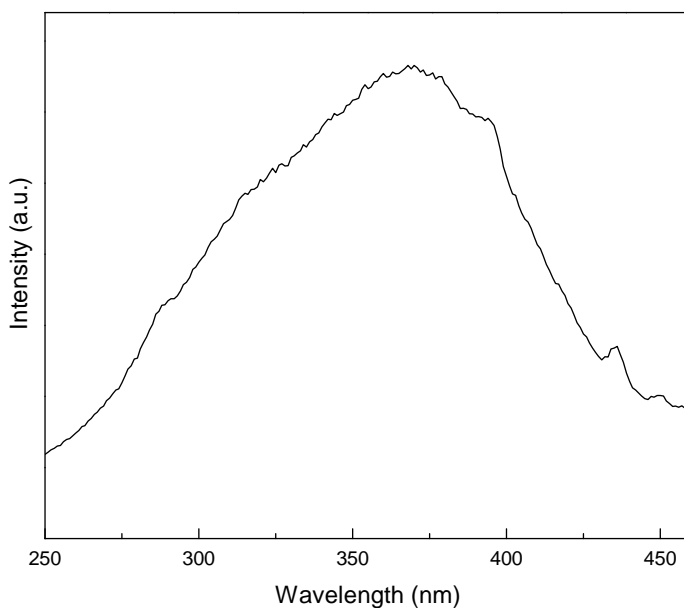


Figure S5. Excitation spectra of dppz-MLG (monitored at 440.0 nm).

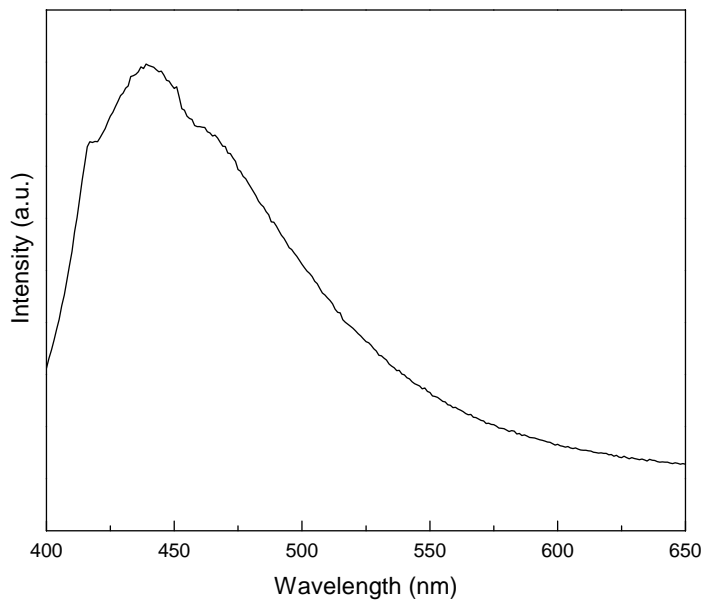


Figure S6. Emission spectra of dppz-MLG (excited at 368.0 nm).

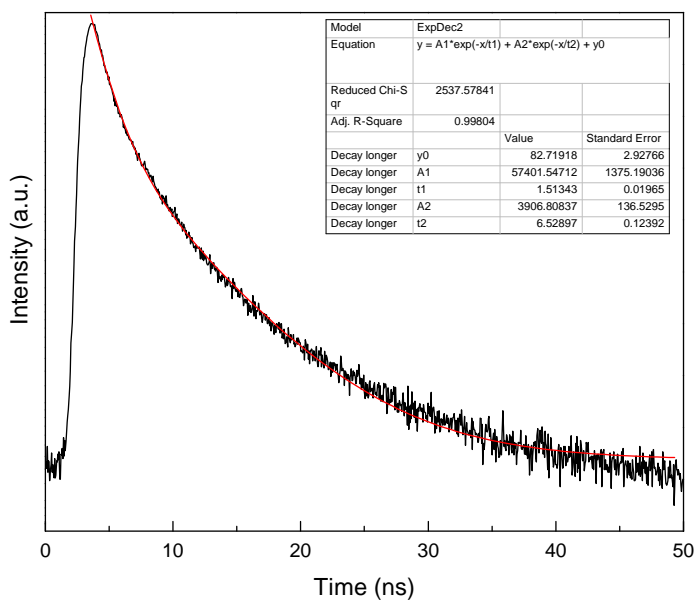


Figure S7. Luminescence decay time for dppz-MLG (excited at 368.0 nm and observed at 440.0 nm).

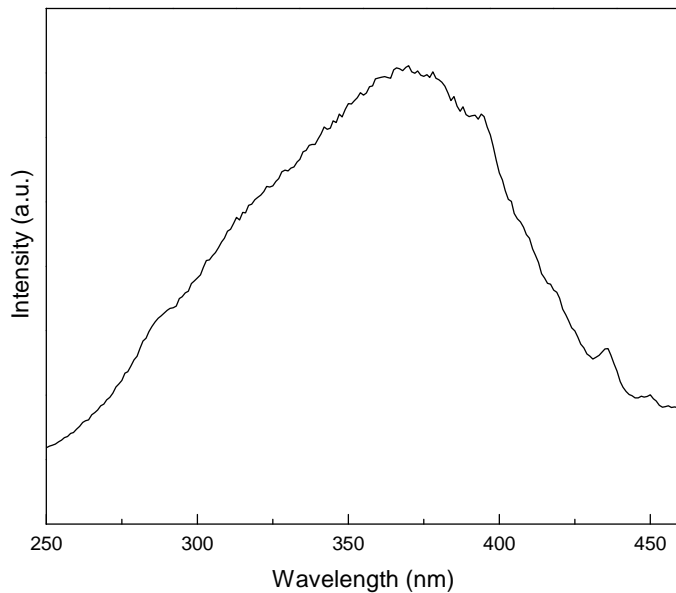


Figure S8. Excitation spectra of dppz-MG (monitored at 440 nm).

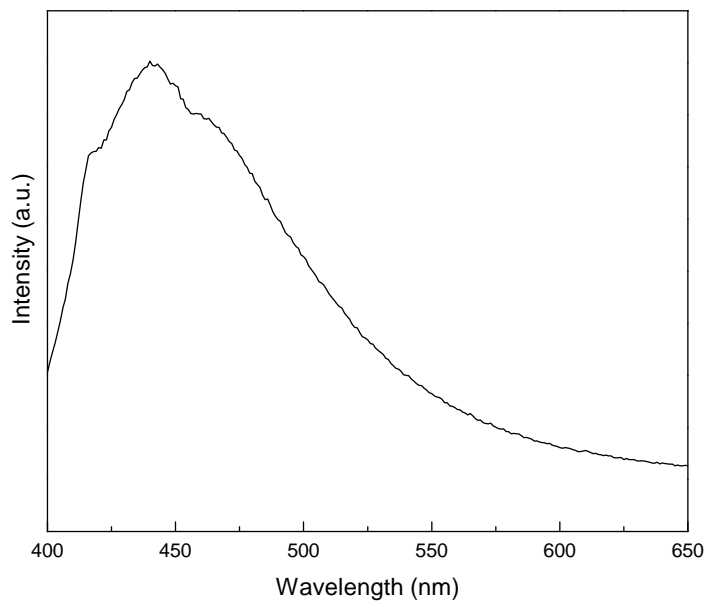


Figure S9. Emission spectra of dppz-MG (excited at 368.0 nm).

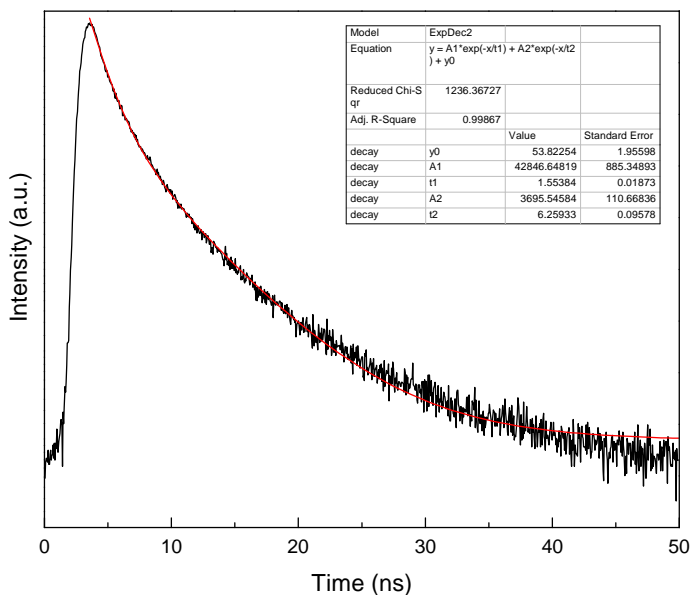


Figure S10. Luminescence decay time for dppz-MG (excited at 368.0 nm and observed at 440.0 nm).

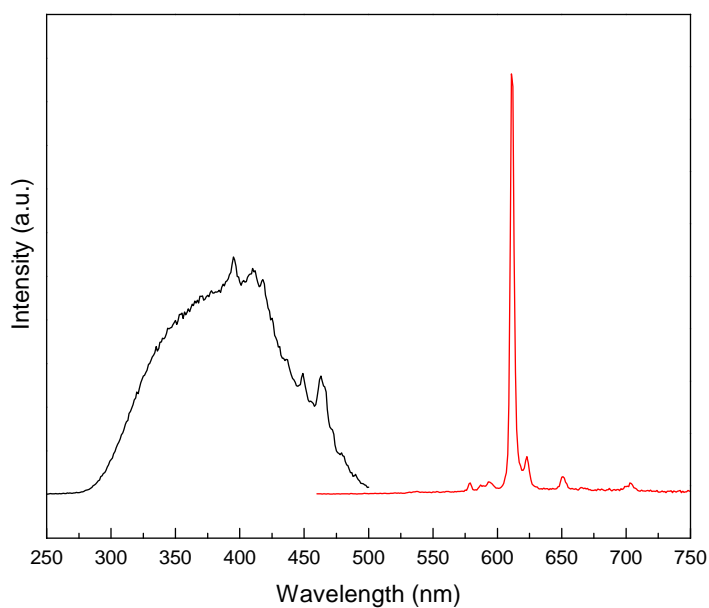


Figure S11. Excitation and emission spectra of $\text{Eu}(\text{dbm})_3(\text{H}_2\text{O})_2$ (excite at 400.0 nm and observed at 612.0 nm).

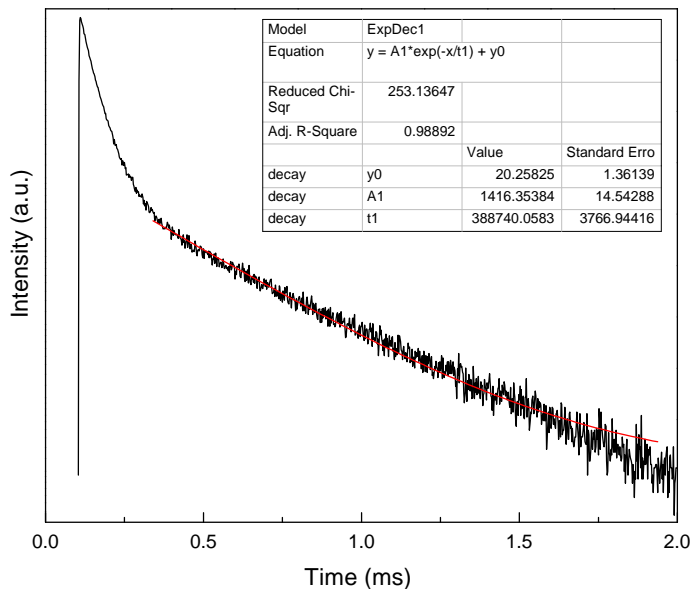


Figure S12. Luminescence decay time for $\text{Eu}(\text{dbm})_3(\text{H}_2\text{O})_2$ (excited at 400.0 nm and observed at 612.0 nm).

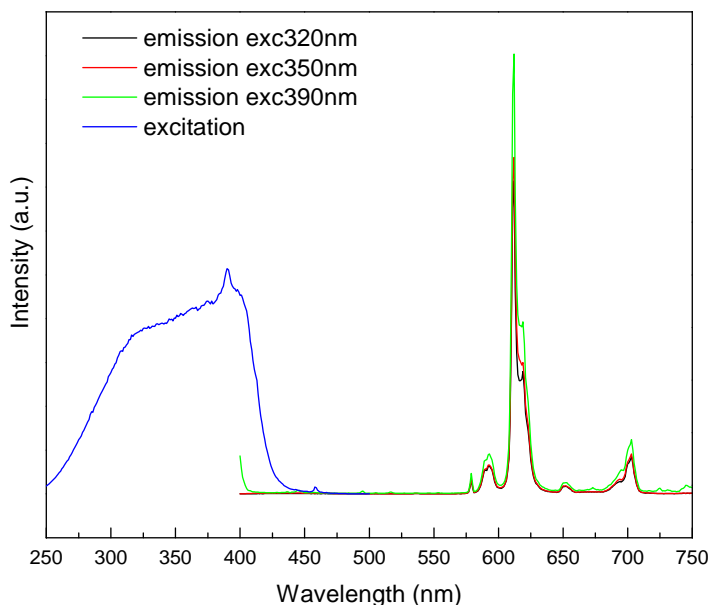


Figure S13. Excitation and emission spectra of $\text{Eu}(\text{dbm})_3@\text{dppz-MLG}$ (excited at 3 different wavelengths: 320.0 nm, 350.0 nm and 390.0 nm and observed at 612.0 nm).

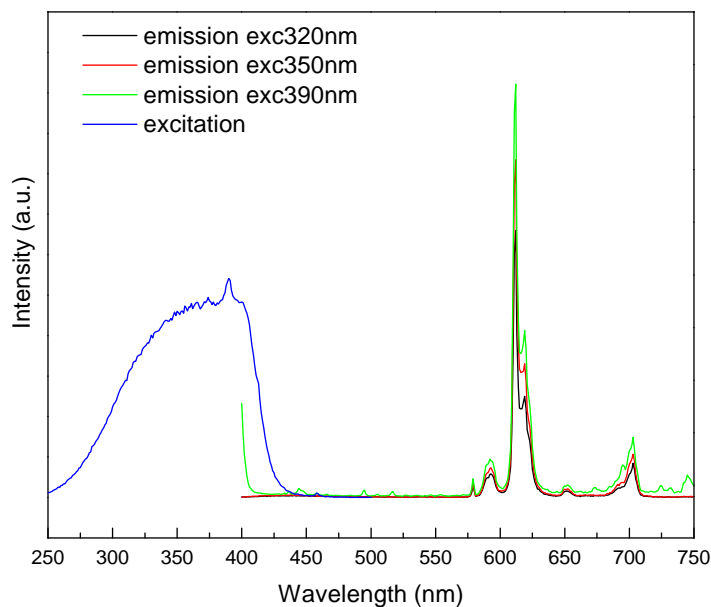


Figure S14. Excitation and emission spectra of $\text{Eu}(\text{dbm})_3@\text{dppz-MG}$ (excited at 3 different wavelengths: 320.0 nm, 350.0 nm and 390.0 nm and observed at 612.0 nm).

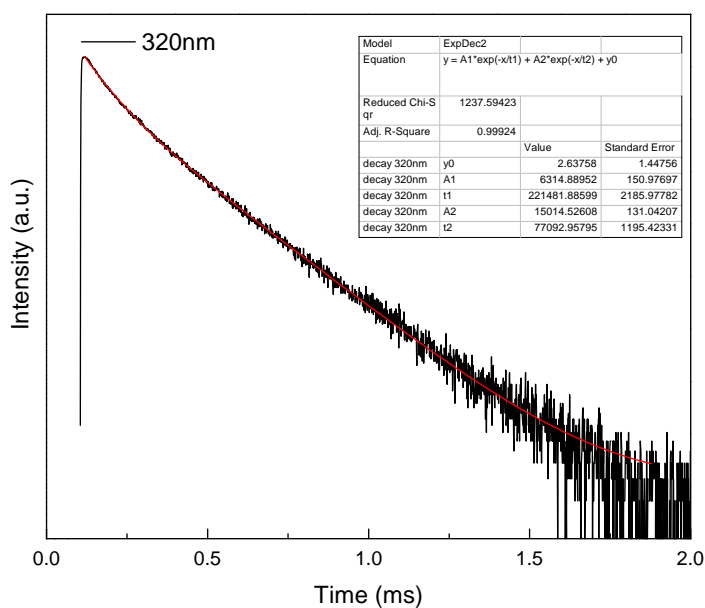


Figure S15. Luminescence decay time for $\text{Eu}(\text{dbm})_3@\text{dppz-FLG}$ (excited at 320.0 nm and observed at 612.0 nm).

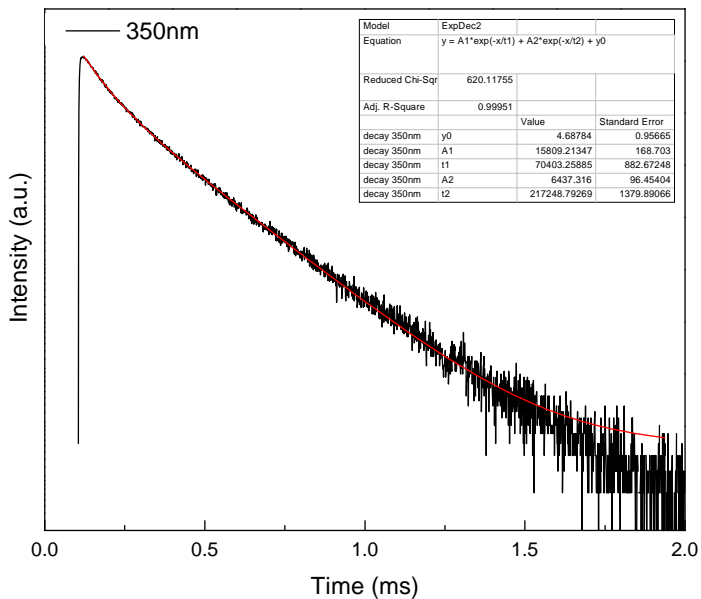


Figure S16. Luminescence decay time for Eu(dbm)₃@dppz-FLG (excited at 350 nm and observed at 612.0 nm).

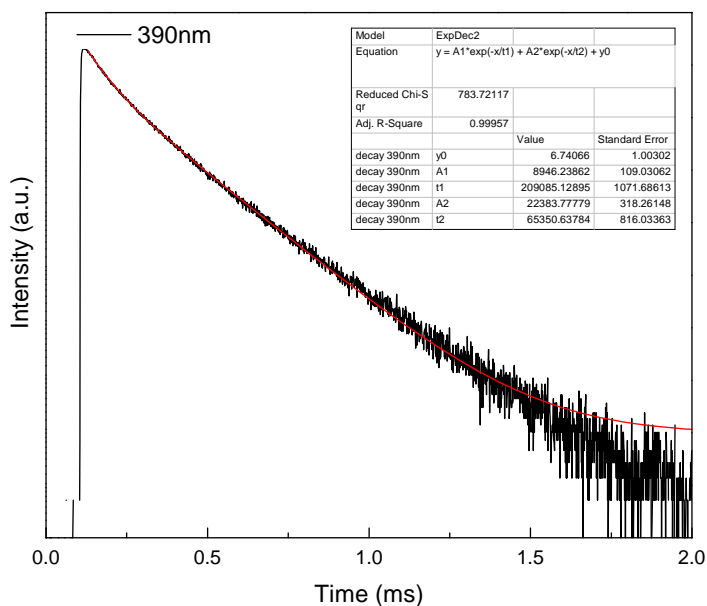


Figure S17. Luminescence decay time for Eu(dbm)₃@dppz-FLG (excited at 390 nm and observed at 612.0 nm).

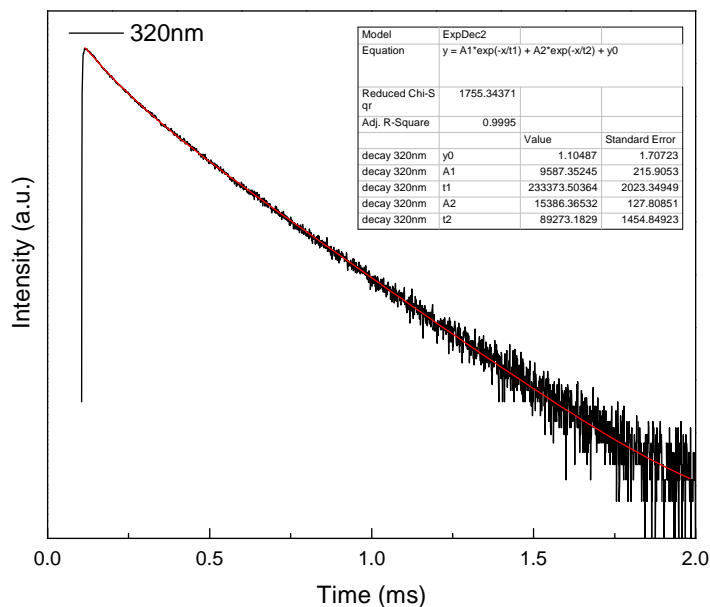


Figure S18. Luminescence decay time for Eu(dbm)₃@dppz-MLG (excited at 320.0 nm and observed at 612.0 nm).

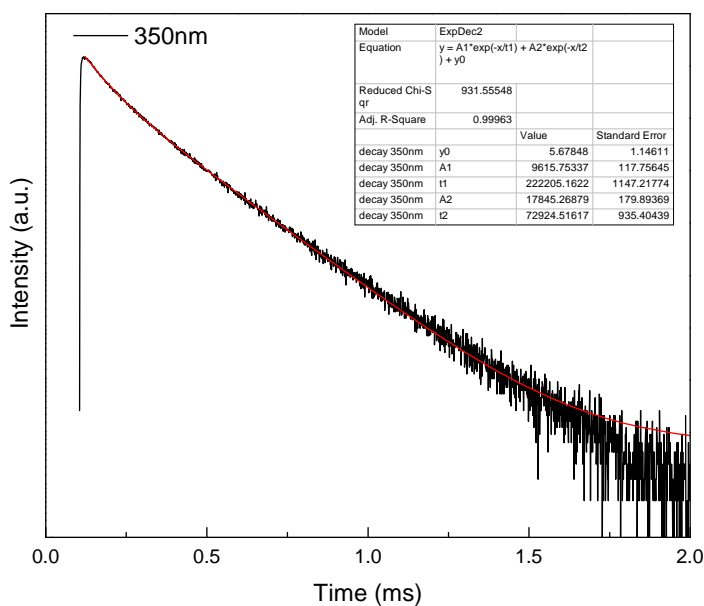


Figure S19. Luminescence decay time for Eu(dbm)₃@dppz-MLG (excited at 350.0 nm and observed at 612.0 nm).

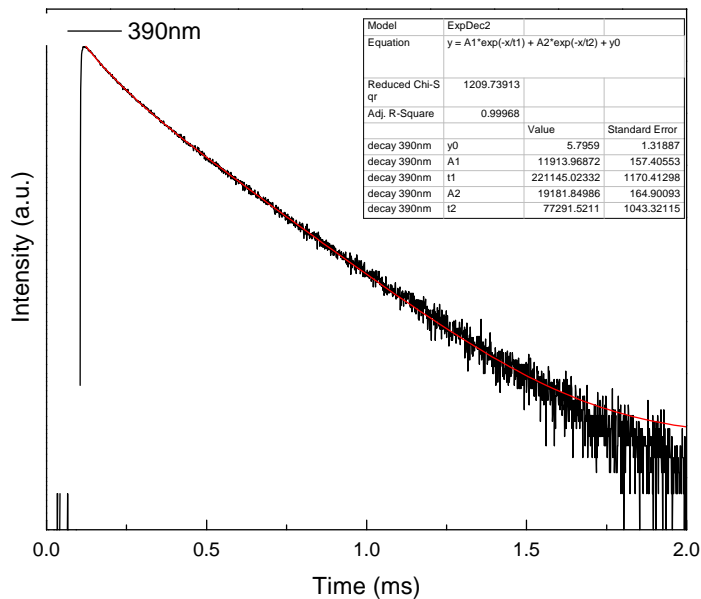


Figure S20. Luminescence decay time for $\text{Eu}(\text{dbm})_3@ \text{dppz-MLG}$ (excited at 390.0 nm and observed at 612.0 nm).

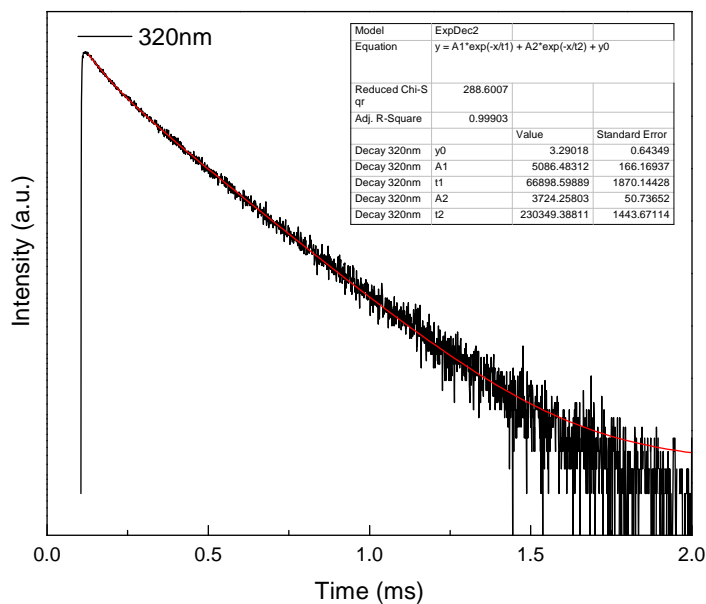


Figure S21. Luminescence decay time for $\text{Eu}(\text{dbm})_3@ \text{dppz-MG}$ (excited at 320.0 nm and observed at 612.0 nm).

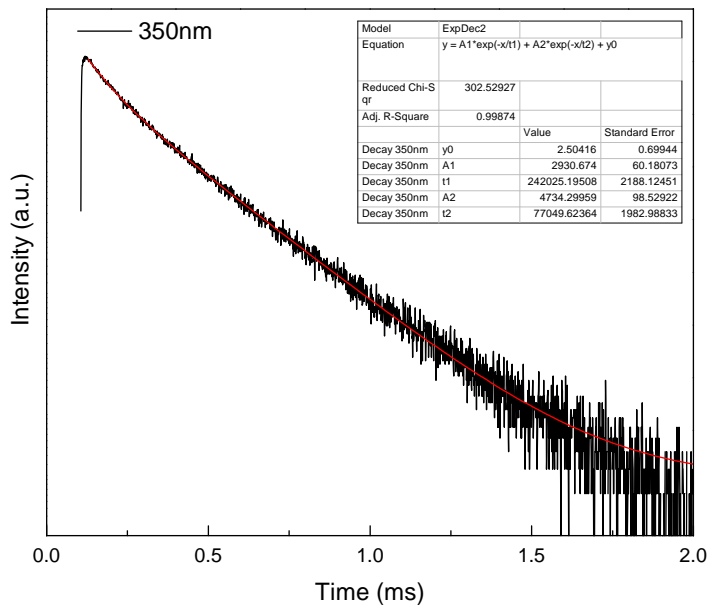


Figure S22. Luminescence decay time for Eu(dbm)₃@dppz-MG (excited at 350.0 nm and observed at 612.0 nm).

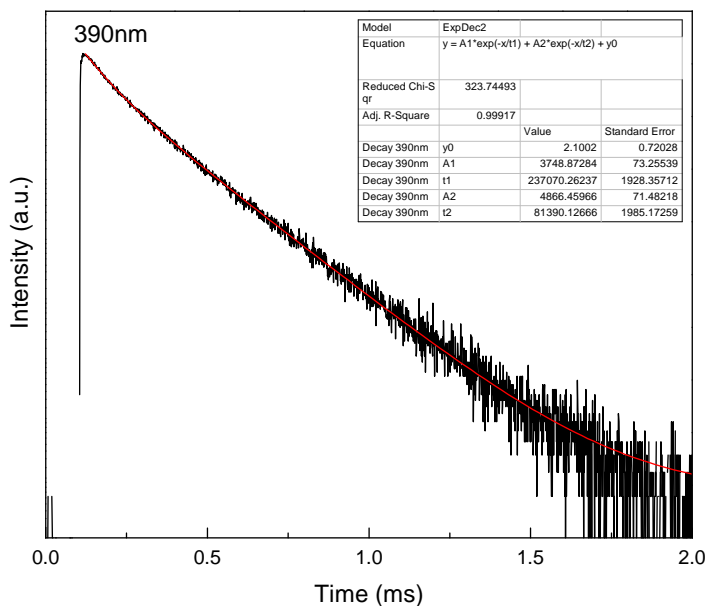


Figure S23. Luminescence decay time for Eu(dbm)₃@dppz-MG (excited at 390.0 nm and observed at 612.0 nm).

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5.3.3. Surface Diels–Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN₄ sites for ORR and OER electrocatalysis

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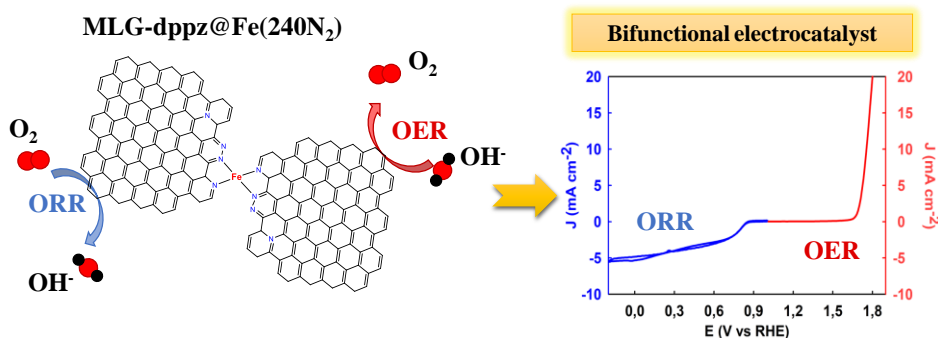
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Published in *Sustainable Energy & Fuels*

Sustainable Energy & Fuels, 2022, vol. 6, no 6, p. 1603-1615

DOI: <https://doi.org/10.1039/D2SE00004K>

Abstract

The assembly of atomically dispersed iron-nitrogen (FeN_4) sites into graphitic structures is a promising approach for sustainable production of bifunctional electrocatalysts for oxygen electroreduction (ORR) and oxygen evolution (OER) reactions. In addition, single-atom FeN_4 sites at the edges of carbon substrates provide higher electrocatalytic performance than those in plane. Unfortunately, the conventional high-temperature pyrolysis method does not allow the generation of edge-enriched FeN_4 single-atom sites. Herein, a novel low-temperature and solvent-free mechanochemical synthesis based on the use of dipyridylpyridazine (dppz) functionalized multilayer graphene as starting material is proposed for precisely engineered location of these FeN_4 active sites at the edges. After carefully characterization of these dppz-based materials, the ORR and OER electrocatalytic performance was investigated, demonstrating the efficient formation of FeN_4 sites at the edges as well as their excellent bifunctional behavior for ORR and OER. This work paves the way for the development of sustainable approaches for the generation of edge-enriched FeN_4 single atom sites on multilayer graphene structures.

Keywords: Multilayer graphene, Diels-Alder functionalization, FeN_4 active site, bifunctional electrocatalyst.

5.3.3.1. Introduction

The growing demand for renewable, clean and sustainable energy to counteract the depletion of fossil fuels and reduce CO₂ emissions as well as mitigate global warming has led the scientific community to focus great attention on the development of low-cost and efficient alternative energy resources and energy storage systems. The plenty of hydrogen in the universe and its relatively easy H₂ gas production from water by electrolysis makes it an ideal energy carrier. However, the use of the electricity from renewable energy sources (such as solar or wind power) to split water into hydrogen, which is subsequently employed in fuel cells, requires the development of efficient and low-cost electrocatalyst materials.¹⁻³

For these reasons, the design of non-noble-metal or metal-free catalysts showing enhanced performance towards the critical reactions involved in these electrocatalytic processes is crucial for the rapid advance of the hydrogen economy.^{4,5} In this sense, highly-active bifunctional electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) are of increasing interest due to their extensive applicability in a wide variety of renewable energy technologies such as rechargeable metal-air batteries, water splitting or reversible fuel cells.⁶⁻¹⁰ To date, Pt- and Ru/Ir-based catalysts are generally regarded as the benchmarked commercial catalysts for ORR and OER reactions, respectively appropriate.¹¹

Carbon-based electrocatalysts are promising materials for the above mentioned electrocatalytic processes, due to their good stability, high surface area, excellent electrical conductivity, and flexibility for the introduction of dopants.^{12,13} Accordingly, a hot topic in electrocatalysis is focused on the appropriate doping of carbon-based materials with heteroatoms (e.g. N, S, P) and transition metals (e.g. Fe or Co) to obtain optimal electronic and geometric structures.¹⁴⁻²¹ More concretely, density functional theory (DFT) calculations suggested that co-doping of Fe and N in the form of possible FeN₄ sites on a graphitic substrate could be as active as Pt for O₂ adsorption and subsequent O=O bond breaking during the ORR.²²⁻²⁵ In this sense, nitrogen-containing functional groups on graphitic matrix also play a fundamental role in the performance and electronic conductivity of electrocatalytic processes.²⁶⁻²⁸ Indeed, the pyridinic-N enhances the potential onset while the graphitic-N greatly improves the limiting current density for ORR in N-doped graphene and N-doped carbon

materials.^{29,30} Furthermore, the pyridinic-N species are responsible for coordinating Fe atoms to generate an FeN₄ bridging structure which, together with the synergistic effect of the graphitic-N active sites, contributes to improve the ORR electrocatalytic activity.^{31–35} On the other hand, DFT calculations have confirmed that graphitic-N species created on N-doped graphene showed a low overpotential and were identified as the optimal active sites for OER electrocatalytic reactions,³⁶ while the reactivity of the coordinated FeN₄ species in carbon-based structures contributes positively by reducing potential barriers and improving the electrocatalytic OER activity.³⁷ In principle, high-performance Fe–N/C electrocatalysts should be designed by arranging N and Fe atoms to form optimal FeN₄ sites uniformly dispersed into graphitic structure.^{38–43}

The preparation of this type of carbon-based materials is mainly based on two different strategies: the template-sacrifice method through metal-organic frameworks^{44–49} and silica support^{50–53} or the built-in FeN₄ active sites on a carbon matrix such as carbon nanotube, graphene or activated carbon.^{54–58} Generally, all of these studies have reported that N-containing carbon materials can be prepared by doping with the use of ammonia, amines or N-containing organic compounds carrying out these processes by simultaneously heat-treating of an iron salt, a nitrogen precursor and a carbon support at high temperature. Consequently, the resulting types of N-sites present in those materials are mostly unpredictable and are characterized a posteriori using different techniques.

In addition, Liu and co-workers suggested in a computational study that the local carbon structure surrounding FeN₄ moiety plays a key role in determining the final catalytic properties, with FeN₄ located at the edge superior to the one in plane.⁵⁹ These results were confirmed experimentally by Xiao et al., who used a self-sacrificed templating approach to obtain enriched-edge FeN₄ sites onto graphitic nanosheets.⁶⁰ Herein, we report a novel strategy based on the use of a dipyridylpyridazine (dppz) functionalized multilayer graphene as starting material for the preparation of carbon derivatives bearing N and edge-enriched FeN₄ sites, employing low-temperature and solvent-free mechanochemical synthesis method. The dppz motifs at the edge of the carbon structure exhibit a rich coordination chemistry and are capable of coordinating a great variety of metal ions due to their similarity to bipyridine-like ligands.^{61–65} The synthesized materials by this method have been characterized and applied as bifunctional oxygen electrocatalysts for ORR and OER reactions.

5.3.3.2. Experimental Section

5.3.3.2.1. Materials

Graphite powder extra fine (GP), 2-pyridinecarbonitrile ($C_6H_4N_2$, 99%), hydrazine hydrate (reagent grade, N_2H_4 50-60 %), acetic acid (CH_3COOH , ReagentPlus, $\geq 99.99\%$), sodium nitrite ($NaNO_2$, ACS reagent, $\geq 97.0\%$), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ, 98%) and sulfuric acid (H_2SO_4 , ACS reagent, 95.0-98.0%) were purchased from Sigma Aldrich. Iron (III) nitrate nonahydrate pure ($Fe(NO_3)_3 \cdot 9H_2O$, 98%) was obtained from PanReac AppliChem. Dichloromethane (CH_2Cl_2 , anhydrous, $\geq 99.8\%$, contains 40-150 ppm amylene as stabilizer), chloroform ($CHCl_3$, anhydrous, $\geq 99\%$, contains 0.5-1.0% ethanol as stabilizer) and ethanol were purchased from Labbox Labware S.L. All the reagents and solvents were used as received without further purification. 3,6-Di(2-pyridyl)-1,2,4,5-tetrazine (dptz) were synthesized by a previously reported procedure.⁶⁴

5.3.3.2.2. Mechanochemical-based synthesis

Synthesis of MLG-dppz: The MLG-dppz material was obtained according to the following experimental procedure, which is a modified synthesis for obtaining multilayer graphene adapted from that previously reported by Amaro et al.⁶¹ 2 g of GP and 0.5 g of dptz (2 mmol) were introduced into a planetary ball mill (Retsch PM100, Retsch GmbH, Haan, Germany). The dry milling process was carried out at 600 rpm with reversal of rotation every 30 min during 24 h. Subsequently, the solid obtained was washed twice at room temperature and at 40 °C with 150 mL of CH_2Cl_2 to remove excess unreacted dptz and then dried at 120 °C under vacuum overnight. After that, the product was aromatized using DDQ with a solid:DDQ weight ratio of 4:1 in 150 mL of $CHCl_3$ for 24 h at room temperature. The solid was washed five times with $CHCl_3$ by successive redispersions to eliminate excess of DDQ. The resulting material, named MLG-dppz, was dried under vacuum at 120 °C overnight. Further details about the Diels-Alder reaction between 3,6-di(2-pyridyl)-1,2,4,5-tetrazine and different graphene-based materials with several activation processes and reaction times were previously reported.⁶¹

Synthesis of MLG-dppz@Fe. For the preparation of MLG-dppz@Fe, 2 g of MLG-dppz and excess amount of $Fe(NO_3)_3 \cdot 9H_2O$ (0.404 g, 1 mmol) were reacted by dry ball milling process (Retsch PM100, Retsch

GmbH, Haan, Germany) at 600 rpm with reversal of rotation every 30 min during 24 h. After this process, the solid was washed with a 0.1 M H₂SO₄ solution to remove excess unreacted iron salt. The dispersion was filtered and then washed several times with distilled water. Finally, the material was dried at 120 °C under vacuum overnight.

Synthesis of MLG-dppz(240N₂). MLG-dppz (1 g) was subjected to a pyrolysis treatment in a tubular furnace (Carbolite Gero CTF, Parsons Lane, Hope Valley, UK) at 240 °C under a nitrogen atmosphere using a heating ramp of 10 °C·min⁻¹ for 1 h. The pyrolyzed sample was named MLG-dppz(240N₂).

Synthesis of MLG-dppz@Fe(240N₂). MLG-dppz@Fe (0.8 g) was treated under the same heating conditions as the MLG-dppz(240N₂) obtaining the material MLG-dppz@Fe(240N₂).

Synthesis of MLG-dppz@Fe(240air). MLG-dppz@Fe (0.8 g) was subjected to a thermal treatment in a tubular furnace (Carbolite Gero CTF, Parsons Lane, Hope Valley, UK) at 240 °C under an air atmosphere using a heating ramp of 10 °C·min⁻¹ for 1 h. The resulting material was named MLG-dppz@Fe(240air).

5.3.3.2.3. *Characterization*

Iron loadings in MLG-dppz@Fe based materials were quantified by ICP-MS analysis in an ICP Mass Spectrometer model NexION™ 350X, PerkinElmer Inc. The analytical procedure was carried out dissolving 1 mg of MLG based materials in a mixture of 200 mL of 69 % HNO₃ (Merck, Suprapur), 50 mL of 30 % H₂O₂ (Fluka, TraceSELECT@Ultra), 20 mL of 40 % HF (Merck, Suprapur) and Milli-Q ultrapure water up to a total volume of 5 mL using an Ultrawave Single Reaction Chamber Microwave Digestion System, Milestone Inc. at 1500 W and temperature up to 220 °C. The nitrogen content was determined by CHNS elemental analysis in an elemental analyzer TruSpec Micro CHNS, LECO. In a typical experimental, 2 mg of material were combusted with pure oxygen at a maximum temperature of 1050 °C and the products were analyzed by means of an infrared cell (CO₂, H₂O and SO₂) or a thermal conductivity cell (N₂). The samples morphology was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM images were recorded on a JEOL JEM-1400 transmission electron microscope operated at an accelerating voltage of 120 kV. Samples were ultrasonically

dispersed in isopropanol and subsequently deposited on holey carbon films supported on copper grids (Agar Scientific Ltd). JEOL JSM-7800F scanning electron microscope was used to obtain SEM images. X-Ray Diffraction (XRD) patterns were recorded on a BrukerD8 Discover A25 X-ray diffractometer by using filtered Cu K α radiation within a 2 θ angle range between 5° and 80° at a rate of 1.05 s per step with a step size of 0.04° in continuous mode. Thermogravimetric analysis (TGA) was performed in a Mettler Toledo TGA/DSC equipment (Mettler-Toledo, Columbus, OH, USA) under nitrogen or oxygen atmosphere, heating the samples from 30 to 900 °C at 10 °C·min⁻¹. Raman spectra were recorded in a Renishaw Raman instrument (InVia Raman Microscope) equipped with a Leica microscope and a Renishaw CCD Camera (578x400) using a green laser light excitation source (532 nm). A total of 20 scans per spectrum were acquired to improve the signal-to-noise ratio, 10 s of exposure time and laser power of 10 % over the maximum provided. Specific surface areas, pore sizes and pore volumes were examined from the N₂ adsorption–desorption isotherms with an Autosorb iQ/ASiQwin (Quantachrome Instruments, Boynton Beach, FL, USA). The samples were previously outgassed under vacuum at 120 °C overnight. X-ray photoelectron spectroscopy (XPS) was performed on a SPECS mod. PHOIBOS 150 MCD spectrometer using monochromatic Mg K α radiation and a multichannel detector. Previously, the samples were outgassed under vacuum in an ultra-high vacuum (UHV) multipurpose surface analysis system SpecsTM. All spectra were fitted to Gauss–Lorentz curves to adequate identification of the different functional groups and iron oxidation states in each material. The charging effect was corrected by taking the adventitious carbon to 284.8 eV as a reference. High resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging was performed on a double aberration corrected (AC), monochromated, FEI Titan3 Themis 60–300 microscope operated at 300 kV.

5.3.3.2.4. *Electrocatalytic measurements*

Both ORR and OER electrochemical activities of the different synthesized MLG-dppz electrocatalyst materials and its constituent components were evaluated by a Potentiostat/Galvanostat (EmStat 3, PalmSens electrochemical analyzer) using a three-electrode configuration. A graphite sheet and an Ag/AgCl electrode were used as counter and reference electrodes, respectively. Whilst a glassy carbon (GC) disk of 5

mm in diameter (Pine Instruments Company) was used as the working electrode. A water dispersion of 5 mg·mL⁻¹ of sample concentration was prepared and sonicated for 15 min. Pt/C sample (10 % wt. Pt) was prepared in a similar manner (i.e. without Nafion). Then, 25 μL of the latter suspension was drop-casted onto the clean surface of the GC and was dried slowly overnight at room temperature. The ORR electrocatalytic measurements were conducted in N₂ or O₂ saturated 0.5 M KOH electrolyte, whilst the OER measurements were performed in 0.5 M KOH under air conditions. Current densities were normalized according to the geometric surface area of GC. OER potentials (vs. Ag/AgCl) were calibrated with reference to the reversible hydrogen electrode (RHE) using the Nernst equation.^{66–68}

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.1976 + 0.059 \text{ pH} \quad (1)$$

ORR analyses were performed by cyclic voltammetry (CV). For this, room temperature electrochemical measurements were recorded in the potential range from 0.00 to -1.2 V (vs. Ag/AgCl) at a scan rate of 10 mV·s⁻¹, and under static or dynamic conditions. The different rotation rates used were from 250 to 2500 rpm. The ORR kinetics parameters were analyzed using Koutecky-Levich (K-L) equations:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_k} \quad (2)$$

$$J_k = nFkC_0 \quad (3)$$

$$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6} = B^*n \quad (4)$$

where J is the measured current density, J_k and J_L are the kinetic and diffusion limiting current densities, respectively, at 0.0 V vs. RHE, ω is the electrode rotation rate, n is the overall number of electrons transferred in oxygen reduction, F is the Faraday constant, C_0 is the bulk concentration of O₂ dissolved in the electrolyte (1.03·10⁻³ mol·L⁻¹ for 0.5 M KOH), D_0 is the diffusion coefficient of O₂ (1.63·10⁻⁵ cm²·s⁻¹ for 0.5 M KOH), ν is the kinematic viscosity of the electrolyte (0.01 cm²·s⁻¹ for 0.5 M KOH), and k is the electron transfer rate constant during ORR. B^* is a constant (2.76·10⁻² A·cm⁻²·rpm^{-1/2}) for all the performed experiments.^{117,118}

For OER analyses, linear-sweep voltammetry (LSV) was performed. These measurements were recorded using a scan rate of 2 mV·s⁻¹

¹ and a rotation rate of 1600 rpm. Tafel slope was determined to further analyse the mechanism and kinetics of the OER rate-determining step. The analysis of the number of active sites of the different materials was inferred through the electrocatalytic surface area (ECSA), which is proportional to some previously reported cases.¹¹² Typically, several cyclic voltammograms (CVs) were measured in a narrow potential window of -0.717 V to -0.817 V vs. RHE (i.e., where no faradaic reactions occurred) at different scan rates, from 12 to 48 mV·s⁻¹ at an interval of 4 mV·s⁻¹. Sequentially, the slope of the resulting line (areal capacitance) for plotting the scan rate (X axis) against the J anodic-J cathodic (at -0.767 V vs. RHE – Y axis) was proportional to the ECSA. In addition, electrochemical impedance spectroscopy (EIS) was performed to analyse the charge-transfer resistance (R_{ct}) of the different MLG-dppz samples, aiming to identify the synthesized material with the most efficient charge transport (i.e., lower R_{ct} value).

5.3.3.3. Results and discussion

In a previous study, we reported a ball-milling synthetic procedure (i.e. a mechanochemical synthesis method) starting with graphite powder and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine to produce a dipyridylpyridazine derived multilayer graphene, MLG-dppz.⁶¹ This synthetic process involved a Diels-Alder cycloaddition between such tetrazine as an electron-deficient diene and the carbon-carbon double bonds on the edges of the graphene sheets as dienophiles. The initial adduct underwent a retro-Diels-Alder reaction with release of N₂, thus resulting in a dihydropyridazine adduct that is subsequently dehydrogenated to the corresponding pyridazine by the action of the oxidizing agent 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The dipyridylpyridazine adducts on the edges of the graphene sheets can act as ligands for the coordination of metals. Coordinated iron sites have received much attention in recent years due to their applicability as catalysts in the energy field in substitution of expensive noble metal catalysts, mainly consisting of platinum.⁶⁶⁻⁶⁹ Accordingly, Fe(III) nitrate was contacted with MLG-dppz to produce MLG-dppz@Fe, whose structure is tentatively proposed in **Fig. 1** by analogy to iron-bipyridine complexes, which have been used for the activation of dioxygen to oxygenate unsaturated hydrocarbons.^{70,71} Thermal treatment of MLG-dppz@Fe at 240°C under a nitrogen or air atmosphere gave MLG-dppz@Fe(240N₂) and MLG-dppz@Fe(240air), respectively, whose structures are also represented in **Fig. 1**. Under these conditions, the formation of N-quaternary and

tetracoordinated iron sites occurs in the graphene sheets (*vide infra*). The MLG-dppz material subjected to heat treatment at 240°C under nitrogen atmosphere, and so without Fe atoms, MLG-dppz(240N₂), was synthesized as a reference material to analyse the structural changes that take place in the different steps of the synthetic route.

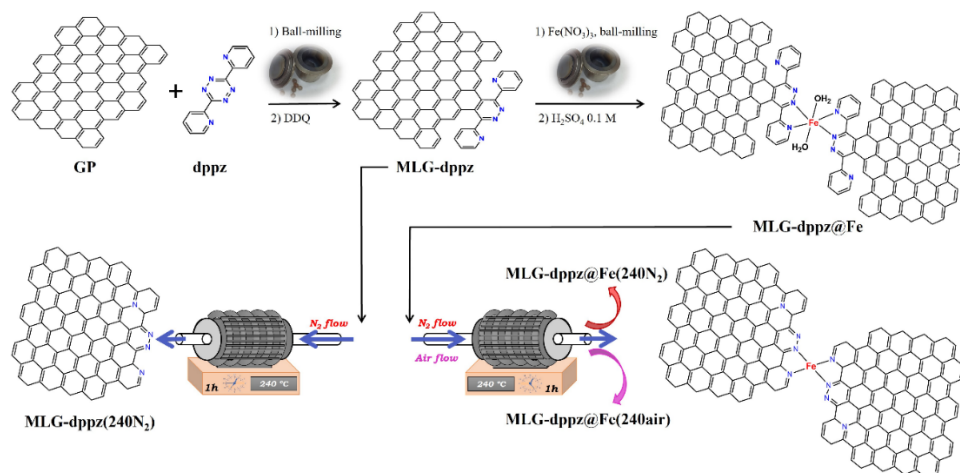


Fig. 1 Schematic diagram for the synthetic route for the preparation of MLG-dppz materials and tentative structures.

TGA analyzes were performed for MLG-dppz and MLG-dppz@Fe confirming the thermal stability of these materials at temperatures above 240 °C (**Fig. S1**). XRD spectra of the sample MLG-dppz@Fe(240N₂) exhibited the same diffraction pattern as the starting graphite powder (**Fig. S2**) showing a strong peak at ca. 26.5°, which corresponds to the (002) graphite reflection plane and four weak peaks over 42.0°, 43.5°, 54.5° and 77.0°, attributed to the (100), (101), (004) and (110) reflections.^{72–75} However, the intensity of the peak corresponding to the (002) plane decreased significantly for MLG-dppz@Fe(240N₂) compared to the pristine graphite powder, denoting exfoliation of the starting graphite to multilayer graphene.⁷⁶

The multilayered structure composed of numerous individual graphene sheets was corroborated by TEM images at different magnifications (**Fig. S3**), confirming the effectiveness of the mechanochemical synthesis process to obtain multilayer graphene with sheet average size of approximately 200 nm.^{61,77,78}

Elemental analysis of the five samples gave the C, H and N contents while the amount of Fe incorporated in these materials was quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (**Table 1**). The N content ranged between 1.3 and 2.2 wt.% whereas the Fe content was ca. 0.7 wt.%. Thus, the N/Fe molar ratio was ca. 8 in materials MLG-dppz@Fe, MLG-dppz@Fe(240N₂) and MLG-dppz@Fe(240air), in accordance with the coordination of one Fe atom to two dipyridylpyridazine units at the edges of two different graphene sheets forming FeN₄-like sites, as represented in **Fig. 1**.

Table 1 Elemental composition of synthesized MLG-dppz materials and N/Fe molar ratio.

Sample reference	wt.% C	wt.% H	wt.% N	wt.% Fe	N/Fe molar ratio
MLG-dppz	81.97	0.19	2.18	-	-
MLG-dppz@Fe	87.31	0.24	1.61	0.76	8.4
MLG-dppz(240N ₂)	87.85	0.15	1.85	-	-
MLG-dppz@Fe(240N ₂)	89.45	0.20	1.48	0.73	8.1
MLG-dppz@Fe(240air)	86.83	0.19	1.35	0.69	7.8

The surface area and pore structure of graphene-based materials play a significant role in the electrochemical behaviour for ORR and OER reactions.^{14,79,80} Thus, N₂ adsorption/desorption isotherms of all materials were measured (**Fig. S4**). All isotherms exhibited a hysteresis loop characteristic of type IV isotherms in the Brunauer-Deming-Deming-Teller (BDDT) classification, which is typical of mesoporous solids. The pore size distribution analyzed by the DFT model is shown in **Fig. S5**. As observed, the thermal treatment favored the appearance of micropores. Specifically, it has been reported to be beneficial for the isolation of FeN₄ sites by preventing aggregation phenomena.⁸¹ Brunauer-Emmett-Teller (BET) surface area, pore volume and pore diameter are given in **Table S1**. These data demonstrated that the incorporation of Fe atoms in the graphene structure promoted an increase in surface area (ca. 100 m²·g⁻¹) and pore volume (ca. 0.2 cm³·g⁻¹),⁸² as a result of the porous structure generated by formation of FeN₄ sites, as observed by SEM microscopy (**Fig. S6**).⁸³ A high specific surface area provides more exposed active sites to promote electrocatalytic processes, while abundant mesopores together with a slight

contribution of micropores favour the penetration of electrolytes to the catalytic centers and the effective mass transfer of the reaction intermediates.⁸⁴

Raman spectroscopy was carried out to obtain further structural information of these materials, allowing to analyze the degree of graphitization. **Fig. 2** shows typical Raman spectra of graphitic materials highlighting two main bands centered at 1350 cm^{-1} and 1580 cm^{-1} that are commonly referred to as D-band and G-band. The D-band is attributed to the disorder degree of graphite-based materials promoted by several factors such as structural defects on the graphene sheets, the discontinuity at the edges of the graphitic planes and the functionalization reactions on the sp^2 carbon bonds. Instead, G- band corresponds to the first-order Raman scattering of E_{2g} phonon mode in the Brillouin zone for sp^2 hybrid carbon atoms and represents the degree of crystallinity for materials with graphitic structure.^{74,85,86} Accordingly, the relative intensity ratio of the D and G peaks (I_D/I_G) provides a quantitative analysis of the structural disorder of these materials, revealing the structural changes that have taken place in each of the synthesis steps. The I_D/I_G values increased from 0.24 for the starting graphite to 0.35 for the MLG-dppz material functionalized by the Diels-Alder reaction. Following the procedure reported by J. N. Coleman et al. to measure flake thickness of exfoliated graphene by Raman spectroscopy based on the shape and intensity of the 2D band,⁸⁷ the number of sheets in MLG-dppz was 8. Accordingly, this material can be classified as multilayer graphene according to the nomenclature proposed by R. H. Hurt.⁸⁸ The incorporation of Fe atoms (MLG-dppz@Fe) or the thermal treatment (MLG-dppz(240N₂)) increased the degree of structural disorder with I_D/I_G values of 0.40 and 0.47, respectively. The level of defects in the graphitic structure was more accentuated in those materials with coordinated Fe subjected to a subsequent thermal treatment at 240 °C. The highest I_D/I_G ratio value of 0.67 was obtained for MLG-dppz@Fe(240N₂). Therefore, this material has a greater number of defects that are considered potentially conducive to promoting crucial mass transfer phenomena in the ORR electrocatalytic process.^{84,89} Additionally, the exposure of more edged planes and thus more nitrogen binding sites that result in the formation of more FeN_4 sites suggests a potential improvement of its ORR electrocatalytic performance.^{85,90} This argument is corroborated by elemental analysis, which accounted for a higher content of N and Fe in MLG-dppz@Fe(240N₂) than in MLG-dppz@Fe(240air).

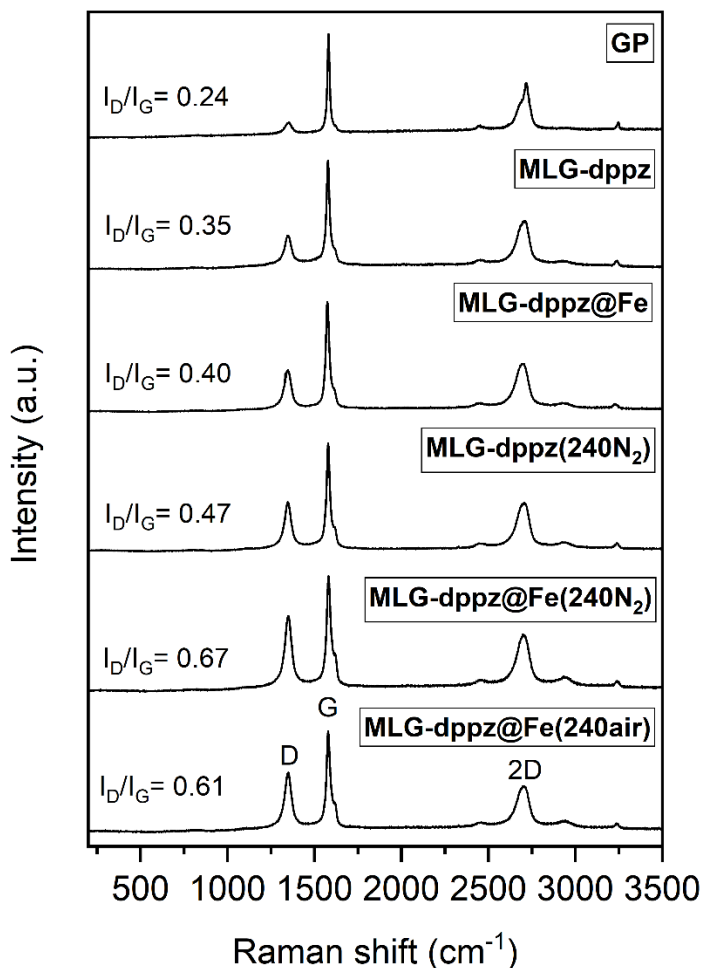


Fig. 1 Raman spectra of the different materials.

The evolution of the chemical changes produced in the different stages of the synthetic route was analyzed by X-ray photoelectron spectroscopy (XPS). C1s high-resolution XPS spectra of the different materials were deconvoluted into six components (**Fig. S7**). The contributions and binding energies of each component used in the fitting of the C1s photoemission peak are given in **Table S2**. All materials gave similar contributions. The main one (ca. 70%) corresponded to C=C (sp² centers) and C-C (sp³ centers) bonds, whose deconvoluted peak was fitted to the adventitious carbon signal at 284.8 eV. The contribution at 285.8 eV was assigned to C-N bonds (ca. 11%), mainly from pyridinic and N-graphitic species. The carbon-oxygen functional groups had a lower contribution and appeared at higher binding energies, i.e. 286.7, 287.8 and

289.1 eV associated with C-O (ca. 7%), C=O (ca. 5%) and O-C=O (ca. 4%) groups, respectively. The contribution at 291.0 eV was assigned to satellite π - π^* transitions (ca. 3.5%).

Several studies have reported that the formation of FeN₄ active site bridging structures linked through two adjacent graphitic sheets is feasible at high temperature mainly due to the presence of pyridine and graphitic (quaternary) nitrogen heteroatoms.^{90,91} The HR-XPS spectra of N1s (**Fig. 3**) provided the detailed analysis of the structural nitrogen evolution for each material.

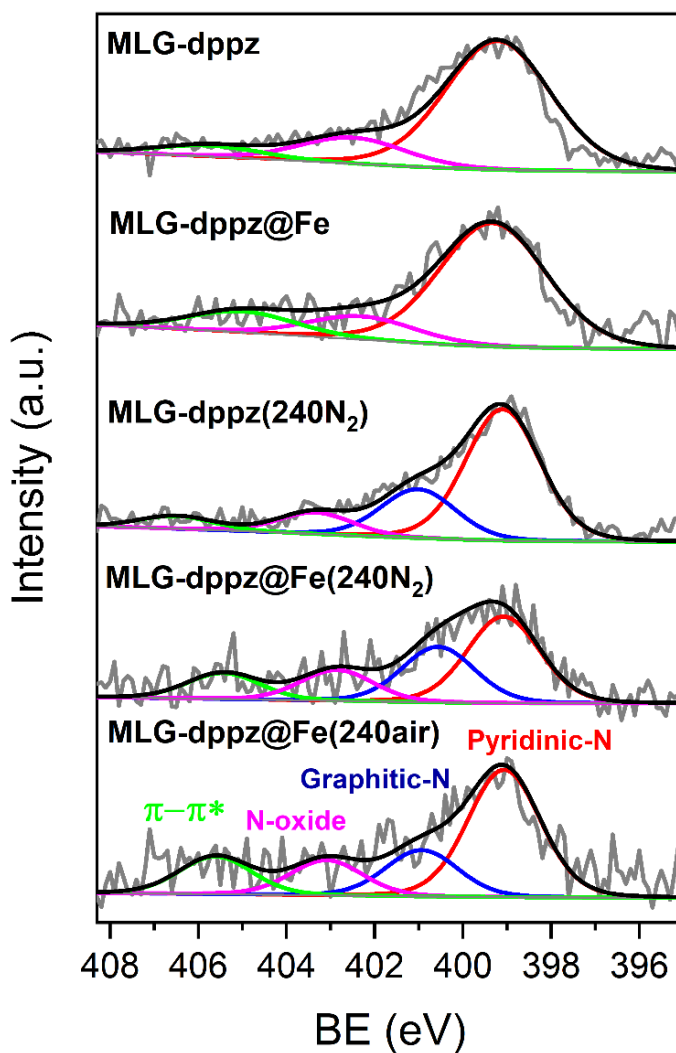


Fig. 2 N1s HR-XPS spectra of the different materials.

The N1s signal of MLG-dppz was fitted into three components. The main contribution centered at 399.2 eV was assigned to N in the pyridine and pyridazine rings because both contributions show the same signal after Diels-Alder reaction between graphite and dptz, in agreement with previous studies.^{61,92} The two remaining lower intensity decomposed bands were assigned to N-oxide groups (402.5 eV) and π - π^* transitions (405.7 eV) from aromatic rings and unsaturated bonds.^{93,94} The coordination of Fe atoms in MLG-dppz@Fe did not produce any significant change in the N1s signal. Nevertheless, the thermal treatment at 240 °C undergone by samples MLG-dppz(240N₂), MLG-dppz@Fe(240N₂) and MLG-dppz@Fe(240air) led to a new component in the N1s signal at ca. 401.0 eV, which can be assigned to graphitic-N (quaternary-N).⁹⁵ This graphitic-N must be generated by an oxidative cyclodehydrogenation promoted by heating (**Fig. 1**). The contribution of each component to the N1s signal is given in **Table 2**.

Table 2 Contribution of the four components used in the fitting of the N1s photoemission peak.

<i>N1s</i>	<i>MLG-dppz</i>		<i>MLG-dppz@Fe</i>		<i>MLG-dppz(240N₂)</i>		<i>MLG-dppz@Fe(240N₂)</i>		<i>MLG-dppz@Fe(240air)</i>	
	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %
Pyridinic-N	399.2	77.8	399.3	77.2	399.1	61.3	399.1	43.5	399.1	51.7
Graphitic-N	-	-	-	-	401.0	22.8	400.6	28.0	400.9	18.8
N-oxide	402.5	15.6	402.3	13.9	403.3	10.0	402.9	15.5	403.1	14.3
π - π^*	405.7	6.6	405.0	12.5	406.5	5.9	405.4	13.1	405.6	15.3

The pyridinic to graphitic N ratio was 2.7 for both MLG-dppz(240N₂) and MLG-dppz@Fe(240air) whereas it was 1.5 for MLG-dppz@Fe(240N₂). A high content of pyridinic-N and graphitic-N is considered a key factor to improve the ORR and OER electrocatalytic performance.^{37,96,97} Accordingly, MLG-dppz@Fe(240N₂), which has the highest content of graphitic-N and iron atoms as well as a large contribution of pyridinic-N (**Table 2**), could be a promising bifunctional catalyst in ORR and OER applications. MLG-dppz@Fe(240air) will be useful to analyze the

slight increase in pyridinic-N and the lower graphitic-N contribution and iron percentage.

The HR-XPS Fe2p spectra are shown in **Fig. 4**. The core-level Fe2p XPS spectra of MLG-dppz@Fe was deconvoluted into three peaks: Fe2p_{3/2} and Fe2p_{1/2} regions at 712.5 eV and 725.8 eV, respectively, assigned to Fe(III) formal oxidation state, and the characteristic Fe³⁺ 2p_{3/2} satellite peak centered at 719.1 eV, in agreement with previously reported works.^{98–103} Fe2p XPS spectra of MLG-dppz@Fe(240N₂) and MLG-dppz@Fe(240air) were fitted into five characteristic contributions (Fe²⁺ 2p_{3/2}, Fe³⁺ 2p_{3/2}, satellite peak, Fe²⁺ 2p_{1/2}, Fe³⁺ 2p_{1/2}). The generation of Fe²⁺ species and the binding energies at ca. 711 and 715 eV, respectively, for the Fe²⁺ 2p_{3/2} and Fe³⁺ 2p_{3/2} signals, similar to those reported in the literature, confirmed the formation of FeN₄ sites in these materials.^{84,104,105}

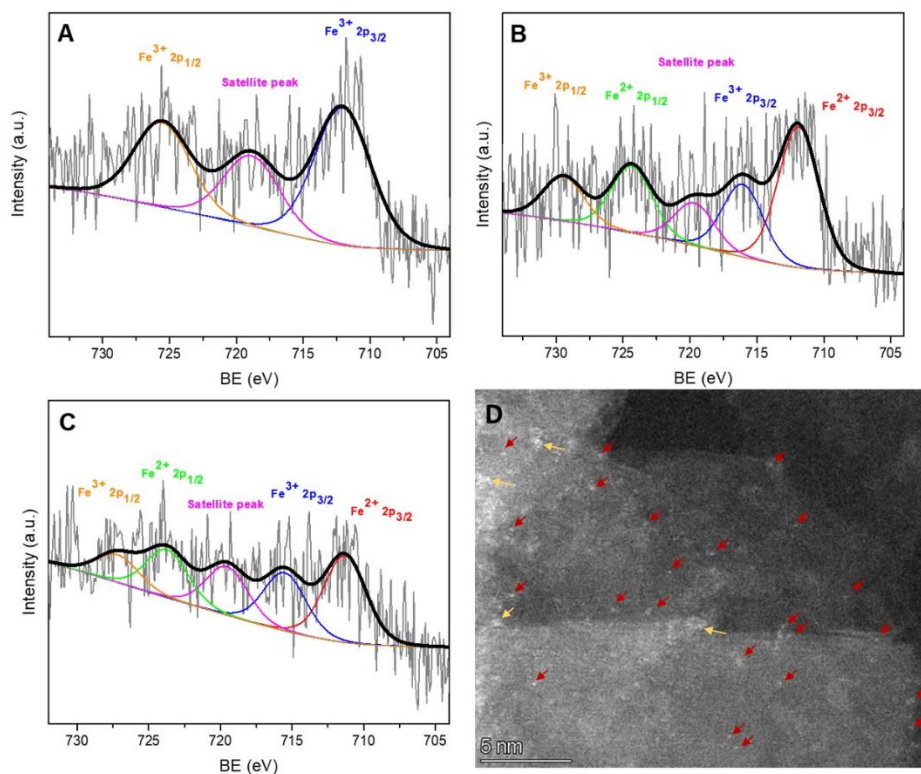


Fig. 4 Fe 2p HR-XPS spectra of (A) MLG-dppz@Fe, (B) MLG-dppz@Fe(240N₂) and (C) MLG-dppz@Fe(240air). (D) Aberration corrected HAADF-STEM image of sample in (B).

Clearly, the generation of reduced Fe^{2+} species was a consequence of the heat treatment at $240\text{ }^\circ\text{C}$.¹⁰⁶ The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was 1.8 and 1.6 for $\text{MLG-dppz@Fe(240N}_2)$ and $\text{MLG-dppz@Fe(240air)}$, respectively. The lower fraction of Fe^{2+} in the latter can be explained by the use of an oxidizing atmosphere during the heat treatment. In fact, FeCl_3 -mediated oxidative cyclodehydrogenation reactions under an inert atmosphere have been reported in the literature for the generation of 6N-doped nanographenes through [2+2+2] cyclotrimerisation routes.¹⁰⁷ Thus, the presence of Fe^{3+} ions under a nitrogen atmosphere promoted the cyclodehydrogenation reaction in $\text{MLG-dppz@Fe(240N}_2)$, for which the lowest pyridinic to graphitic-N ratio was observed.

After exhaustive characterization, the electrocatalytic properties for ORR of the different samples were compared (**Fig. 5**). **Fig. 5A** compares the resulting electrocatalytic performance toward the ORR, reflecting the most effective mechanochemical synthesis route for the incorporation of FeN_4 sites into the graphitic structures. Overall, the maximum current density increased when the heating step at $240\text{ }^\circ\text{C}$ was included during the synthesis because electrocatalytically active graphitic-N species were generated. Additionally, the current density increase was even larger when the heat treatment was carried out under inert atmosphere (a maximum current density value of $-0.83\text{ mA}\cdot\text{cm}^{-2}$). These results can be explained by the presence of oxygen atmosphere during thermal treatment that favored the iron oxidation, providing a worse electrocatalytic performance. Indeed, **Fig. 5B** clearly demonstrated that the corresponding ORR cathodic peaks were not presented under a saturated N_2 environment, revealing the presence of available active Fe(II) ions related to FeN_4 coordinative structure.¹⁰⁸ To further demonstrate it, High resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging was performed on $\text{MLG-dppz@Fe(240N}_2)$. **Fig. 4D** shows a representative HAADF-STEM of this sample using spherical aberration (Cs)-corrected TEM (enlarged in **Fig. S8**). This approach allowed us to observe the presence of sub-nano clusters (yellow narrows) and even individual atoms (red narrows) of relatively heavy iron atoms on a light support such as a multilayer graphene. In addition, we can see homogeneously dispersed white dots that correspond with the iron single atoms stabilized into the FeN_4 coordinative structure. In order to confirm the chemical nature of the observed single atoms, Energy-dispersive X-ray (EDX) analysis were carried out. Due to the detection limits of the EDX

detector, it was not possible to obtain a good spectrum of a single atom. For this reason, elemental mappings of large areas were recorded, and the corresponding sum spectrum was obtained. **Fig. S9** includes a representative EDX spectrum, showing the presence of low contents of both nitrogen and iron, even though in the low magnification HAADF image where it can't be observed the presence of iron nanoparticles.

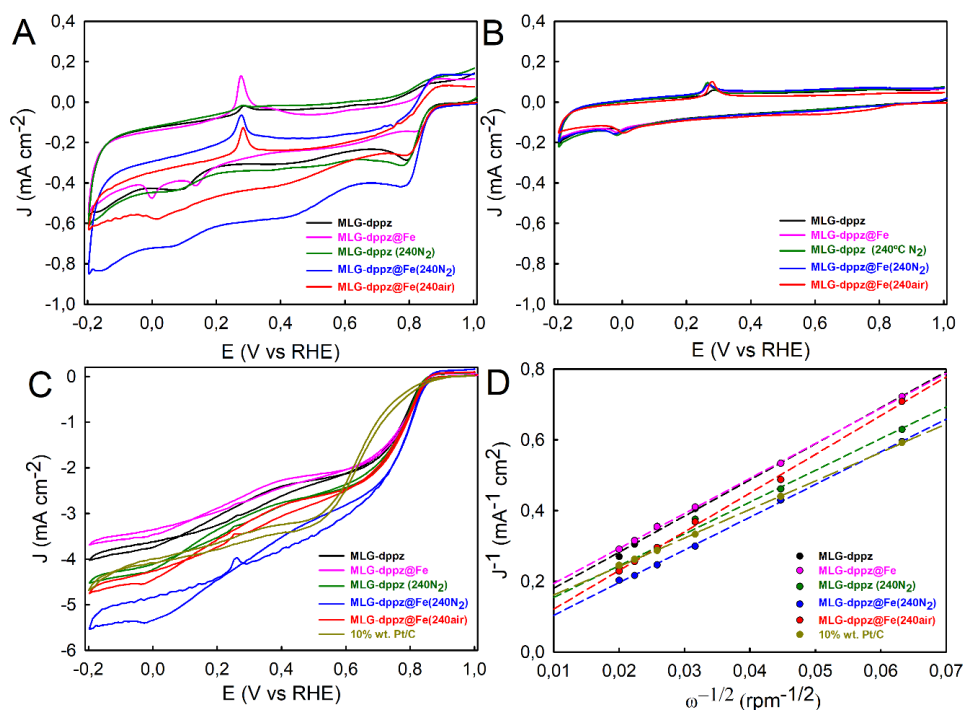


Fig. 5 CV curves obtained for the different synthesized MLG-dppz samples in O₂-saturated (A) and N₂-saturated (B) with 0.5 M KOH at 0.1 V s⁻¹. (C) RDV curves of all MLG-dppz materials at the same rotating rate of 2500 rpm. Scan rate: 10 mV s⁻¹. (D) K–L plots obtained from the RDVs in **Fig. S10** at 0.0 V (vs RHE).

Additionally, in order to gain further insights into the ORR, rotating-disk voltammograms (RDVs) were acquired for the different MLG-dppz derived samples in oxygen-saturated 0.5 M KOH, and at different rotation rates, ranging from 250 to 2500 rpm (**Fig. S10A–E**). As it was expected, the limiting current density in the RDVs curves increased with the increase of rotation speed due to a smaller diffusion layer at high rates, indicating a kinetics-controlled process. **Fig. 5C** compares the resulting RDV curves for the five analyzed MLG-dppz derived materials with

the reference 10 % wt. Pt/C at the same rotation rate of 2500 rpm. The half-wave potentials ($E_{1/2}$) were calculated from the maxima of the derivative plots of the ORR curves shown in **Fig. 5C (Fig. S11)**.¹⁰⁹ The $E_{1/2}$ values obtained for MLG-dppz, MLG-dppz@Fe, MLG-dppz(240N₂), MLG-dppz@Fe(240N₂) and MLG-dppz@Fe(240air) were 0.762, 0.810, 0.800, 0.812 and 0.802 V, respectively. The best $E_{1/2}$ value was obtained with MLG-dppz@Fe(240N₂) sample, being a better value than the reported in the literature for Pt/C (20 % wt. Pt, ca. 0.80 V).¹¹⁰ In summary, the MLG-dppz@Fe(240N₂) material provided the best electrocatalytic performance with an onset potential of 0.89 V vs RHE and a maximum current density of $-5.5 \text{ mA}\cdot\text{cm}^{-2}$ at 0.0 V vs RHE, which were better than those for Pt/C reference catalyst (i. e. 0.81 V vs RHE and $-4.2 \text{ mA}\cdot\text{cm}^{-2}$) and similar to the best reported ORR catalysts (**Table S3**). It should be noted that, in all cases, a hysteresis effect associated to the removal of adsorbed OH species and subsequent O₂ chemisorption from the free active sites at the metal surface can be observed, suggesting a similar reaction mechanism. **Fig. 5D** shows the resulting K-L plots for the different MLG-dppz derived samples at 0.0 V (vs RHE), demonstrating first-order reaction kinetics toward dissolved oxygen due to the excellent linearity of the experimental points.

The resulting slope and y-intercept were used to calculate the average number of electrons transferred (n) per oxygen molecule and other ORR kinetic parameters (**Table 3**).

Table 3 ORR kinetic parameters for ORR of the different synthesized MLG-dppz materials obtained from Fig. 5C and 5D.

Paramet.	MLG-dppz	MLG-dppz@Fe	MLG-dppz(240N ₂)	MLG-dppz@Fe(240N ₂)	MLG-dppz@Fe(240air)	10% wt. Pt/C
E_{onset} (V)	0.872	0.889	0.892	0.892	0.892	0.810
n	3.55	3.66	4.03	3.92	3.31	4.19
J_k (mAcm ⁻²)	-12.80	-10.55	-15.52	-86.59	-84.09	-12.34
K (cm s ⁻¹)	0.13	0.11	0.16	0.87	0.85	0.28

The resulting ORR kinetics parameters (n , J_k and k) of the different synthesized materials suggested the following electrocatalytic performance order: MLG-dppz@Fe < MLG-dppz < MLG-dppz(240N₂) < MLG-dppz@Fe(240air) < MLG-dppz@Fe(240N₂). Therefore, MLG-dppz@Fe(240N₂) is the most suitable electrocatalyst for ORR, providing a

four-electron pathway. These results corroborated the XPS analysis confirming the importance of the inert calcination treatment for the formation of higher content of graphitic-N and coordinated FeN_4 active sites in the multilayer graphene structure, both carrying out a synergistic effect to promote an improved ORR activity.

The OER electrocatalytic performance for the synthesized MLG-dppz derived samples were investigated through LSV curves in 0.5 M KOH electrolyte.

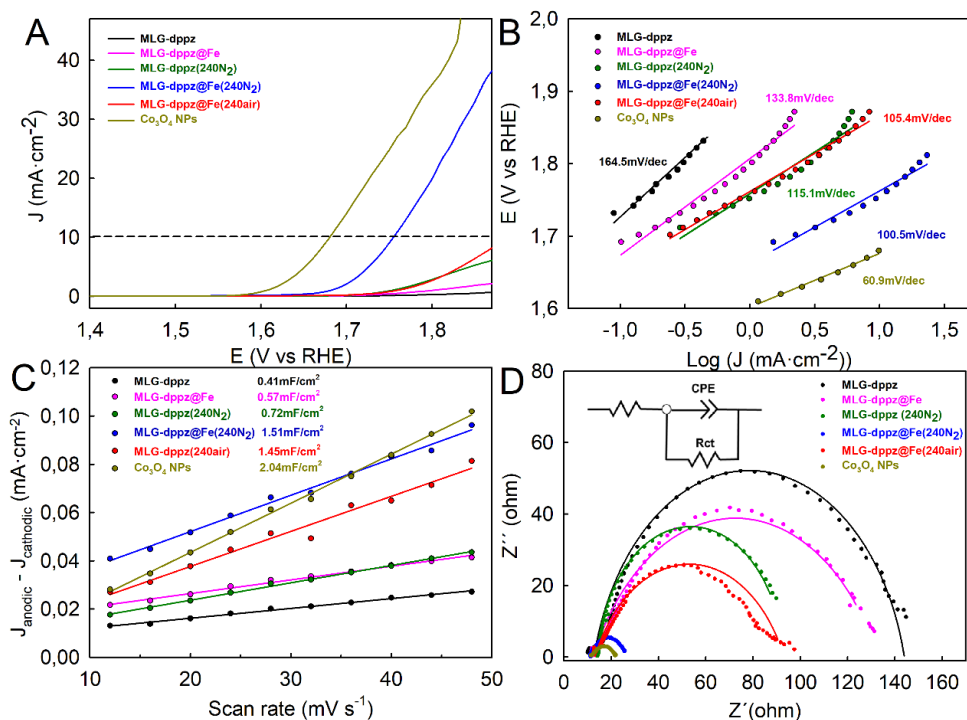


Fig. 6 (A) OER polarization curves obtained for the different MLG-dppz samples and the Co_3O_4 NPs reference material in 0.5 M KOH solution at 2 mV/s. (B) Tafel plot from (A). (C) Plots of difference of anodic and cathodic current density as a function of the scan rate, and (D) EIS curves obtained for the MLG-dppz samples at the overpotential of 700 mV, with frequency from 100 kHz to 1 Hz and amplitude of 5 mV. Dots and lines represent the experimental and simulated data, respectively.

Fig. 6A shows that the resulting current density increased with the potential change for the different materials, as expected for OER anodic processes. For the evaluation of their electrocatalyst activity, the

overpotentials at the geometric current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ were measured.^{111,112} As shown in **Fig. 6A**, the MLG-dppz@Fe(240N₂) showed the lowest overpotential of 500 mV at 10 mA cm^{-2} , which was similar to that of previously reported OER catalysts (**Table S4**). This overpotential was slightly higher than that of the Co₃O₄ NPs reference material (450 mV), which gave a quite similar value to that previously reported by Leal-Rodríguez et al. (430 mV),¹¹² thus demonstrating the excellent electrocatalytic performance of MLG-dppz@Fe(240N₂) despite its very low Fe content (0.73 %). These results can be attributed to the great availability of the highly disperse FeN₄ active centers, which significantly favored the water oxidation process. It further confirmed the most efficient route for the generation of high graphitic-N content during the calcination stage under inert atmosphere, proving to play a key role in OER processes.³⁶ More concretely, the MLG-dppz@Fe(240air) sample provided lower OER electrocatalytic performance than MLG-dppz(240N₂). The calcination stage at 240 °C under inert atmosphere significantly improved the OER electrocatalytic performance of MLG-dppz@Fe, partially avoiding the oxidation of Fe²⁺ to Fe³⁺ observed under oxygen-saturated conditions. These results were more evident when comparing the resulting maximum current density values (**Fig. 6A**). In addition, the Tafel slope was determined to evaluate the OER mechanism and rate-determining step (**Fig. 6B**). The resulting Tafel slope values indicated that the third reaction of the physisorbed hydrogen peroxide based-mechanism for OER in alkaline media was rate-determining step for all samples.^{113,114} Overall, a lower Tafel slope is beneficial for a faster increase in the reaction rate. In this sense, a significant Tafel slope decrease can be observed with the increase of the FeN₄ active centers and graphitic-N species, confirming that the enhance of the electrocatalytic performance is associated to the inert heat treatment to produce the efficient coordination of Fe atoms into the pyridinic-N and the generation of graphitic-N into the multilayer graphene structures.

The total electrode activity was determined by the total number of active sites.¹¹² **Fig. 6C** plots the difference of anodic and cathodic current density against the scan rate, where the resulting slope (areal capacitance) was proportional to their ECSA. Accordingly, MLG-dppz@Fe(240N₂) showed the highest areal capacitance of $1.51 \text{ mF}\cdot\text{cm}^{-2}$ ($2.04 \text{ mF}\cdot\text{cm}^{-2}$ for the reference Co₃O₄ NPs and $2.36 \text{ mF}\cdot\text{cm}^{-2}$ for the previously reported by Leal-Rodríguez et al.¹¹²).

As the number of active sites favor the charge transfer, EIS analysis were conducted for the different samples (**Fig. 6D**), confirming the previous findings. The EIS results were fitted based on the equivalent circuit (**Fig. 6D**, inset), and the obtained solution resistance (R_s), charge-transfer resistance (R_{ct}) and constant phase elements (CPE) are summarized in **Table 4**.¹¹⁵ The CPE-T parameter is referred to pseudo capacitance and CPE-P is related to depressed semicircle in the EIS plot.¹¹⁶ As expected, MLG-dppz@Fe(240N₂) provided the best charge transport efficiency with the smallest R_{ct} of 15.87 $\Omega \cdot \text{cm}^{-2}$, while MLG-dppz showed the highest R_{ct} of 131.00 $\Omega \cdot \text{cm}^{-2}$. The resulting R_{ct} value in the former case was similar to that of the reference material Co₃O₄ NPs (12.35 $\Omega \cdot \text{cm}^{-2}$).

Table 4 Summary data obtained from the simulation of the equivalent circuit for the MLG-dppz samples, and the Co₃O₄ NPs used as reference material.¹¹²

Sample reference	R_s [Ω/cm^2]	R_{ct} [Ω/cm^2]	CPE-T	CPE-P
MLG-dppz	12.80	131.00	5.03×10^{-7}	0.8556
MLG-dppz@Fe	12.44	120.19	1.74×10^{-5}	0.7305
MLG-dppz(240N ₂)	14.34	78.55	3.77×10^{-4}	0.9532
MLG-dppz@Fe(240N ₂)	13.73	15.87	3.98×10^{-4}	0.9040
MLG-dppz@Fe(240air)	13.11	79.97	1.1×10^{-5}	0.7331
Co ₃ O ₄ NPs	18.20	12.35	6.5×10^{-4}	0.6905

5.3.3.4. Conclusions

A novel low-temperature and solvent-free mechanochemical synthesis strategy based on dppz functionalized multilayer graphene for the generation of edge-enriched FeN₄ sites was successfully developed. Our findings demonstrate that dppz adducts on the edges of the graphene sheets can act as ligands for the coordination of iron. The subsequent thermal treatment of MLG-dppz@Fe at 240 °C under a nitrogen atmosphere provided more successful incorporation of edge-enriched FeN₄ sites than that under air conditions. The resulting MLG-dppz@Fe(240N₂) material provides bifunctional electrocatalytic performance for ORR and OER. Our low-temperature synthesis with low-iron content paves the way for the

development of novel sustainable approaches for the generation of edge-enriched FeN₄ single atom sites on multilayer graphene structures with bifunctional electrocatalytic properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors wish to acknowledge the financial support from Ramon Areces Foundation, Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981) and Projects RTI2018-101611-B-I00, CTQ2017-83961-R (MANA), CTQ2017-92264-EXP (JEANS) and PID2020-112744GB-I00 (BIOMINA), Andalusian Regional Government (FQM-346, FQM-175 and FQM-204 groups) and Feder Funds (UCO-1263193 -PAIDI2018- and P20_01151 -PAIDI2020-projects).

5.3.3.5. References

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Appendix VI: Supplementary Information

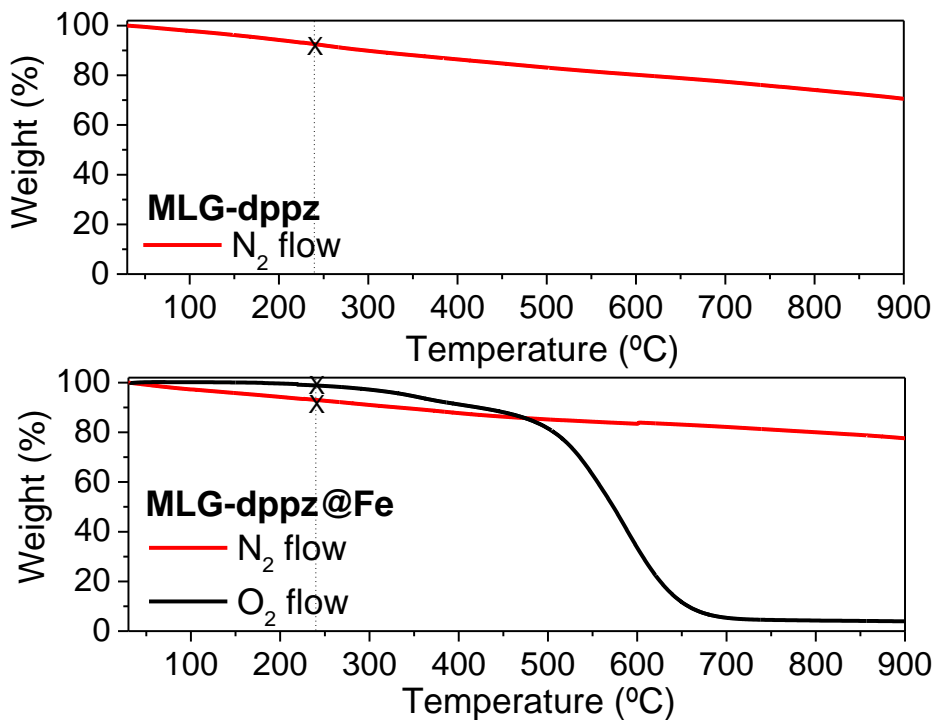


Fig. S1 TGA curves of MLG-dppz (under a nitrogen atmosphere) and MLG-dppz@Fe (in nitrogen and oxygen atmospheres).

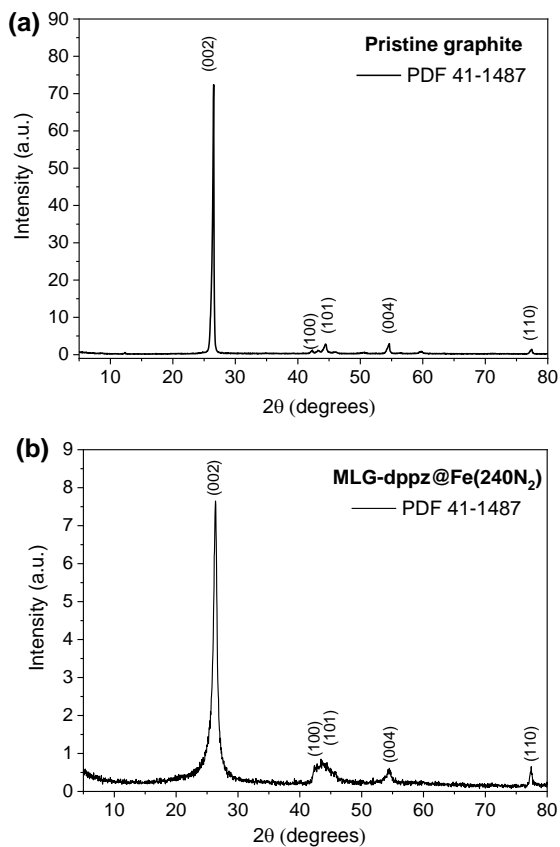


Fig. S2 XRD patterns of (a) pristine graphite powder and (b) MLG-dppz@Fe(240N₂) materials.

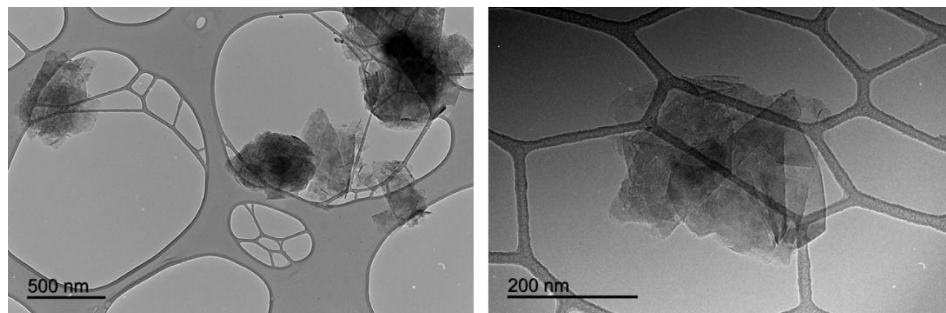


Fig. S3 TEM images of MLG-dppz@Fe(240N₂).

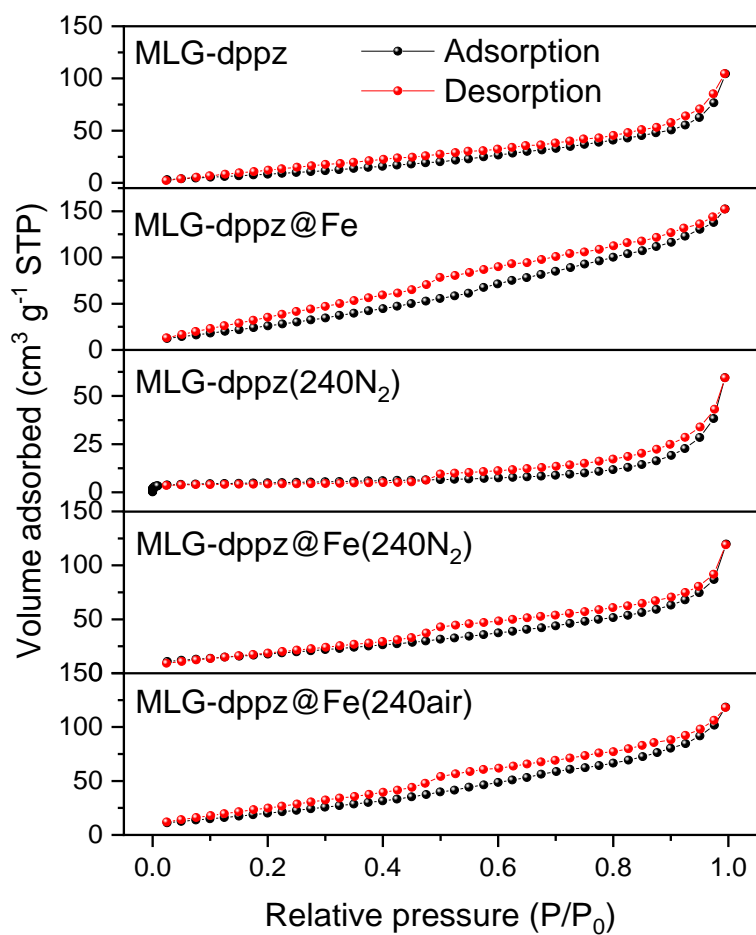


Fig. S4 N₂ adsorption/desorption isotherms of MLG-dppz materials.

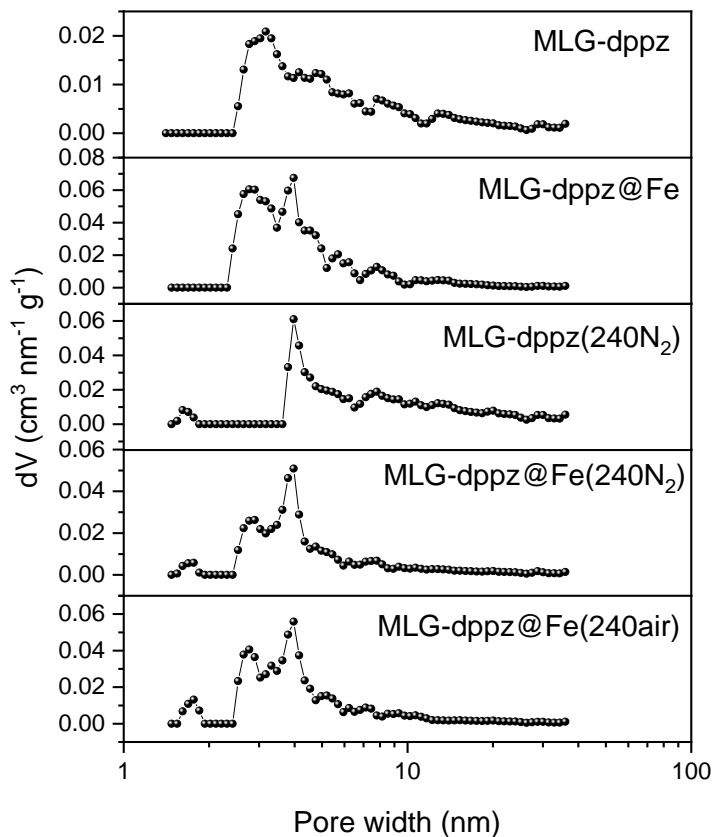


Fig. S5 Pore size distribution of MLG-dppz materials.

Table S1 Textural data of MLG-dppz materials.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{T} ($\text{cm}^3 \text{g}^{-1}$)	D_{pore} (nm)
MLG-dppz	50	0.161	13
MLG-dppz@Fe	128	0.236	7
MLG-dppz(240N ₂)	18	0.092	21
MLG-dppz@Fe(240N ₂)	74	0.185	10
MLG-dppz@Fe(240air)	92	0.183	8

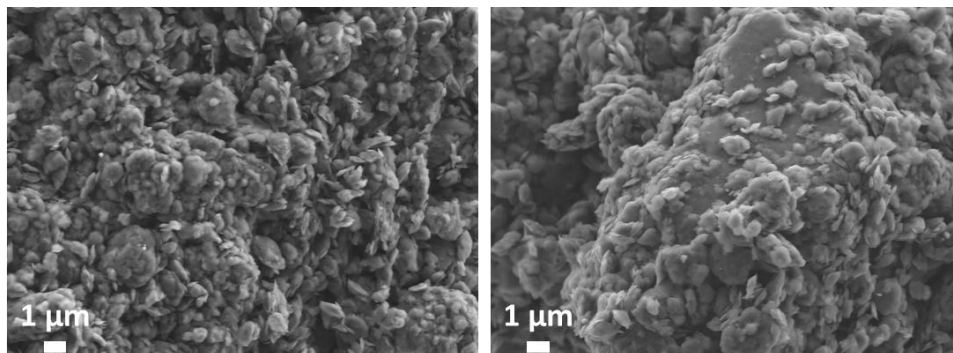


Fig. S6 SEM representative images of MLG-dppz@Fe(240N₂).

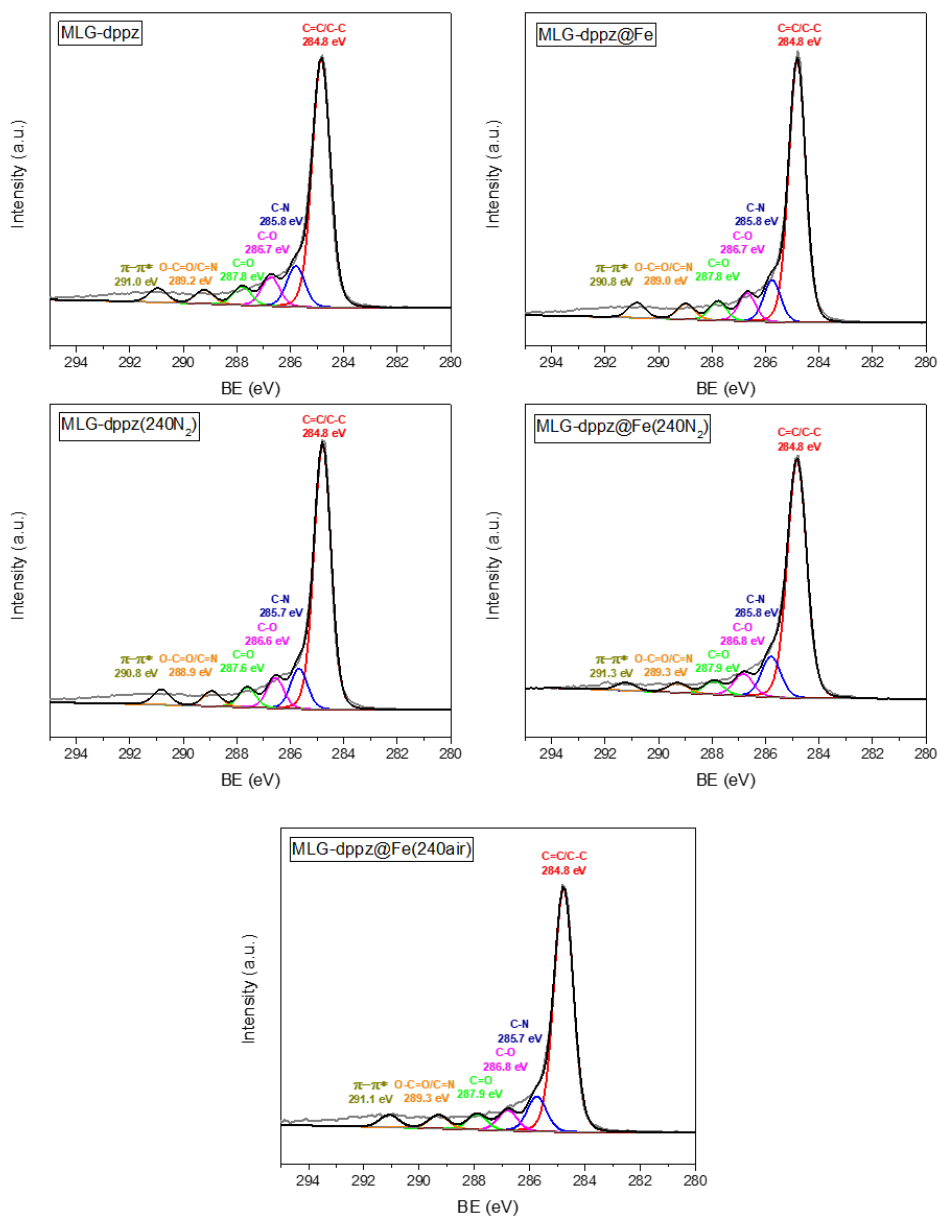
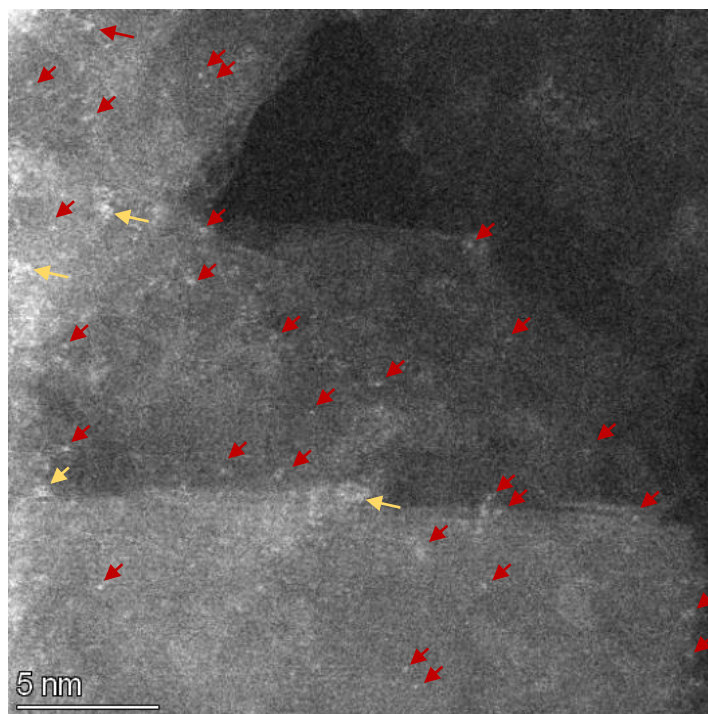


Fig. S7 XPS spectra for the C1s photoemission peak of MLG-dppz materials.

Table S2 Contribution of the six components used in the fitting of the C 1s core level signal.

C1s	MLG-dppz		MLG-dppz@Fe		MLG-dppz(240N ₂)		MLG-dppz@Fe(240N ₂)		MLG-dppz@Fe(240air)	
	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %	BE (eV)	Atom %
C=C/C-C	284.8	68.1	284.8	68.9	284.8	68.6	284.8	71.7	284.8	71.6
C-N	285.8	11.3	285.8	11.0	285.7	10.5	285.8	12.2	285.7	10.3
C-O	286.7	8.0	286.7	7.3	286.6	7.9	286.8	6.7	286.8	5.9
C=O	287.8	5.1	287.8	4.9	287.6	5.1	287.9	4.0	287.9	4.6
O-C=O/C=N	289.2	3.8	289.0	4.0	288.9	3.9	289.3	3.0	289.3	4.0
π - π^*	291.0	3.9	290.8	4.0	290.8	4.0	291.3	2.4	291.1	3.7

**Fig. S8** Aberration corrected HAADF-STEM image of MLG-dppz@Fe(240N₂) sample (showed in **Fig. 4D**).

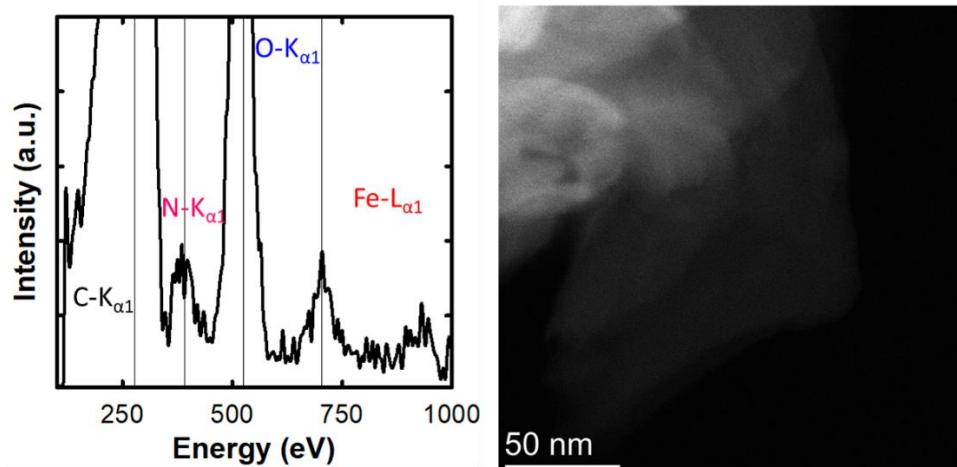


Fig. S9 Sum EDX spectrum of the area included in the HAADF image.

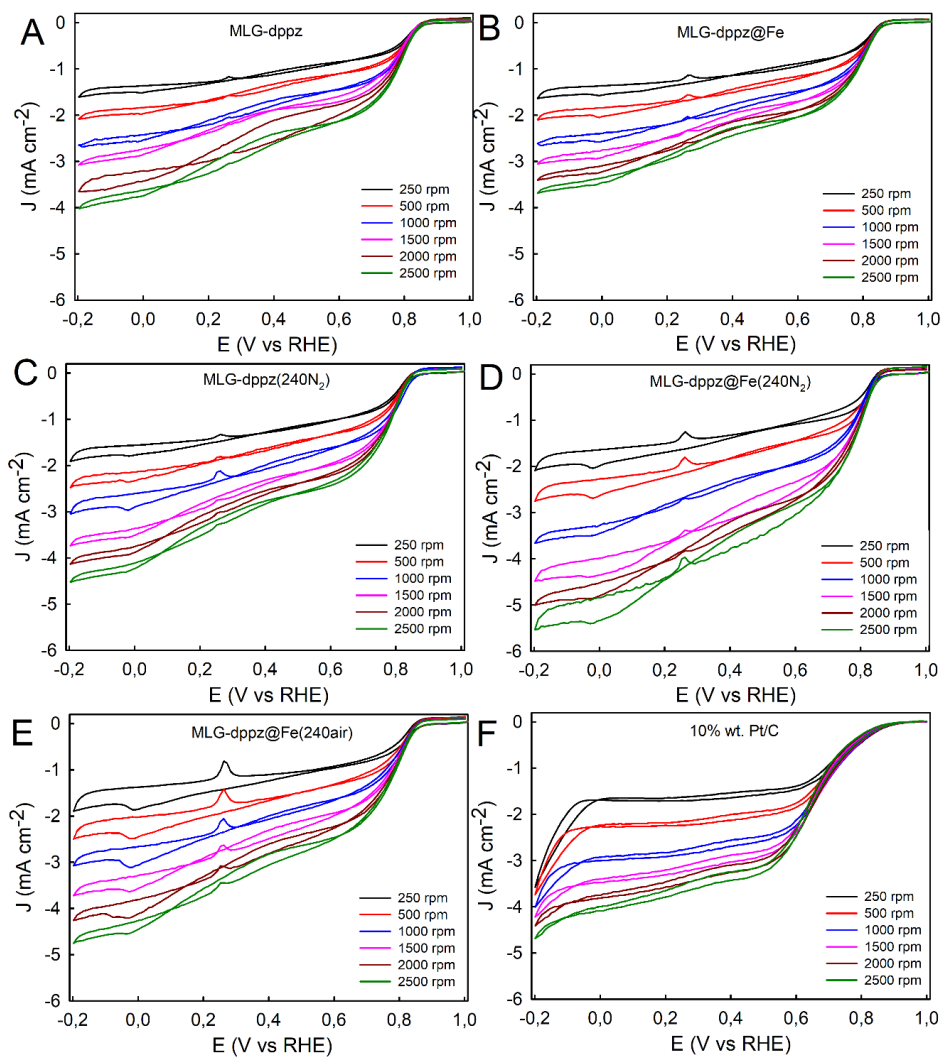


Fig. S10 Rotating-disk voltammograms at different rotation rates for (A) MLG-dppz, (B) MLG-dppz@Fe, (C) MLG-dppz(240N₂), (D) MLG-dppz@Fe(240N₂), (E) MLG-dppz@Fe(240air) and (F) 10 % wt. Pt/C in O₂ saturated 0.5 M KOH at scan rate of 10 mV·s⁻¹.

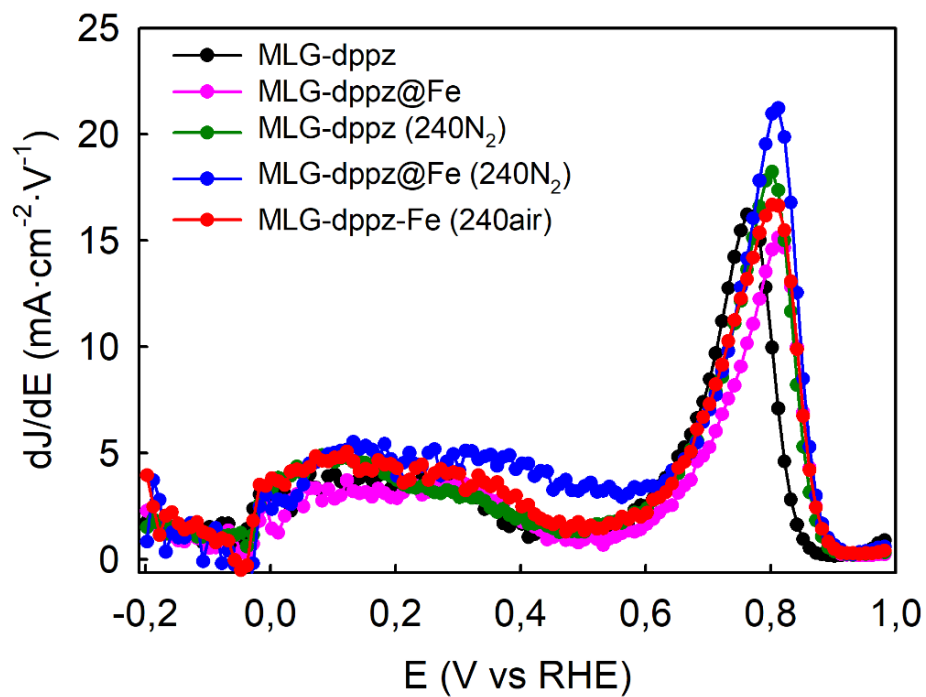


Fig. S11 Derivatives of the ORR data shown in **Fig. 5C** to obtain the half-wave potentials.

Table S3 Summary table of ORR electrocatalysts based on NC and Fe-NC materials.

C/Fe based electrocatalyst	Fe Wt%	J (mA·cm ⁻²) and ω (rpm)	E _{onset} (V)	J _k (mA·cm ⁻²)	n	Potential (V)	Electrolyte	Reference electrode	Working electrode	Ref.
BINOL-CTF-10-500	-	-3.00 and 2400	0.79	9.00	4.04	0.23	0.1M KOH	RHE (SCE)	GC	[1]
Fe ₂ O ₃ -NPCS	21.00	-5.80 and 2500	1.06	31.8	3.85	0.90	0.1M KOH	RHE (Ag/AgCl)	GC	[2]
CNT/PC	2.90	-6.00 and 1600	0.95	4.3	3.98	0.90	0.1M KOH	RHE (Ag/AgCl)	GC	[3]
Fe-N-CNT@RGO	30.00	-4.44 and 1600	0.93	1.85	4.00	0.85	0.1M KOH	RHE (SCE)	GC	[4]
Co,N-PCL	-	-5.20 and 1600	0.93	-	3.99	0.30	0.1M KOH	RHE (Ag/AgCl)	GC	[5]
Fe ₃ C/NG-800	0.81	-6.40 and 2500	1.03	100	3.70	0.70	0.1M KOH	RHE (SCE)	GC	[6]
Fe-N-C-800acid	2.20	-4.30 and 1600	0.93	-	3.70	0.56	0.1M KOH	RHE (Ag/AgCl)	GC	[7]
Fe _{1.6} -N-HCNS/rGO-900	1.60	-5.70 and 1600	0.7-0.9	-	4.02	0.70	0.1M KOH	RHE (SCE)	GC	[8]
Fe ₃ C/C-800	15.00	-5.50 and 2500	1.05	-	3.80 - 4.00	0.99	0.1M KOH	RHE (SCE)	GC	[9]
Fe-N-C-800	0.24	-4.90 and 2025	0.98	-	3.95	0.75	0.1M KOH	RHE (Ag/AgCl)	GC	[10]
Fe-N-C/rGO	0.15 (atom)	-4.50 and 2025	0.94	-	4.00	0.60	0.1M KOH	RHE (Ag/AgCl)	GC	[11]
Fe@C-NG/NCNTs	0.42	-5.00 and 1600	0.93	-	4.00	0.80	0.1M KOH	RHE (SCE)	GC	[12]*
C-COP-C-Fe	4.95	-5.70 and 2025	0.89	4.00	3.93	0.75	0.1M KOH	RHE (SCE)	GC	[13]
Fe ₃ C-Co/NC	1.70	-5.50 and 1600	0.94	-	3.9	0.80	0.1M KOH	RHE (Ag/AgCl)	GC	[14]*
N-doped CoCx/FeCo@C/rGO	-	-7.00 and 2500	1.02	-	3.84	0.46	0.1M KOH	RHE (SCE)	GC	[15]*
M-2	-	-7.90 and 2500	0.97	-	-	-	0.1M KOH	RHE (Ag/AgCl)	GC	[16]*
FeCo/N-DNC	52.80 (atom)	-6.20 and 1600	0.89	-	3.92	0.2	0.1M KOH	RHE (Ag/AgCl)	GC	[17]*
FeS/Fe ₃ C@N-S-C-800	2.17	-6.80 and 2500	1.02	-	3.9	0.2	0.1M KOH	RHE (Ag/AgCl)	GC	[18]*
MLG-dppz@Fe (240N ₂)	0.73	-5.50 and 2500	0.89	86.59	3.92	1.00	0.5M KOH	RHE (Ag/AgCl)	GC	This work*

*Materials with bi- or tri-functional character.

Table S4 Summary table of OER electrocatalysts based on NC and Fe-NC materials.

C/Fe based catalyst	Fe Wt%	η_{10} (mV)	Tafel Slope (mV/dec)	Electrolyte	Reference electrode	Working electrode	Ref.
Fe/Fe ₃ C-MC	2.40	320	51.0	1M KOH	RHE	GC	[19]*
Fe@C-NG/NCNTs	0.42	450	163.0	1M KOH	RHE (SCE)	GC	[12]*
Fe ₃ C-Co/NC	1.70	340	108.8	1M KOH	RHE (Ag/AgCl)	GC	[14]*
Fe ₃ O ₄ /NiS@CC	1.18	310	82.0	1M KOH	RHE (Ag/AgCl)	GC	[20]
N-doped CoCx/FeCo@C/rGO	-	390	77.1	0.1M KOH	RHE (SCE)	GC	[15]*
PNG-NiCo	-	564	156.0	0.1M KOH	RHE (Ag/AgCl)	Hybrid films	[21]
M-2	-	710	54.0	0.1M KOH	RHE (Ag/AgCl)	GC	[16]*
N-doped SWNT	-	430	-	0.1M KOH	RHE	GC	[22]
FeCo/N-DNC	52.80 (atom)	390	68.0	0.1M KOH	RHE (Ag/AgCl)	GC	[17]*
FeS/Fe ₃ C@N-S-C-800	2.17	570	81.0	1M KOH	RHE (Ag/AgCl)	GC	[18]*
Fe ₃ C@C-N	3.50	608	89.0	0.1M KOH	RHE (SCE)	GC	[23]
Ni _{1.95} Fe-MOP@CNTs	2.69	256	58.0	1M KOH	RHE (Ag/AgCl)	GC	[24]
Co ₃ O ₄ /N-C	-	390	44.0	1M KOH	RHE (Ag/AgCl)	GC	[25]
Fe/C-doped-MoS ₂ /Ni ₃ S ₂ -450	-	273	66.0	1M KOH	RHE (SCE)	GC	[26]
MLG-dppz@Fe (240N ₂)	0.73	500	100.5	0.5M KOH	RHE (Ag/AgCl)	GC	This work*

*Materials with bi- or tri-functional character.

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Capítulo 6

Conclusiones

En esta Tesis Doctoral se han diseñado y sintetizado materiales híbridos orgánico-inorgánicos de diferente naturaleza empleando una gran variedad de estrategias de síntesis. En función de sus características estructurales y fisicoquímicas, la presente memoria se ha dividido en tres bloques principales: *1) polímeros de coordinación, 2) materiales híbridos orgánico-inorgánicos basados en sílices y 3) materiales híbridos basados en grafeno.*

Se han llevado a cabo diversos procesos de funcionalización con objeto de impartir propiedades concretas a algunos de estos materiales híbridos, que han sido de gran importancia en aplicaciones específicas. Asimismo, se ha abordado una profunda caracterización estructural, textural, morfológica y de composición química mediante una gran variedad de técnicas instrumentales, que ha servido para elucidar el singular comportamiento de los materiales sintetizados en campos de investigación de especial relevancia en el sector industrial como la (foto/electro)catálisis, adsorción, luminiscencia o energía.

De esta labor realizada, **de acuerdo con los objetivos planteados al comienzo de esta Memoria**, las **conclusiones** obtenidas de los artículos plasmados en cada una de las secciones que conforman el *Capítulo 4: Resultados y Discusión* han sido las siguientes:

- **Sección 1: Polímeros de coordinación-Metal Organic Frameworks (MOFs):**
 - En el artículo “*Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions*” fueron preparados polímeros de coordinación basados

en zirconio con diferentes ligandos orgánicos quirales (ácido L-tartárico, ácido dibenzoil-L-tartárico y ácido L-málico) bajo condiciones solvotermales a reflujo o presión autógena en autoclave. Las propiedades texturales y estructurales de los polímeros resultantes estuvieron directamente relacionadas con la naturaleza del ligando quiral, las condiciones de síntesis y la relación metal:ligando. Estos polímeros de coordinación fueron activos en la reacción de cianosililación de benzaldehído con TMSiCN, particularmente los que contuvieron ácido málico sintetizados a 110 °C en autoclave estableciendo proporciones estequiométricas metal:ligando (Z_1M_1-110A), dando lugar a conversiones elevadas (96%). Respecto a la enantioselectividad mostrada por Z_1M_1-110A , se ha observado un exceso enantiomérico de hasta el 12.6% utilizando dietiléter como disolvente sin requerir la presencia del agente promotor. Adicionalmente, se han utilizado diferentes benzaldehídos *p*-sustituidos como sustratos que se transforman a la cianohidrina correspondiente, en general, con buena conversión y enantioselectividad variable, sobre todo aquellos con sustituyentes electroaceptores. Por lo tanto, estos materiales pueden considerarse catalizadores muy prometedores para procesos orgánicos catalizados por ácidos de Lewis.

- En el artículo “*Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents*” se ha optimizado un método de ultrasonido para sintetizar cristales del MOF MIL-88A con elevada cristalinidad y superficie específica. Dependiendo del tratamiento con ultrasonidos y los tiempos de reacción aplicados, se obtuvieron

partículas con diferente morfología, área superficial y porosidad. Los materiales obtenidos mediante sondas de ultrasonidos presentaron tamaños de partícula más pequeños que los sintetizados en baño de ultrasonidos. Sin embargo, estos últimos exhibieron mayores áreas superficiales y mayor proporción de microporos. Adicionalmente, las partículas MIL-88A actuaron como sitios activos ácidos de Lewis en procesos de adsorción de etileno y conservaron su integridad estructural tras varios ciclos de adsorción. Más concretamente, Fe-fum-B1 exhibió una adsorción específica de etileno comparable a otros MOFs ampliamente reportados en literatura, aunque su adsorción en términos absolutos fue menor debido a su área superficial moderada. Esto los convierte en materiales muy prometedores para la captura y eliminación controlada de etileno en el envasado de frutas, lo que resulta especialmente atractivo e importante para el sector agroalimentario.

- El artículo “*MIL-88A Metal-Organic Framework as a stable sulfur-host cathode for long-cycle Li-S batteries*” supuso una extensión de la investigación anterior en la que se sintetizó el MOF MIL-88A mediante un procedimiento rápido asistido por sonda ultrasónica, que dio lugar a la generación de partículas cristalinas de tamaño reducido con una elevada superficie específica y volumen de poro. Estas características texturales y estructurales lo convirtieron en un material adecuado para ser utilizado como matriz hospedadora de azufre (S) en el componente catódico de las baterías de Li-S, logrando alojar un 40 % de S en su estructura. El composite MIL-88A@S demostró una óptima capacidad de almacenamiento energético a elevadas

densidades de corriente y una respuesta electroquímica excelente en condiciones de ciclaje prolongado de hasta 1000 ciclos de carga y descarga, proporcionando una capacidad específica promedio de 300 mAh g^{-1} a una velocidad de corriente considerable de 0.5 C. Por lo tanto, los resultados sugirieron que este composite, formado por un MOF prístino MIL-88A como matriz hospedadora de S, podría ser un componente catódico prometedor para las baterías Li-S, lo que supone un avance en el área de investigación de dispositivos de conversión y almacenamiento de energía.

- **Sección 2: Materiales híbridos orgánico-inorgánicos basados en sílice-Periodic Mesoporous Organosilicas (PMOs):**

- El artículo de revisión “*Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production*” ha puesto de manifiesto que los sistemas fotocatalíticos basados en modelos biomiméticos del sitio activo de [FeFe]-hidrogenasa han evolucionado sustancialmente durante las últimas dos décadas. De este artículo, se puede concluir que las estrategias de síntesis para reproducir arquitecturas análogas a las que se encuentran en la enzima hidrogenasa natural, la elucidación mecanística del papel del hidruro estructural, la modificación de sus diferentes esferas de coordinación y la investigación electroquímica de los complejos [2Fe2S] han tenido un impacto decisivo en el ajuste de sus propiedades electrónicas y fotofísicas que determinan su

aplicación como catalizadores en la producción de hidrógeno asistida por luz visible. El desafío en el futuro en esta área de investigación consiste en acoplar las semirreacciones de reducción y oxidación para construir sistemas fotosintéticos artificiales completos de división de agua para la conversión de energía solar en combustibles químicos. Estas investigaciones supondrán una nueva inspiración para las tecnologías energéticas basadas en el fascinante mundo de la fotocatalisis y la biomimética.

- El trabajo previo de revisión estableció las bases conceptuales previas para abordar el artículo *“Hydroxyl-decorated diiron complex as a [FeFe]-hydrogenase active site model complex: Light-driven photocatalytic activity and heterogenization on ethylene-bridged periodic mesoporous organosilica”* en el que se ha sintetizado y caracterizado un complejo modelo biomimético [FeFe]-hidrogenasa de sitio activo (FeFeOH), con un puente de etileno y un grupo hidroxilo, y posteriormente investigado con éxito por primera vez como un catalizador potencial para la evolución de hidrógeno impulsada por la luz visible. Además, se diseñó y preparó un precursor novedoso basado en un carbamato trietoxisilano portador de un ditiolato de dihierro (NCOFeFe) para ser incorporado mediante un procedimiento *“grafting”* sobre un soporte sólido, concretamente en una organosílice periódica mesoporosa (PMO) con puentes orgánicos etileno (EthanePMO), obteniendo el material EthanePMO@NCOFeFe con una carga de hierro de 0.235 mmol Fe/g PMO. Las diferentes variables que influyen en la reacción fotocatalítica fueron optimizadas exitosamente bajo la irradiación de una luz LED: pH, flujo de

fotones, concentración de catalizador y concentración de fotosensibilizador. La sustitución del sistema de iluminación por una lámpara de xenón con mayor intensidad lumínica y un mayor intervalo de longitud de onda supuso una excelente mejora de la producción de hidrógeno asistida por luz, alcanzando valores de TON de 70 y 37 para FeFeOH y NCOFeFe, respectivamente. Se sugirió que los fenómenos de agregación molecular debidos a la naturaleza hidrofóbica del precursor NCOFeFe provocaron la disminución de la actividad fotocatalítica en comparación con la mostrada por FeFeOH. Por su parte, la inmovilización de NCOFeFe en EthanePMO permitió estabilizar el complejo catalítico y así poder trabajar en un medio completamente acuoso, pero condujo a menores rendimientos en la generación de hidrógeno, probablemente debido al bloqueo de algunos sitios activos. Sin embargo, los resultados de actividad catalítica obtenidos en término de TON para este catalizador heterogéneo EthanePMO@NCOFeFe, fueron comparable a los obtenidos por otros modelos biomiméticos de [FeFe]-hidrogenasa inmovilizados en soportes heterogéneos bajo condiciones experimentales análogas reportados previamente en literatura.

- **Sección 3: Materiales híbridos basados en grafeno:**

- En el artículo “*A comparative study of particle size distribution of graphene nanosheets synthesized by an ultrasound-assisted method*” se ha llevado a cabo la exfoliación asistida por ultrasonidos de un micrografito a nanoláminas de grafeno (GNS). Este proceso fue confirmado mediante diferentes técnicas, como la difracción de rayos X, microscopia de transmisión electrónica

y espectroscopia Raman. Respecto a la distribución del tamaño de partícula de las GNS, inicialmente fue determinada por dispersión dinámica de la luz (DLS), que proporcionó el radio hidrodinámico y la polidispersidad de las GNS. Posteriormente, dos técnicas diferentes, el análisis de seguimiento de nanopartículas (NTA) y el fraccionamiento de flujo de campo asimétrico (AF4), se aplicaron por primera vez en el estudio de grafenos. NTA proporcionó una resolución más alta que DLS, así como concentraciones aproximadas. Además, se demostró que mediante DLS se obtuvo un tamaño de partícula promedio cuya intensidad estaba sesgada hacia las partículas de grafeno de mayor tamaño. Por su parte, AF4 permitió separar varias poblaciones de GNS con diferentes radios de giro y, además, proporcionó información sobre la estructura y la forma de las partículas. Claramente, la aplicación de NTA y AF4, además de DLS, permitió recopilar información muy rica sobre las partículas de grafeno. Las ventajas mencionadas anteriormente para NTA y AF4 han revelado su utilidad para la determinación de la polidispersidad real en preparaciones de grafeno, la evaluación de sus procedimientos sintéticos y la determinación del tamaño y fraccionamiento en medios acuosos para estudios relacionados con aplicaciones biológicas, detección y toxicidad.

- En el artículo “*Luminescent graphene-based materials via europium complexation on dipyridylpyridazine-functionalized graphene sheets*” fue efectuada una reacción de hetero-Diels-Alder entre 3,6-di(2-piridil)-1,2,4,5-tetrazina y materiales basados en grafeno proporcionando sitios de coordinación bien definidos para la coordinación de metales en láminas de grafeno.

A partir del mismo grafito de partida, tres procedimientos diferentes con energías de activación alternativas (ultrasonido, molienda de bolas y calentamiento) dieron como resultado grafenos de pocas capas (FLG), grafeno multicapa (MLG) y grafito (MG) funcionalizados con unidades de dipiridilpiridazina. Todos ellos han demostrado ser ligandos útiles para la formación de complejos de europio. Las propiedades de emisión de estos materiales fueron estudiadas antes y después de su unión a complejos $\text{Eu}(\text{dbm})_3$, observando una fuerte emisión roja en el visible de Eu^{3+} con una amplia gama de longitudes de onda de excitación. Por lo tanto, esta metodología podría permitir el marcaje de materiales basados en grafeno para bioimágenes independientemente de su tamaño de partícula. La extensión de esta estrategia de síntesis a otros complejos grafeno-metal puede dar lugar a materiales con aplicaciones potenciales en química organometálica, catálisis, biomedicina, imagenología y detección, entre otras.

- En el artículo *“Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN_4 sites for ORR and OER electrocatalysis”* se desarrolló con éxito una nueva estrategia de síntesis mecanoquímica a baja temperatura y sin disolventes para la generación de sitios de FeN_4 enriquecidos en los bordes a partir de grafeno multiláminas funcionalizado con unidades de dipiridilpiridazina (dppz) mediante una reacción de Diels-Alder. Los hallazgos encontrados en este trabajo demostraron que los aductos dppz en los bordes de las láminas de grafeno pudieron actuar como ligandos para la coordinación de átomos de hierro. El tratamiento térmico

posterior a 240 °C bajo atmósfera de nitrógeno proporcionó una incorporación específica más exitosa de los sitios de FeN₄ en los bordes de las láminas que en condiciones oxidantes en presencia de aire. Basado en esto, el material resultante MLG-dppz@Fe(240N₂), aunque presentó un bajo contenido de hierro, proporcionó un rendimiento electrocatalítico bifuncional inédito para las reacciones de reducción (ORR) y oxidación (OER) de oxígeno, ambas de vital importancia en una amplia gama de dispositivos de conversión y almacenamiento de energía. Esta estrategia sintética permitirá allanar el camino en el desarrollo de nuevos enfoques sostenibles para la generación de sitios de un solo átomo, como los centros FeN₄ enriquecidos en los bordes de estructuras de grafeno multiláminas con propiedades electrocatalíticas bifuncionales.

➤ **CONSIDERACIONES FINALES:**

Los aspectos tratados en esta Tesis Doctoral no agotan, ni mucho menos, todas las posibilidades de estudio que pueden abordarse en este tipo de materiales híbridos orgánico-inorgánicos con nuevas estructuras y características singulares.

En términos generales, estas investigaciones contribuirán a avanzar en el conocimiento de estos materiales, desde su diseño estructural hasta la elección de las estrategias de síntesis óptimas para otorgar al híbrido resultante las características deseadas. Las propiedades fisicoquímicas presentadas por cada uno de ellos han permitido adentrarnos en campos aplicativos novedosos de enorme interés actual para la comunidad científica. Entre ellos, podemos destacar:

a) Los polímeros de coordinación y redes metal-orgánicas presentan especies metálicas, que actúan como ácidos de Lewis muy eficientes en procesos catalíticos y de adsorción, y ligandos orgánicos, que suministran un entorno capaz de interactuar, incluso de forma enantioselectiva, y adsorber moléculas orgánicas.

b) Las organosílices periódicas mesoporosas muestran una red inorgánica, que aportan el sostén estructural del material, y fragmentos orgánicos, que exhiben carácter hidrofóbico y otorgan funcionalidad, resultando así materiales silíceos dotados de gran estabilidad y centros activos catalíticos.

c) Los materiales grafénicos híbridos aúnan las características propias de los grafenos con las amplias propiedades fotofísicas y catalíticas de los fragmentos organometálicos.

Aunque en algunos casos los resultados obtenidos no hayan alcanzado las expectativas inicialmente previstas, los trabajos llevados a cabo en esta Tesis a escala de laboratorio han sentado las bases y etapas fundamentales para que, en un futuro inmediato, se pueda continuar profundizando en los estudios enmarcados en las líneas de investigación contenidas en la presente Memoria.

Nuestra sociedad no conoce el límite de sus demandas; por tanto, se considera fundamental que la comunidad científica las vaya resolviendo a medida que aquélla las plantea; muchas de ellas, en el campo de la energética, de la catálisis, de la adsorción selectiva de gases y contaminantes emergentes, de la dosificación controlada de fármacos, de la alimentación, de la biología, de la farmacoquímica, de la informática, de la remediación ambiental y de la química industrial, entre otros. Muchas de estas

necesidades que van surgiendo exponencialmente con el paso de los años directamente ligadas al desarrollo de la humanidad, tendrán su solución en el área de la Química de Materiales. Para ello, el futuro de los materiales híbridos orgánico-inorgánicos estará fuertemente marcado por el descubrimiento de nuevos procedimientos de síntesis que proporcionen al material resultante mayor estabilidad a lo largo del tiempo, mayor resistencia al reuso, elevada especificidad y menores costes económicos de producción. Así, sus novedosas aplicaciones, que tendrán gran impacto en el sector industrial, contribuirán al sostenimiento del bienestar y a la mejora de la economía global.

Chapter 6

Conclusions

In this Doctoral Thesis, organic-inorganic hybrid materials of different nature have been designed and synthesized using a wide variety of synthesis strategies. Depending on their structural and physicochemical characteristics, the present report has been divided into three main blocks: **1) coordination polymers, 2) silica-based organic-inorganic hybrid materials and 3) graphene-based hybrid materials.**

Several functionalization processes have been carried out in order to impart particular properties to some of these hybrid materials, which have been of great importance in specific applications. Likewise, a deep structural, textural, morphological and chemical composition characterization has been accomplished by means of a wide variety of instrumental techniques, which have served to elucidate the unique behaviour of the synthesized materials in research fields of special relevance to the industrial sector such as (photo/electro)catalysis, adsorption, luminescence or energy.

From this work, **in accordance with the objectives set out at the beginning of this Report**, the **conclusions** obtained from the articles included in each of the sections that make up **Chapter 4: Results and Discussion** are as follows:

- **Section 1: Coordination polymers-Metal Organic Frameworks (MOFs):**
 - In the paper "*Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions*" coordination polymers based on zirconium with different chiral organic ligands (L-tartaric acid, dibenzoyl-L-tartaric acid and L-

malic acid) were prepared under solvothermal conditions at reflux or autogenous pressure in autoclave. The textural and structural properties of the resulting polymers were directly related to the nature of the chiral ligand, the synthesis conditions and the metal:ligand ratio. These coordination polymers were active in the cyanosilylation reaction of benzaldehyde with TMSCN, particularly those containing malic acid synthesized at 110 °C in autoclave with stoichiometric metal:ligand ratios (Z_1M_1 -110A), resulting in high conversions (96%). Regarding the enantioselectivity shown by Z_1M_1 -110A, an enantiomeric excess of up to 12.6% has been observed using diethyl ether as solvent without requiring the presence of the promoting agent. Additionally, different *p*-substituted benzaldehydes have been used as substrates that are transformed to the corresponding cyanohydrin, in general, with good conversion and variable enantioselectivity, especially those with electron withdrawing substituents. Therefore, these materials can be considered very promising catalysts for Lewis acid-catalyzed organic processes.

- In the paper "*Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents*" an ultrasound method has been optimized to synthesize MOF MIL-88A crystals with high crystallinity and specific surface area. Depending on the ultrasound treatment and the reaction times applied, particles with different morphology, surface area and porosity were obtained. The materials obtained by ultrasound probes presented smaller particle sizes than those synthesized in an ultrasonic bath. However, the latter exhibited larger surface areas and a higher proportion of micropores.

Additionally, MIL-88A particles acted as Lewis acid active sites in ethylene adsorption processes and retained their structural integrity after several adsorption cycles. More specifically, Fe-fum-B1 exhibited specific ethylene adsorption comparable to other MOFs widely reported in literature, although its adsorption in absolute terms was lower due to its moderate surface area. This makes them very promising materials for the controlled capture and removal of ethylene in fruit packaging, which is particularly attractive and important for the agri-food sector.

- The paper "*MIL-88A Metal-Organic Framework as a stable sulfur-host cathode for long-cycle Li-S batteries*" was an extension of the previous research in which the MIL-88A MOF was synthesized by a fast ultrasonic probe-assisted procedure, resulting in the generation of small-sized crystalline particles with high specific surface area and pore volume. These textural and structural characteristics made it a suitable material to be used as a sulfur (S) host matrix in the cathode component of Li-S batteries, achieving to host 40 % of S in its structure. The MIL-88A@S composite demonstrated optimum energy storage capacity at high current densities and excellent electrochemical response under prolonged cycling conditions of up to 1000 charge-discharge cycles, providing an average specific capacity of 300 mAh g⁻¹ at a substantial current rate of 0.5 C. Therefore, the results suggested that this composite, consisting of a pristine MIL-88A MOF as sulphur-host matrix, could be a promising cathode component for Li-S batteries, which is a breakthrough in the research area of energy conversion and storage devices.

- **Section 2: Silica-based organic-inorganic hybrid materials-Periodic Mesoporous Organosilicas (PMOs):**

- The review paper "*Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production*" has highlighted that photocatalytic systems based on biomimetic models of the [FeFe]-hydrogenase active site have evolved substantially over the last two decades. From this article, it can be concluded that synthesis strategies to reproduce analogous architectures to those found in the natural hydrogenase enzyme, mechanistic elucidation of the role of the structural hydride, modification of their different coordination spheres and electrochemical investigation of the [2Fe2S] complexes have had a decisive impact on tuning their electronic and photophysical properties that determine their application as catalysts in visible light-assisted hydrogen production. The challenge in the future of this research area is to couple the reduction and oxidation half-reactions to construct complete artificial photosynthetic water splitting systems for the conversion of solar energy into chemical fuels. This research will provide new inspiration for energy technologies based on the fascinating world of photocatalysis and biomimetics.
- The previous review work laid the conceptual foundations to address the article "*Hydroxyl-decorated diiron complex as a [FeFe]-hydrogenase active site model complex: Light-driven photocatalytic activity and heterogenization on ethylene-bridged periodic mesoporous organosilica*" in which a biomimetic [FeFe]-hydrogenase active site model complex (FeFeOH), with

an ethylene bridge and a hydroxyl group, has been synthesized and characterized, and subsequently successfully investigated for the first time as a potential catalyst for visible light-driven hydrogen evolution. In addition, a novel precursor based on a triethoxysilane carbamate carrying a diiron dithiolate (NCOFeFe) was designed and prepared to be incorporated by a "grafting" procedure on a solid support, namely on a periodic mesoporous organosilica (PMO) with ethylene bridges (EthanePMO), thus obtaining the material EthanePMO@NCOFeFe with an iron loading of 0.235 mmol Fe/g PMO. The different variables influencing the photocatalytic reaction were successfully optimized under the irradiation of an LED light: pH, photon flux, catalyst concentration and photosensitizer concentration. Replacing the illumination system with a xenon lamp with higher light intensity and longer wavelength range led to an excellent improvement of the light-assisted hydrogen production, reaching TON values of 70 and 37 for FeFeOH and NCOFeFe, respectively. It was suggested that molecular aggregation phenomena due to the hydrophobic nature of the NCOFeFe precursor caused the decrease in photocatalytic activity compared to that shown by FeFeOH. Moreover, the immobilization of NCOFeFe on EthanePMO allowed stabilizing the catalytic complex, which was able to work in a fully aqueous medium, but led to lower yields in hydrogen generation, probably due to the blocking of some active sites. However, the catalytic activity results obtained in terms of TON for this heterogeneous EthanePMO@NCOFeFe catalyst were comparable to those obtained by other biomimetic models of [FeFe]-hydrogenase

immobilized on heterogeneous supports under analogous experimental conditions previously reported in literature.

- **Section 3: Graphene-based hybrid materials:**

- In the paper "*A Comparative Study of Particle Size Distribution of Graphene Nanosheets Synthesized by an Ultrasound-Assisted Method*" the ultrasound-assisted exfoliation of a micrographite to graphene nanosheets (GNS) has been carried out. This process was confirmed by different techniques, such as X-ray diffraction, transmission electron microscopy and Raman spectroscopy. Regarding the particle size distribution of the GNS, it was initially determined by dynamic light scattering (DLS), which provided the hydrodynamic radius and polydispersity of the GNS. Subsequently, two different techniques, nanoparticle tracking analysis (NTA) and asymmetric flow field flow fractionation (AF4), were applied for the first time in the study of graphene. NTA provided higher resolution than DLS as well as approximate concentrations. In addition, it was shown that DLS yielded an average particle size whose intensity was biased towards the larger graphene particles. AF4, on the other hand, allowed the separation of several GNS populations with different radii of gyration and, in addition, provided information on particle structure and shape. Clearly, the application of NTA and AF4, in addition to DLS, allowed the collection of very rich information about the graphene particles. The advantages mentioned above for NTA and AF4 have revealed their usefulness for the determination of the actual polydispersity in graphene preparations, the evaluation of their synthetic

procedures and the determination of size and fractionation in aqueous media for studies related to biological applications, sensing and toxicity.

- In the paper "*Luminescent Graphene-Based Materials via Europium Complexation on Dipyridylpyridazine-Functionalized Graphene Sheets*" a hetero-Diels-Alder reaction between 3,6-di(2-pyridyl)-1,2,4,5-tetrazine and graphene-based materials was performed providing well-defined sites for metal coordination in graphene sheets. Starting from the same graphite, three different procedures with alternative activation energies (ultrasound, ball-milling and heating) resulted in few-layer graphene (FLG), multilayer graphene (MLG) and graphite (MG) functionalized with dipyridylpyridazine units. All of them have proven to be useful ligands for the formation of europium complexes. The emission properties of these materials were studied before and after their binding to $\text{Eu}(\text{dbm})_3$ complexes, observing strong red Eu^{3+} emission in the visible with a wide range of excitation wavelengths. Therefore, this methodology could allow the labelling of graphene-based materials for bioimaging regardless of their particle size. The extension of this synthesis strategy to other graphene-metal complexes may lead to materials with potential applications in organometallic chemistry, catalysis, biomedicine, imaging and sensing, among others.
- In the paper "*Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN_4 sites for ORR and OER electrocatalysis*" a novel low-temperature solvent-free mechanochemical synthesis strategy for the

generation of edge-enriched FeN₄ sites from multilayer graphene functionalized with dipyridylpyridazine (dppz) units by a Diels-Alder reaction was successfully developed. The findings found in this work demonstrated that the dppz adducts at the edges of graphene sheets were able to act as ligands for the coordination of iron atoms. Subsequent heat treatment at 240 °C under nitrogen atmosphere provided a more successful specific incorporation of FeN₄ sites at the edges of the sheets than under oxidizing conditions in the presence of air. Based on this, the resulting MLG-dppz@Fe(240N₂) material, although exhibiting low iron content, provided unprecedented bifunctional electrocatalytic performance for oxygen reduction (ORR) and oxidation (OER) reactions, both of which are of vital importance in a wide range of energy conversion and storage devices. This synthetic strategy will pave the way in the development of new sustainable approaches for the generation of single-atom sites, such as FeN₄ centers enriched at the edges of multilayered graphene structures with bifunctional electrocatalytic properties.

➤ CONCLUDING REMARKS:

The aspects dealt with in this Doctoral Thesis do not exhaust, far from it, all the possibilities of study that can be addressed in this type of organic-inorganic hybrid materials with new structures and unique characteristics.

In general terms, these investigations will contribute to advance in the knowledge of these materials, from their structural design to the choice of the optimal synthesis strategies to give the resulting hybrid the desired characteristics. The physicochemical properties presented by each of them

have allowed us to enter into novel application fields of great current interest for the scientific community. Among them, we can highlight:

a) Coordination polymers and metal-organic frameworks present metal species, which act as very efficient Lewis acids in catalytic and adsorption processes, and organic ligands, which provide an environment capable of interacting, even enantioselectively, and adsorbing organic molecules.

b) Periodic mesoporous organosilicas show an inorganic network, which provides the structural support of the material, and organic fragments, which exhibit hydrophobic character and provide functionality, thus resulting in siliceous materials endowed with great stability and catalytic active centers.

c) Hybrid graphene materials combine the characteristics of graphenes with the broad photophysical and catalytic properties of organometallic fragments.

Although in some cases the results obtained have not reached the initially foreseen expectations, the work carried out in this Thesis at laboratory scale has laid the foundations and fundamental stages so that, in the immediate future, it will be possible to continue deepening the studies framed in the lines of research contained in this Report.

Our society does not know the limit of its demands; therefore, it is considered essential that the scientific community is going to solve them as they arise; many of them, in the field of energy, catalysis, selective adsorption of gases and emerging pollutants, controlled dosing of drugs, food, biology, pharmacology, informatics, environmental remediation

and industrial chemistry, among others. Many of these needs, which have been arising exponentially over the years, directly attributed to the humanity development, will have their solution in the area of Materials Chemistry. To this end, the future of organic-inorganic hybrid materials will be strongly marked by the discovery of new synthesis procedures that provide the resulting material with long-term stability, higher reusability and specificity, and lower economic production costs. Thus, its novel applications, which will have a major impact on the industrial sector, will contribute to sustaining the welfare and improving the global economy.

Anexo 1

Producción científica

I.I. Indicios de calidad

A continuación, quedan recogidos los índices de calidad de los artículos científicos que conforman el compendio de publicaciones de la presente Tesis Doctoral, cuya información de impacto se obtuvo de la base de datos *Journal Citation Reports (JCR)* de ISI Web of Knowledge (*Web Of Science*, WOS):

- **Sección 1: Polímeros de coordinación-Metal Organic Frameworks (MOFs):**

Título	Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions
Autores	Juan Amaro-Gahete; Dolores Esquivel; José Rafael Ruiz; César Jiménez-Sanchidrián; Francisco José Romero-Salguero.
Revista	Applied Catalysis A: General
Año, volumen, páginas	2019, 585, 117190
Editorial	Elsevier
DOI	10.1016/j.apcata.2019.117190
Índice de impacto (2019)	5.006
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Environmental sciences: 41/265 (Q1) Chemistry/physical: 47/159 (Q2)

Título	Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents
Autores	Juan Amaro-Gahete; Rafael Orlando Klee; Dolores Esquivel; José Rafael Ruiz; César Jiménez-Sanchidrián; Francisco José Romero-Salguero.
Revista	Ultrasonics Sonochemistry
Año, volumen, páginas	2019, 50, 59 - 66
Editorial	Elsevier
DOI	10.1016/j.ultsonch.2018.08.027
Índice de impacto (2019)	6.513
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Acoustics 1/31 (D1) Chemistry, Multidisciplinary: 34/178 (Q1)

Título	MIL-88A Metal-Organic Framework as a Stable Sulfur-host Cathode for Long-cycle Li-S Batteries
Autores	Almudena Benítez*; Juan Amaro-Gahete*; Dolores Esquivel; Francisco José Romero-Salguero; Julián Morales; Alvaro Caballero *Ambos autores contribuyen por igual en este trabajo
Revista	Nanomaterials
Año, volumen, páginas	2020, 10 (3), 424
Editorial	MDPI
DOI	10.3390/nano10030424
Índice de impacto (2020)	5.076
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Physics, Applied: 35/160 (Q1) Chemistry, Multidisciplinary: 55/178 (Q2) Materials science, Multidisciplinary: 103/334 (Q2) Nanoscience & Nanotechnology: 51/106 (Q2)

- **Sección 2: Materiales híbridos orgánico-inorgánicos basados en sílice-Periodic Mesoporous Organosilicas (PMOs):**

Título	Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production
Autores	Juan Amaro-Gahete; Mariia V. Pavliuk; Haining Tian; Dolores Esquivel; Francisco José Romero-Salguero; Sascha Ott
Revista	Coordination Chemistry Reviews
Año, volumen, páginas	2021, 448, 214172
Editorial	Elsevier
DOI	10.1016/j.ccr.2021.214172
Índice de impacto (2020)	24.833
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Chemistry, Inorganic & Nuclear: 1/46 (D1)

Título	Hydroxyl-Decorated Diiron Complex as a [FeFe]-Hydrogenase Active Site Model Complex: Light-Driven Photocatalytic Activity and Heterogenization on Ethylene-Bridged Periodic Mesoporous Organosilica
Autores	Juan Amaro-Gahete; Dolores Esquivel; Mariia V. Pavliuk; César Jiménez-Sanchidrián; Haining Tian; Sascha Ott; Francisco José Romero-Salguero
Revista	Catalysts
Año, volumen, páginas	2022, 12 (3), 254
Editorial	MDPI
DOI	10.3390/catal12030254
Índice de impacto (2020)	4.501
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Chemistry, Physical: 70/163 (Q2)

- **Sección 3: Materiales híbridos basados en grafeno:**

Título	A Comparative Study of Particle Size Distribution of Graphene Nanosheets Synthesized by an Ultrasound-Assisted Method
Autores	Juan Amaro-Gahete; Almudena Benítez; Rocío Otero; Dolores Esquivel; César Jiménez-Sanchidrián; Julián Morales; Álvaro Caballero; Francisco José Romero-Salguero
Revista	Nanomaterials
Año, volumen, páginas	2019, 9 (2), 152
Editorial	MDPI
DOI	10.3390/nano9020152
Índice de impacto (2019)	4.324
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Materials science, Multidisciplinary: 89/314 (Q2) Nanoscience & Nanotechnology: 42/103 (Q2)

Título	Luminescent Graphene-Based Materials via Europium Complexation on Dipyridylpyridazine-Functionalized Graphene Sheets
Autores	Juan Amaro-Gahete; Anna M. Kaczmarek; Dolores Esquivel; César Jiménez-Sanchidrián; Pascal Van der Voort; Francisco José Romero-Salguero
Revista	Chemistry-A European Journal
Año, volumen, páginas	2019, 25, 6823 - 6830
Editorial	Wiley-VCH Verlag GmbH
DOI	10.1002/chem.201900512
Índice de impacto (2019)	4.857
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Materials science, Multidisciplinary: 44/177 (Q1)

Título	Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN ₄ sites for ORR and OER electrocatalysis
Autores	Juan Amaro-Gahete; José Ángel Salatti-Dorado; Almudena Benítez; Dolores Esquivel; Valentín García-Caballero; Miguel López-Haro; Juan José Delgado; Manolo Cano; Juan José Giner-Casares; Francisco José Romero-Salguero.
Revista	Sustainable Energy & Fuels
Año, volumen, páginas	2022, 6, 1603-1615
Editorial	Royal Society of Chemistry
DOI	10.1039/D2SE00004K
Índice de impacto (2020)	6.813
Categorías: Lugar que ocupa/Nº revistas del área temática (Cuartil)	Materials science, Multidisciplinary: 91/345 (Q2) Chemistry, Physical: 47/163 (Q2) Energy & Fuels: 40/119 (Q2)

I.II. Otras publicaciones derivadas de la Tesis Doctoral

Adicionalmente al compendio de publicaciones recogido en el apartado “Chapter 4: Results and discussion” de la presente memoria, el doctorando ha participado en otros trabajos de investigación, así como colaboraciones científicas, de las cuales se han derivado las siguientes publicaciones en revistas internacionales:

I.II.I. Artículos científicos publicados como autor principal

IOP Publishing

Journal of Physics D: Applied Physics

J. Phys. D: Appl. Phys. 53 (2020) 435202 (7pp)

<https://doi.org/10.1088/1361-6463/aba069>

Preparation of graphene-based nanomaterials by pulsed RF discharges on liquid organic compounds

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Received 15 April 2020, revised 19 June 2020

Accepted for publication 26 June 2020

Published 30 July 2020



Abstract

A new pulsed RF plasma reactor has been used for the synthesis of graphene-based nanomaterials under atmospheric pressure conditions. This is an environmental-friendly system, not using catalyst and where no hazardous components are generated. Nanographenes formed upon plasma treatment of some hydrocarbons (cyclohexane, cyclohexene, heptane, hexane, pentane, and toluene), while N-containing organic compounds (cyclohexylamine, pyridine, dipropylamine, and triethylamine) resulted in N-doped graphenes. Synthesis took place in a very fast way, mediated by plasma reactive species.

Keywords: hydrocarbons, graphene, pulsed corona plasma

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Published in *Journal of Physics D: Applied Physics*

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Abstract

A new pulsed RF plasma reactor has been used for the synthesis of graphene-based nanomaterials under atmospheric pressure conditions. This is an environmental-friendly system, not using catalyst and where no hazardous components are generated. Nanographenes formed upon plasma treatment of some hydrocarbons (cyclohexane, cyclohexene, heptane, hexane, pentane, and toluene), while N-containing organic compounds (cyclohexylamine, pyridine, dipropylamine, and triethylamine) resulted in N-doped graphenes. Synthesis took place in a very fast way, mediated by plasma reactive species.

Keywords: hydrocarbons, graphene, pulsed corona plasma

I.II.I.1. Introduction

The study of graphene-based nanomaterials has experienced an extraordinary development in recent years [1–4]. The interest of researchers in this field relies on the outstanding electronic, mechanical, thermal and optical properties of this privileged material [5,6]. The use and commercialization of graphene offer a wide range of possibilities that will entail a real technological revolution.

Graphene is a 2D material consisting of a single graphite sheet with a thickness of a carbon atom formed by a network of hexagonal rings with sp^2 -hybridized carbons. It is an allotropic form of carbon and constitutes the basic elementary 2D unit to build graphitic materials of other dimensions such as carbon nanotubes, fullerenes, and graphite [7].

Small thickness, flexibility, transparency, lightness, high charge-carrier mobilities, and excellent adhesion to surfaces are some of the unique and novel features that these materials have. However, the isolation of individual graphene sheets is a complex task, due to their tendency to agglomerate in solution. Despite this, methods for obtaining single layer graphene, such as chemical vapor deposition (CVD), have been developed producing high-quality monolayer graphene [8,9].

Generally, the term graphene refers to the simple constitutive unit, whereas those formations of nanometric thickness based on graphene are named nanographenes. Although a few-layer and multilayer graphenes are easier to synthesize, they have less flexibility and transparency than monolayer graphene, which limits some of their applications. However, their extraordinary characteristics of conductivity and capacitance have been reported of great relevance in electronic devices, water desalination, and supercapacitors, and they can even be improved with metal doping. Carbonaceous materials formed by aggregates of thickness exceeding nanometers also have good properties from the point of view of their application to electronics, given their structural similarity with graphite, although they are not as extraordinary as graphenes and nanographenes [10].

Various methods of obtaining graphene have been described in the literature, which can be mainly classified into two main groups: *bottom-up* (CVD or chemical synthesis) and *top-down* synthesis. Concerning top-down processes, the general strategy consists in starting with commercial graphite as an elementary unit, in order to obtain graphene compounds. For

this purpose, methods such as liquid-phase exfoliation of graphite, mechanical exfoliation by ball milling, or chemical exfoliation (oxidation process and subsequent reduction of the functional groups) have been investigated and continuously improved at both, scientific and industrial levels, to obtain graphene with different sizes, number of layers, and defects in the sheets [11]. Graphene is commonly synthesized through the Hummers method in which graphene oxide (GO) is produced by reactions of graphite with different oxidizing agents (HNO_3 , KMnO_4 or H_2SO_4). Subsequently, the functional groups present in the GO sheets are reduced by using different reducing agents, such as hydrazine, thus obtaining the reduced graphene oxide (rGO) [12]. A key factor during graphene synthesis processes is the breaking of the attraction forces between the sheets that make up the graphite while avoiding, in turn, a post-synthesis rearrangement. Thus, it is of utmost importance to select a suitable exfoliation method, using an appropriate agent that contributes to the stability of suspended graphene.

In the last 25 years, plasma technology has emerged as a very interesting tool for material synthesis. Plasmas are a source of active species including charged particles (electrons and ions), excited species, radicals, and UV radiation, which allow them to foster traditional chemical reactions and promote new ones, unattainable in conventional chemical reactors. Thus, plasma-enhanced chemical vapour deposition technique has been used to synthesize carbon materials such as diamonds, carbon nanotubes (CNTs), vertically oriented graphene (VG) nanosheets as well as graphene. This method has demonstrated to be very promising for controllable graphene synthesis [13]. Also, different plasmas have been used to synthesize graphenes from different carbon sources in the gas phase [14–16]. For instance, graphene-based materials and carbon quantum dots (CQD) have been obtained by plasma technology through clean, eco-friendly and large-scale processes from alcohols as a carbon source using a microwave (2.45 GHz) plasma source [17–19].

Plasmas have also been applied to the functionalization of different carbon nanostructures, including graphenes. Different types of plasma have been used for this purpose including glow discharges [20], dielectric barrier discharges [21], and hollow cathode discharges [22].

Less often, plasmas have been also used for the functionalization of graphene-derived materials in the liquid phase [23,24]. In addition, different nanomaterials have been synthesized in the plasma-liquid

interface, particularly metal nanoparticles [25]. However, the preparation of graphenes by plasma-liquid interaction remains rather unexplored. The first examples reported in this field refer to arc discharge plasmas originated between two graphite electrodes [26]. Atmospheric pressure microplasmas have also been used for obtaining carbon quantum dots. In this way, Huang and coworkers have reported on the fast synthesis of CQD by using a helium DC microplasma [27]. More recently, colloidal graphene quantum dots have been synthesized through the interaction of an argon DC microplasma with a precursor aqueous solution (organosulfate) [28].

A very versatile reaction system for certain applications is the pulsed corona discharge. These discharges have many advantages since they allow the treatment of complex surfaces, they are easy to handle, and they enable an enhancement of chemical reactions under atmospheric pressure conditions. Based on this, they have been applied to diverse industrial operations, including the generation of ozone [29], surface treatments [30], or gasification of wastes [31].

In this work, we report on the use of a new pulsed RF plasma corona reactor, operating at atmospheric pressure, to obtain nanographenes in one-step at a remarkable short reaction time through its interaction with liquid organic compounds.

I.II.I.2. Experimental section

I.II.I.2.1. System setup and synthesis procedure

A novel pulsed RF plasma corona device and its application to the formation of nanographene from liquid organic compounds with different structures in a specifically designed reactor have been developed. A scheme of the apparatus design is shown in **Figure 1**. A detailed description of this coaxially arranged plasma source may be found elsewhere [32]. This device consisted of a rod electrode with a sharp end inside a quartz tube. A second electrode (ring-shaped) surrounded the end of this tube. The corona plasma created in this cylindrical quartz chamber was the initiator of a second one (main plasma) extending throughout the volume of a second reactor chamber, surrounded by a capacitive structure consisting of a dielectric element (2-20 mm thick) with a metallic coating. Argon (with a purity $\geq 99,995\%$) was used as main and auxiliary gas of the discharges in both chambers due to its inert and easy ionizable character.

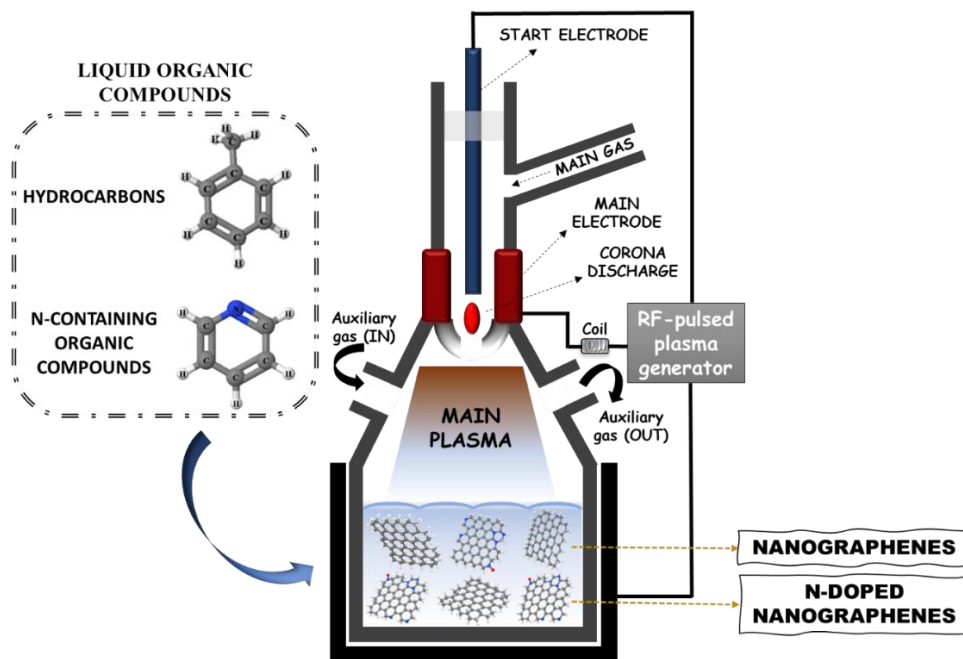


Figure 1. Configuration of the pulsed plasma reactor

The pulsing device mainly consisted of: (i) an oscillator configured to provide the RF signal (13.56 MHz); (ii) a pulse generator; (iii) and a power amplifier circuit designed to amplify the power of the oscillator output RF signal. This system delivered 5 kW through single RF bursts (peak voltage ~ 10 kV), 50 ms long, thus allowing a fast expansion of the plasma in the second chamber, and a reduction of its gas temperature. The distance from the outlet of the corona discharge to the organic liquid surface was 20 mm. The distance between the tip of the initial electrode and the main electrode was optimized around 2 mm in order to achieve breakdown when the RF voltage was applied. The synthesis was carried out inside polypropylene tubes, where 1 mL of different organic compounds was placed. Thus, 6 tubes were arranged in series and two discharges were applied per tube until reaching a total of 6 discharges of 50 ms in each of them. Next, the contents of these tubes, which contained the starting reagent in addition to suspended carbonaceous particles, were collected in a vial. To purify and isolate the graphene material obtained, the suspension was centrifugated at 3500 rpm for 10 minutes.

The isolated solid was washed twice with the starting organic compound. After it, the graphene-based material was dried in an oven at

120 °C until complete elimination of the remaining organic residues. Cyclohexane, cyclohexene, heptane, hexane, pentane, and toluene were chosen as starting hydrocarbons. Additionally, cyclohexylamine, pyridine, dipropylamine, and triethylamine were used as starting N-containing organic compounds. Therefore, the application of plasma pulses on each of the liquid organic compounds produced a suspension from which a small amount of a black solid, i.e nanographenes and N-doped graphenes, was isolated.

I.II.I.2.2. Characterization techniques

A Renishaw Raman instrument (InVia Raman microscope) was used to obtain the Raman spectra by excitation with a green laser light (532 nm). A total of 10 scans per spectrum were acquired to improve the signal-to-noise ratio with an exposure time of 25 s. The laser power used was 1% with 1800 l/mm grating at 50x magnification. For the sample preparation, 50 μL organic suspension of nanographenes previously sonicated in an ultrasound bath for 5 min was deposited in a glass slide. After evaporation of the solvent, the spectra were acquired by inciding the laser on the resulting particles. Transmission electron microscopy (TEM) images were recorded on a Jeol JEM-1400 transmission electron microscope operated at an accelerating voltage of 120 kV. The measurements were made in a magnification range between 200x a 1.200.000x with an instrument resolution of 0.38 nm between points. XPS spectra were recorded on a SPECS mod. PHOIBOS 150 MCD spectrometer using monochromatic Mg $K\alpha$ radiation and a multichannel detector. All spectra were fitted to Gauss–Lorentz curves and were corrected with respect to the adventitious carbon reference at 284.8 eV using CasaXPS software. The solid powder samples were placed on stainless steel cylinders with a surface of 0.5 cm^2 and analyzed under ultra-high vacuum conditions.

I.II.I.3. Results and discussion

The application of corona plasma discharges resulted in the successful production of nanographenes from hydrocarbons and N-containing organic compounds. Raman spectroscopy is a fundamental characterization technique providing very useful structural information on carbon-based materials. All Raman spectra recorded from 700 to 3000 cm^{-1} showed the typical bands of graphene-based materials (**Figure 2**).

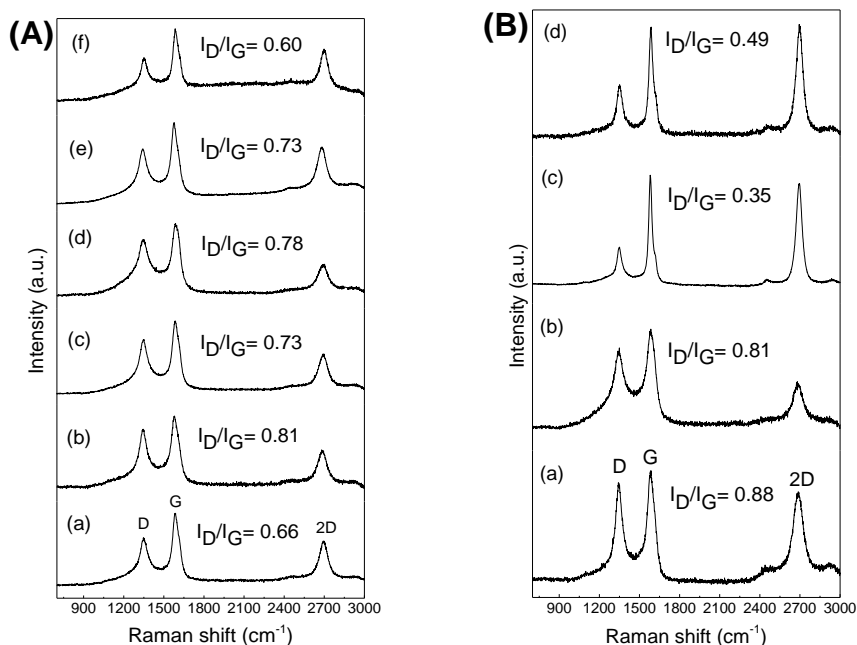


Figure 2. Raman spectra of graphene-based materials obtained from hydrocarbons (A): cyclohexane (a), cyclohexene (b), heptane (c), hexane (d), pentane (e) and toluene (f); and from N-containing compounds (B): cyclohexylamine (a), pyridine (b), dipropylamine (c) and triethylamine (d).

Three fundamental bands can be distinguished: (i) the G band, associated to splitting of the E_{2g} stretching mode, confirming sp^2 hybridized carbon atoms in the graphitic structure; (ii) the D band characteristic of C-C single bonds with sp^3 -hybridized carbon atoms in a cubic diamond crystalline form, related to the double resonant process, which arises from intervalley phonons, indicating the amount of defects in the graphene material (edges, vacancies, etc.) [33]; and (iii) the 2D band, which is an overtone of the D band, very useful to calculate the number of layers in graphene samples [34]. The degree of disorder of the layers in graphene-based materials can be estimated by calculating the ratio of intensities of the D band to the G band [35]. A perfectly ordered structure of highly oriented pyrolytic graphite (HOPG) has an I_D/I_G ratio close to 0 [36]. An increase in the D band with respect to the G band indicates the introduction of defects in the graphene structure, thus increasing the level of disorder. In this work, the most ordered materials were obtained from toluene ($I_D/I_G = 0.60$), in the case of hydrocarbons, and from dipropylamine ($I_D/I_G = 0.35$), in the case of N-containing organic compounds. Typical I_D/I_G ratios for

graphene oxide (GO) and reduced graphene oxide (rGO) are around 0.97 and 1.05, respectively, suggesting that the obtained graphene-based materials present higher structural order of layers [37,38]. In addition, the intensity of the G band was higher than that of the D band for all samples indicating that most of the carbons in the nanographenes had sp^2 hybridization [19].

The number of layers in graphene-based materials is directly related to the intensity ratio of the G and 2D bands, as reported by Das et al. [39] following the equation: $I_G/2I_D = 0.14 + n/10$, where n is the number of graphene layers. In all cases, the number of layers formed ranged from 8 to 22 (**Figure 3**). Thus, few-layer graphene (FLG, less than 10 layers) were obtained with dipropylamine and triethylamine, whereas multilayer graphenes (MLG, >10 layers) were produced with the rest of organic compounds [40].

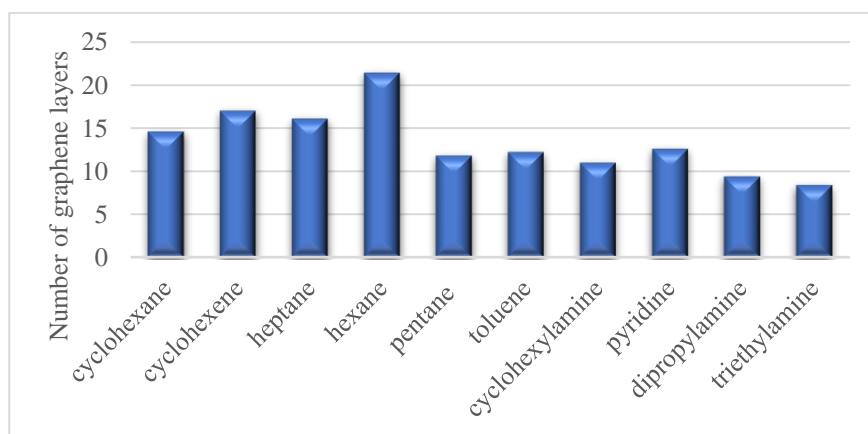


Figure 3. Number of layers in nanographenes obtained by pulsed plasma discharges on different organic compounds.

TEM images of graphenes obtained from all of the studied organic compounds showed particles of diameter below 100 nm (**Figure 4**). Those from toluene and pyridine gave larger particles with sizes between 50 and 100 nm, whereas those from the rest of compounds produced smaller particles between 10 and 30 nm. Spherical carbon nanoparticles (**Figure 4c**) and graphene flakes (**Figure 4c**, inset) seemed to be present in those materials produced from toluene. This mixture of different products has also been obtained using a magnetically rotating arc plasma by methane or propane decomposition under an Ar atmosphere [41,42]. Instead, folded graphene sheets were clearly evidenced for those coming from other

organic compounds (**Figure 4**), which exhibited a similar morphology to other reported in the literature, such as those generated from different aliphatic linear alcohols (from ethanol to decanol) using a radiofrequency thermal plasma jet [43]. The inset in **Figure 4b** shows a magnification of the graphene flakes agglomerates obtained from hexane.

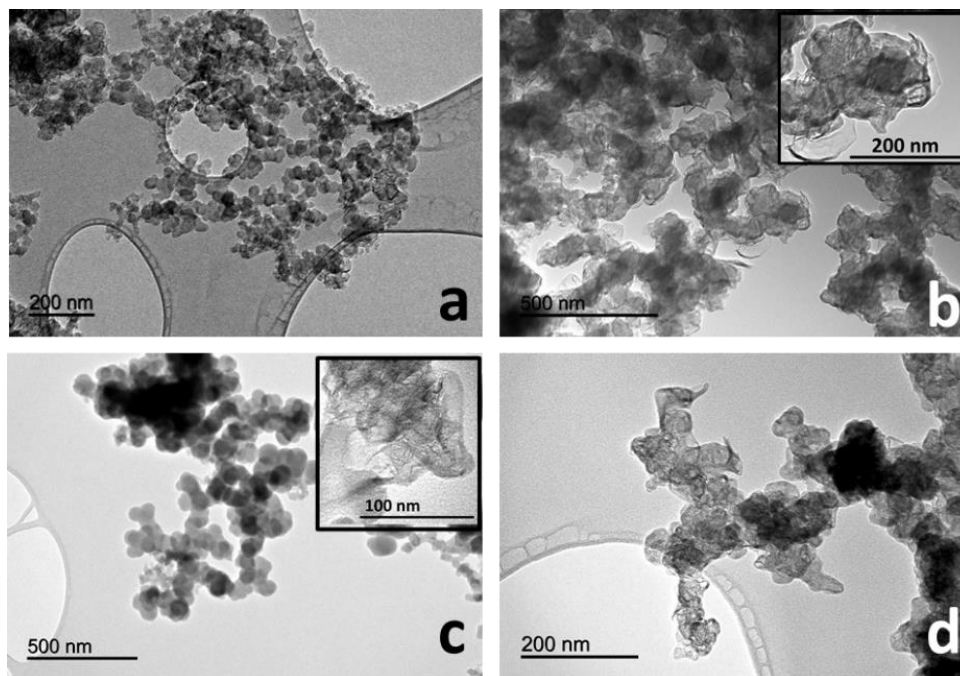


Figure 4. Representative TEM images of nanographenes obtained from cyclohexene (a), hexane (b), toluene (c) and pyridine (d).

Under the conditions studied, aromatic compounds, i.e. toluene and pyridine, gave rise to a higher yield of graphene-based materials in relation to the other organic compounds. Around 2 mg of graphene were obtained in a reaction cycle (6 vials, 6 pulses each) from these two organic compounds and their composition was determined by elemental analysis of XPS survey spectra (**Figure 5**). Results revealed 97.1 wt% C and 2.9 wt% O for graphene derived from toluene and 95.6 wt% C, 1.9 wt% O and 2.5 wt% N for that from pyridine. Remarkably, N content was quite high as compared with other graphene materials obtained in a microwave plasma reactor at atmospheric pressure using ethanol and ammonia as carbon and nitrogen precursors, respectively, which gave 0.4% N [44].

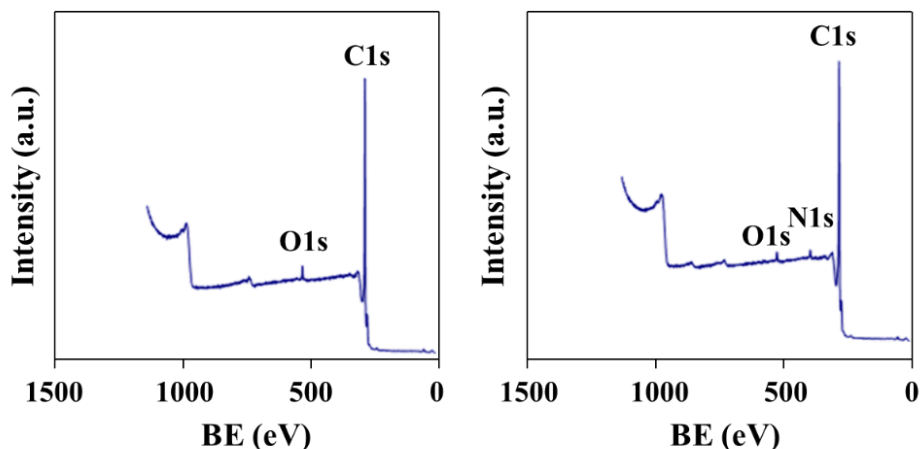


Figure 5. XPS survey for nanographenes obtained from toluene (right) and pyridine (left).

The C1s signal of the graphene obtained from toluene (**Figure 6**) displayed three components corresponding to graphitic C-C (285 eV), C-O alkoxy (285.9 eV) and C=O (289.7 eV), respectively [38]. The O1s signal corroborated the presence of C-O bonds (533.7 eV) and carboxylic groups (535.3 eV). Similar C1s and O1s XPS signals were observed for the material synthesized from pyridine (**Figure 7**). Additionally, the N1s signal was decomposed into three main components, i.e. pyridinic N (399.5 eV), quaternary N (401.2 eV) and pyridinic N-oxide (402.8 eV) [45,46]. This corroborates the production of N-doped graphenes by the interaction of plasma with liquid N-containing organic compounds.

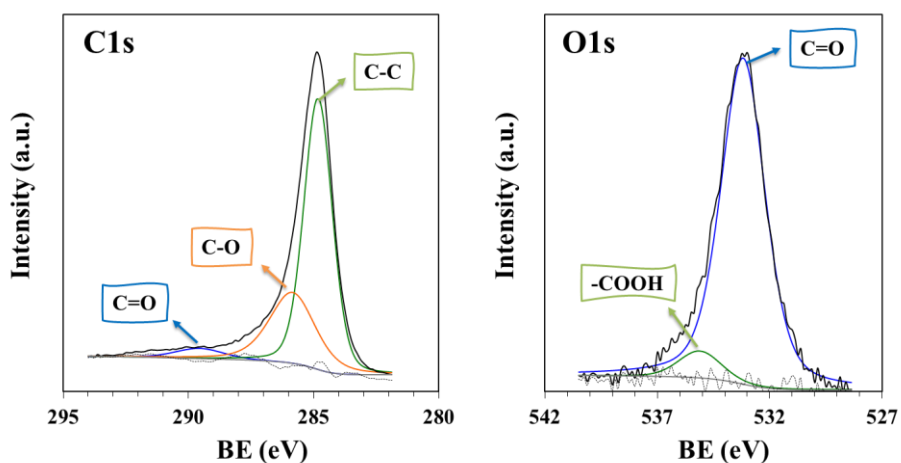


Figure 6. XPS spectra for the C1s and O1s photoemission peaks of nanographenes obtained from toluene.

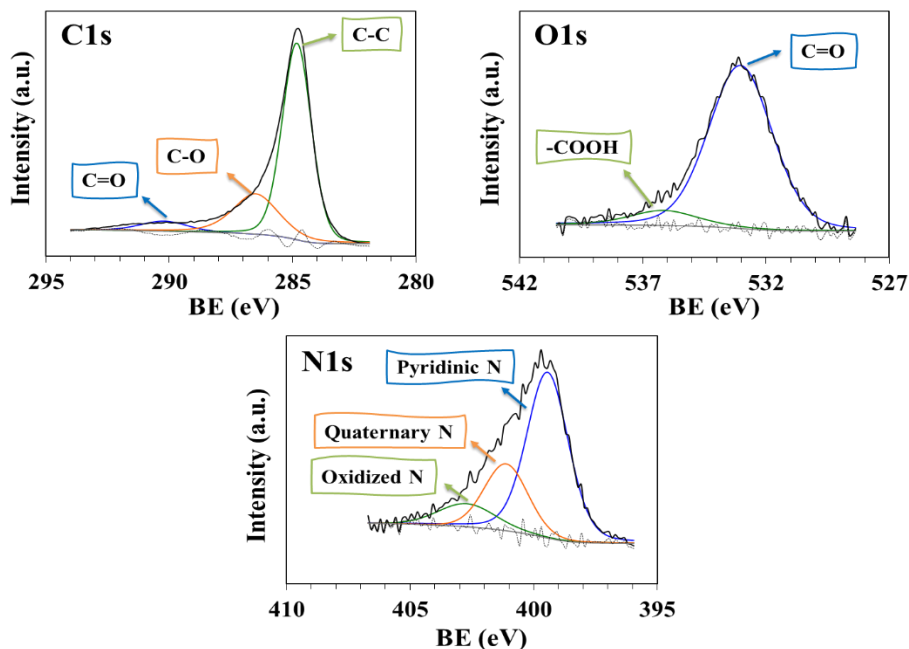


Figure 7. XPS spectra for the C1s, O1s and N1s photoemission peaks of nanographenes obtained from pyridine.

Energetic electrons and argon excited species from the plasma likely play an outstanding role in the interaction of the plasma with the liquid hydrocarbon. Yang et al [28] have shown that electrons play an outstanding role in the synthesis of CQDs from an argon DC microplasma in contact with an aqueous precursor. By analogy with other processes where plasma discharges interact with liquids [47], argon excited species might cause the dissociation of C-H bonds leading to radicals that react and/or combine with organic molecules. These intermediates would evolve losing hydrogen and finally forming graphene sheets with sp^2 hybridized carbon atoms. Accordingly, organic molecules only containing sp^2 carbon atoms, that is, toluene and pyridine, provided a higher yield to graphenes.

This methodology opens up new perspectives for the preparation of graphene derivatives. The energy supplied by the plasma discharge, the number of pulses and/or the duration of each pulse are some of the variables that can allow tailoring the graphene structure (morphology, particle size, number of layers). Likewise, graphenes incorporating different heteroatoms, such as S, B, and P, could be obtained using appropriate organic compounds with these elements in their structure.

I.II.I.4. Conclusions

In this work we have reported on the successful fast synthesis of nanographenes using a new RF plasma reactor operating at atmospheric pressure. The interaction of pulsed plasma discharges with a variety of liquid organic compounds produced nanographenes, specifically few-layer or multilayer graphenes, with 8 to 22 layers and particle size between 10 and 100 nm, depending on the starting compound. Interestingly, the incorporation of heteroatoms present in the starting organic compound has been proven. This procedure constitutes a new bottom-up strategy for the synthesis of graphene-based materials with a great versatility.

Acknowledgements

The authors wish to acknowledge the financial support from Ramon Areces Foundation (Spain), Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981) and project RTI2018-101611-B-I00, Andalusian Regional Government (FQM-346 group), Feder Funds, the technical staff from the Instituto Universitario de Investigación en Química Fina y Nanoquímica (IUNAN) and Servicio Central de Apoyo a la Investigación (SCAI). We thank Engineer Nicolaas Van Dijk for his technical support.

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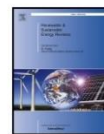
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Recent advances in lithium-sulfur batteries using biomass-derived carbons as sulfur host

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ARTICLE INFO

Keywords:

Activated carbon
Biomass
Li-S batteries
Sustainable materials
Sulfur hosts
Bio-waste

ABSTRACT

While biomass waste is generated in abundance, these materials and their production processes are generally environmentally friendly, low cost, non-hazardous and easily scalable. These advantages position biomass materials as excellent candidates to solve problems of environmental pollution, primarily by substitution of less sustainable counterparts. This also applies to energy storage systems such as batteries, where several components have large environmental impacts. Lithium-Sulfur batteries have, in this context, been extensively researched to cope with the growing energy needs, and are expected to foresee a growing commercialization. Specifically, advances in the use of renewable cathode materials for Li-S batteries is a field that has been widely addressed in recent years, with carbonaceous materials (C) and/or activated carbons (AC), obtained from biomass, being intensively studied. We here reviewed this field through a classification and discussion of carbonaceous materials from natural waste according to the type of biomass: (1) woody, (2) herbaceous and agricultural, (3) aquatic, (4) animal and human, and (5) contaminated and industrial biomass waste materials. In addition, all porous carbons or activated carbons used as sulfur hosts have been exhaustively evaluated in terms of origin, synthesis parameters, physical properties, and electrochemical performance in Li-S batteries. The purpose is to provide a general description of the progress in the preparation of carbons from biomass resources, examine the textural and electrochemical properties of these materials focusing on the last decade, and also to present an outlook for future research in this developing area.

1. Introduction

From the discovery of fire to modern civilization, energy has played a fundamental role in our lives. In fact, its importance has reached such an extent that in today's society, the availability of energy is strongly linked to well-being, economy, health, and even life expectancy. However, the global energy system is still dominated by non-renewable fossil fuels (oil, coal and natural gas) and nuclear energy [1] which are finite and have limited reserves. We must therefore consider how the next generations will sustain themselves energetically in the future. Although this has been known for centuries, humanity has not yet been able to develop new technologies with the same power as the traditional ones [2].

It should be noted that coal has generally been the resource that has

come to the rescue for energy throughout modern civilizations. However, this resource is unsustainable since the amount of carbon that needs to be stored to meet current energy demands is enormous, and, so far, the Carbon Capture and Storage (CCS) is not an effective enough process [3]. The environmental problems associated with the use of these types of fossil fuels, due to their combustion, are well known: generation of pollutants such as sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide, carbon dioxide (an important greenhouse gas or GHG), hydrocarbons, and particles that affect air quality, leading to photochemical smog, soot and acid rain, and therefore posing a risk to the health of humans, animals and plants [4]. Nuclear energy in turn, in addition to safety concerns exemplified by Chernobyl and Fukushima, presents the serious problem of the management of spent fuel, which has

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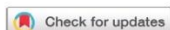
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<https://doi.org/10.1016/j.rser.2021.111783>

Received 29 April 2021; Received in revised form 18 September 2021; Accepted 15 October 2021

Available online 29 October 2021

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Cite this: *Dalton Trans.*, 2022, **51**,
4884

Copper-complexed dipyriddy-pyridazine functionalized periodic mesoporous organosilica as a heterogeneous catalyst for styrene epoxidation

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A new heterogeneous catalyst has been synthesized by immobilization of a copper complex on dipyriddy-pyridazine functionalized periodic mesoporous organosilica (dppz-vPMO). This ordered support was first prepared by a co-condensation reaction between vinyltriethoxysilane and 1,2-bis(trimethoxysilyl)ethane and further post-functionalized through a hetero Diels-Alder reaction with 3,6-di-2-pyridyl-1,2,4,5-tetra-zine. Techniques such as XRD, N₂ isotherms, TEM, ¹³C NMR, XPS and DRIFT, among others, were employed to characterize the surface functionalized materials. These results have proven the ordered mesostructure of the materials as well as the presence of novel nitrogen-chelating heterocyclic compounds on the pore surface after the post-modification process. Additionally, the successful anchoring of a copper complex on the dipyriddy-pyridazine (dppz) ligands has been confirmed. The resulting material was evaluated as a heterogeneous catalyst in the epoxidation of styrene using *tert*-butylhydroperoxide (TBHP) as an oxidant. Under the optimized reaction conditions, Cu@dppz-vPMO showed a high styrene conversion (86.0%) and a remarkable selectivity to styrene oxide (41.9%). Indeed, this catalyst provided excellent catalytic results in terms of stability, reaction rate, conversion and selectivity compared to other bipyridine-like copper catalysts.

Received 3rd January 2022,
Accepted 23rd February 2022
DOI: 10.1039/d2dt00018k

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1. Introduction

Epoxidation of olefins is one of the most relevant reactions in organic synthesis since the resultant epoxide products are important and versatile intermediates for the synthesis of a wide variety of fine chemicals, pharmaceuticals, agrochemicals, and perfumes, among others.¹⁻⁴ While traditional methods for the synthesis of epoxides are characterized using stoichiometric amounts of harmful oxidants (peracids) and generate enormous waste,⁵⁻⁷ the recent synthetic methodologies in this field are focused to overcome them. Thus, the use of safer oxidizing agents, such as *tert*-butyl hydroperoxide (TBHP), molecular oxygen or hydrogen peroxide in styrene epoxidation provides an economical and environment friendly alternative. However, their characteristic low reactivity and selectivity in this type of reaction when they are used alone have led to the use of such oxidants in combination with tran-

sition-metal catalysts.^{3,8} Over the last few decades, a wide variety of ions, oxides and complexes of transition metals have been explored through homogeneous catalytic processes. Although these systems lead to high yields in the epoxidation reactions, their immobilization on solid supports has gained much more attention from an environmental and economic perspective due to their potential applications in industry.⁹⁻¹⁴ Nowadays, the development of efficient heterogenized catalytic systems for the epoxidation of olefins remains a challenge.^{4,15-17} Different types of porous materials, such as zeolites,¹⁸ polymers,¹⁹ mesoporous silicas,¹⁴ activated carbons²⁰ or MOFs,²¹ have been employed as supports of transition metal complexes for liquid phase epoxidation of olefins.

Studies on epoxidation reactions catalysed by heterogenized Schiff-bases and other Cu(II)-complex-based catalysts have received a great deal of attention during recent years. Depending on the support, different synthetic approaches have been adopted to integrate them on their framework for the oxidation of olefins. Thus, Spodine *et al.*²² were the first who reported the synthesis of a MOF with Cu(II) centers coordinated to bipy (2,2'-bipyridine) and H₄btec (1,2,4,5-benzenetetracarboxylic acid) ligands as a heterogeneous catalyst for oxi-

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Tailoring Bifunctional Periodic Mesoporous Organosilicas for Cooperative Catalysis

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Cite This: *ACS Appl. Nano Mater.* 2020, 3, 2373–2382

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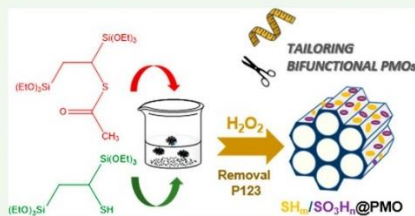
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ABSTRACT: This paper presents a novel approach to create bifunctional periodic mesoporous organosilicas containing thiol and sulfonic acid groups ($\text{SH}_m/\text{SO}_3\text{H}_n@\text{PMO}$) by co-condensation reactions of an own designed bis-silane precursor $(\text{EtO})_2\text{Si}-\text{CH}_2\text{CH}(\text{SH})-\text{Si}(\text{OEt})_3$ containing thiols groups with its predecessor $(\text{EtO})_2\text{Si}-\text{CH}_2\text{CH}(\text{SCoCH}_3)-\text{Si}(\text{OEt})_3$. This bifunctional strategy involves the in situ oxidation of thiol to sulfonic acid groups during the formation of the mesostructure followed by the hydrolysis of the $-\text{SCoCH}_3$ to $-\text{SH}$ groups during the subsequent surfactant extraction process. The good structural ordering and mesoporosity of the bifunctional materials were confirmed by powder X-ray diffraction (PXRD) and nitrogen adsorption-desorption measurements, respectively. The successful incorporation of dual functionality in the pore walls was confirmed by elemental analysis, X-ray electron spectroscopy (XPS), and solid-state nuclear magnetic resonance of ^{13}C (^{13}C CP/MAS NMR) and ^{29}Si (^{29}Si NMR) measurements. The existence of cooperative effect between both functional groups was evaluated in the bisphenol A formation. The catalytic data showed that the bifunctional materials present a better selectivity to the p,p'-isomer of bisphenol A compared to materials containing only one functionality, reaching the optimal value in the material with a thiol/sulfonic acid ratio of 1:1.

KEYWORDS: dual functionality, PMOs, cooperative catalysis, regioselectivity, bisphenol A



INTRODUCTION

One of the most challenging tasks in the design of solid supports is the search of new and creative approaches toward incorporating multiple active sites into heterogeneous catalysis. On the basis to this aim, an encouraging route is to design more efficient catalytic materials taking account of the principles of enzymatic catalysis. Enzymes are capable of dramatically enhancing the rate and the specificity of catalytic processes by specific cooperative interactions between functional groups positioned at a certain distance within the active center. The development of molecular structures that mimic enzyme reactivity has meant a great progress in the design of imprinted polymers and supramolecular complexes.^{1–3}

In the field of silica-based materials, different methodologies have also been conducted to understand the cooperative interactions among different functional groups located on the solid surface.⁴ In 2003, Dufaud and Davis explored the catalytic behavior in the bisphenol A formation of SBA-15 materials containing thiol and sulfonate ester functional groups positioned at certain distances with each other.⁵ Nevertheless, it was not until 2006 when new studies elucidated the nature of such cooperative effects. The findings of homogeneous reactions and bifunctional solids containing thiol and sulfonic

acid groups suggested that the origin to achieve higher reaction rates and selectivities in this cooperative reaction was due to the immobilization of a thiol group close to a sulfonic acid group.^{6,7} Furthermore, the existence of bifunctional cooperativity has been explored in numerous catalytic processes.^{8–10}

Among different solid supports reported in literature to immobilize dual functionalities, mesoporous silicas represent the most significant solid supports because of their great stability, well-defined mesoporous structure, and the numerous possibilities for surface modification.^{11,12} Either through direct synthesis or postsynthetic modification, different functional organic groups have been successfully anchored on the surface of these materials for different purposes.^{13–15} Despite it, both traditional functionalization methods are well-known to present some important drawbacks. As an alternative, the synthesis of periodic mesoporous organosilicas (the so-called

Received: December 16, 2019

Accepted: February 28, 2020

Published: February 28, 2020

Article

Coumarin Derivatives Solvent-Free Synthesis under Microwave Irradiation over Heterogeneous Solid Catalysts

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Received: 31 October 2017; Accepted: 23 November 2017; Published: 28 November 2017

Abstract: A suitable methodology of synthesis of coumarin derivatives by Pechmann reaction over heterogeneous solid acid catalysts in a free solvent media under microwave irradiation is described. Resorcinol, phenol and ethyl acetoacetate were selected as model reactants in the Pechmann condensation. The catalytic activity of several materials—Amberlyst-15, zeolite β and sulfonic acid functionalized hybrid silica—in solvent-free microwave-assisted synthesis of the corresponding coumarin derivatives has been investigated in detail. 7-Hydroxy-4-methylcoumarin and 4-methylcoumarin were obtained in 97% and 43% yields, respectively, over Amberlyst-15. This was the most active catalyst in the Pechmann reaction under studied conditions.

Keywords: phenol; ethyl acetoacetate; solvent-free; microwave irradiation; heterogeneous acid catalysts

1. Introduction

Coumarins are an important family of oxygen-containing heterocycles with a 1-benzopyran-2-one moiety, originally found as secondary metabolites in some plants (*Rutaceae* and *Umbelliferae* family) and microorganisms [1]. Coumarin derivatives have displayed widespread therapeutic applications including antibacterial [2,3], anti-inflammatory [4], antioxidant [5], anticoagulant [6], anticancer [7,8] and anti-HIV [9], among others [10,11]. Additionally, these compounds have attracted a great interest in other fields, such as fragrance and cosmetic [12], agrochemical [13], food and dyes industries [14].

Due to their applicability, several methods have been developed over the years to synthesize coumarin derivatives such as Pechmann condensation [15], Knoevenagel [16], Perkin, Witting, Reformatsky reactions and by flash vacuum pyrolysis [17] or via carbon suboxide [18]. Among these methods, the Pechmann reaction is a simple and widely used method for the synthesis of 4-substituted coumarins, since it requires simple and inexpensive starting materials, i.e., phenols and β -ketoesters. This reaction proceeds in acidic media, using either homogenous Brønsted acid catalysts like H_2SO_4 , HCl, H_3PO_4 and CF_3COOH [19] or Lewis acid catalysts such as $InCl_3$, $Sm(NO_3)_3$, $ZrCl_4$, $BiCl_3$ and FeF_3 , among others [20–23]. However, these catalysts require drastic conditions, long reaction times and large quantities to reach high yields. In addition, they are corrosive, hard to remove from the reaction mixture, non recoverable and pollutants for the environment.

I.III. Comunicaciones a Congresos Científicos

Seguidamente, se recogen las contribuciones realizadas en diferentes congresos científicos durante el periodo pre-doctoral:

1- Participación en Congreso Nacional II Encuentro de Jóvenes Investigadores de la SECAT 2016 con:

- Una Comunicación Oral titulada: *“In situ SO₃H-etano PMO: un eficaz catalizador reciclable para catálisis ácida”*

Autores: Dolores Esquivel; María Isabel López; Daniel Cosano; Juan Amaro Gahete; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- Una Comunicación Póster titulada: *“Uso de materiales periódicos mesoporosos organosilícicos (PMOs) funcionalizados con grupos tioles como soportes para la reacción de acoplamiento cruzado de Suzuki”*

Autores: María Isabel López; Dolores Esquivel; Manolo Mora; Daniel Cosano; Juan Amaro Gahete; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: Del 27 al 29-junio-2016

Lugar de celebración: Ciudad Real, Castilla-La Mancha, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Catálisis como herramienta en procesos sostenibles. Año: 2016; Capítulos: 15, 38; Páginas: 15 – 16, 21 – 22. Editorial: Sociedad Española de Catálisis (SECAT). II Encuentro de Jóvenes Investigadores de la Sociedad Española de Catálisis. ISBN: 978-84-608-8766-9

2- Participación en Congreso Nacional I Congreso de Investigadores Noveles de la Universidad de Córdoba con una Comunicación Póster titulada: *“Preparación de nanomateriales híbridos quirales y su aplicación a la resolución de mezclas racémicas”*

Autores: Juan Amaro Gahete; Daniel Cosano; María Isabel López Martínez; Dolores Esquivel; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: 11-noviembre-2016

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Investigando por un futuro mejor. Año: 2016; Capítulo: 22; Páginas: 101 – 105. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-291-7

3- Participación en Congreso Nacional V Congreso Científico de Investigadores en Formación de la Universidad de Córdoba con una Comunicación Póster titulada: *“Síntesis de materiales híbridos orgánico-inorgánicos laminares con capacidad quirral”*

Autores: Daniel Cosano; Juan Amaro Gahete; María Isabel López Martínez; Dolores Esquivel; Francisco José Romero Salguero; César Jiménez Sanchidrián; José Rafael Ruiz

Fecha: Del 30-noviembre al 2-diciembre-2016

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Creando Redes Doctorales: Volumen V. Año: 2016; Páginas: 387 – 390. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-271-9

4- Participación en Congreso Nacional Sexto Edición del Encuentro sobre Nanociencia y Nanotecnología de Investigadores y Tecnólogos Andaluces (NANOUCO VI) con:

- Una Comunicación Oral titulada: *“Optimización de la intercalación de materiales con capacidad quirral en sólidos híbridos orgánico-inorgánicos laminares”*

Autores: Daniel Cosano; María Isabel López Martínez; Manuel Mora; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

- Tres Comunicaciones Póster tituladas:

- 1) *“Materiales híbridos orgánico-inorgánicos y su empleo en adsorción y catálisis”*

Autores: Juan Amaro Gahete; Daniel Cosano; María Isabel López Martínez; Dolores Esquivel; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- 2) *“Aplicación de organosílices periódicas mesoporosas con grupos sulfónicos en catálisis ácida”*

Autores: Dolores Esquivel; María Isabel López Martínez; Daniel Cosano; Juan Amaro Gahete; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- 3) *“Síntesis de materiales periódicos mesoporosos organosilícicos (PMOS) funcionalizados con grupos tioles para su uso como soportes catalíticos en la reacción de acoplamiento cruzado de Suzuki”*

Autores: María Isabel López Martínez; Dolores Esquivel; Manuel Mora; Daniel Cosano; Juan Amaro Gahete; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: 25 y 26-enero-2017

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Sexta Edición del Encuentro sobre Nanociencia y Nanotecnología de Investigadores y Tecnólogos Andaluces. NANOUCO VI. Año: 2017; Capítulos: 17, 20, 27, 30; Páginas: 46, 82, 89, 92. Editorial: Copisterías Don Folio, S.L. Pedro del Río Obejo. ISBN: 978-84-16017-89-8

5- Participación en Congreso Internacional Reunión BIENAL de la Sociedad Española de Catálisis (SECAT 2017) con seis Comunicaciones Póster tituladas:

- 1) *“Síntesis de polímeros de coordinación de zirconio con conectores quirales para su aplicación como catalizadores heterogéneos”*

Autores: Juan Amaro Gahete; Dolores Esquivel; María Isabel López Martínez; Daniel Cosano; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- 2) *“PMOs funcionalizados con grupos tioles como soportes catalíticos en la reacción de acoplamiento cruzado de Suzuki”*

Autores: María Isabel López Martínez; Dolores Esquivel; Daniel Cosano; Juan Amaro Gahete; Manuel Mora; José Rafael Ruiz; Francisco José Romero Salguero; César Jiménez Sanchidrián

- 3) *“Estudio de la actividad catalítica de diferentes catalizadores ácidos en la reacción de Pechmann entre fenol y acetoacetato de etilo”*

Autores: Souad Bouasla; Dolores Esquivel; Daniel Cosano; Juan Amaro Gahete; María Isabel López Martínez; Manuel Mora; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- 4) *“Estudio de la actividad catalítica de complejos RECuL en la oxidación de ciclohexano”*

Autores: Anna M. Kaczmarek; Tineke Mortier; Dolores Esquivel; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; Rik Van Deun; Kristof Van Hecke.

- 5) *“Optimización de la intercalación del Sulfato de β -Ciclodextrina en Hidróxidos Dobles Laminares”*

Autores: Daniel Cosano; Dolores Esquivel; María Isabel López Martínez; Manuel Mora; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

- 6) *“Estudio de la adsorción de nitratos en LDHs calcinadas mediante espectroscopia Raman”*

Autores: Daniel Cosano; Dolores Esquivel; María Isabel López Martínez; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

Fecha: 26 y 27-junio-2017

Lugar de celebración: Oviedo, Principado de Asturias, España

6- Participación en Congreso Nacional II Congreso de Investigadores Noveles de la Universidad de Córdoba con una Comunicación Oral titulada: *“Síntesis de polímeros de coordinación de zirconio con conectores quirales: Caracterización y aplicación como catalizadores heterogéneos en reacciones de cianosililación”*

Autores: Juan Amaro Gahete; Dolores Esquivel; Daniel Cosano; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: 15-noviembre-2017

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Investigadores de hoy para los retos de mañana. Año: 2018; Capítulo: 8; Páginas: 39-42. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-386-0

7- Participación en Congreso Nacional VI Congreso Científico de Investigadores en Formación de la Universidad de Córdoba con una Comunicación Oral titulada: *“Eliminación de nitratos de aguas por adsorción”*

Autores: Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

Fecha: 18 y 19-enero-2018

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Creando redes doctorales. Vol. VI: La generación del conocimiento. Año: 2018; Capítulo: 29; Páginas: 113 – 117. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-239-9

8- Participación en Congreso Nacional III Encuentro de Jóvenes Investigadores de la SECAT 2018 con:

- Una Comunicación Oral titulada: *“Aplicación de polímeros de coordinación quirales en reacciones de cianosililación”*

Autores: Juan Amaro Gahete; Dolores Esquivel; María Isabel López; Daniel Cosano; Rafael Klee; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- Tres Comunicaciones Póster tituladas:

1) *“Síntesis de cumarinas sobre catalizadores ácidos mediante activación por microondas”*

Autores: Souad Bouasla; Juan Amaro Gahete; Dolores Esquivel; María Isabel López; José Rafael Ruiz; César Jiménez Sanchidrián; M. Teguique; Francisco José Romero Salguero

2) *“Síntesis de nuevos materiales organo-LDHs asistidos por microondas”*

Autores: Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

3) *“Transferencia catalítica de hidrógeno empleando óxidos mesoporosos obtenidos a partir de hidrotalcitas”*

Autores: Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

Fecha: Del 24 al 26-junio-2018

Lugar de celebración: Valencia, Comunidad Valenciana, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro**: Catálisis para un futuro sostenible. Año: 2018; Capítulos: 9, 23, 36, 46; Páginas: 64 – 65, 120 – 121, 133 – 134, 143 – 144. Editorial: Universidad Politécnica de Valencia (UPV). Sociedad Española de Catálisis (SECAT). III Encuentro de Jóvenes Investigadores de la Sociedad Española de Catálisis. ISBN: 978-84-09-03041-5

9- Participación en Congreso Internacional Graphene Week 2018 con una Comunicación Póster titulada: *“Ultrasound-assisted synthesis and characterization of graphene nanosheets”*

Autores: Juan Amaro Gahete; Almudena Benítez; Rocío Otero Martínez; Dolores Esquivel; César Jiménez Sanchidrián; Álvaro Caballero; Julián Morales; Francisco José Romero Salguero

Fecha: Del 09 al 14-septiembre-2018

Lugar de celebración: San Sebastián, País Vasco, España

10- Participación en Congreso Internacional XXVI Congresso Ibero-Americano de Catálise (CICAT 2018) con una Comunicación Oral titulada: *“Aplicación de catalizadores de Pd soportado en organosílices periódicas mesoporosas funcionalizadas con grupos tioles en la reacción de acoplamiento cruzado de Suzuki”*

Autores: María Isabel López Martínez; Dolores Esquivel; Juan Amaro Gahete; Daniel Cosano; Rafael Klee; José Rafael Ruiz; César Jiménez Sanchidrián; Pascal Van der Voort; Francisco José Romero Salguero

Fecha: Del 09 al 14-septiembre-2018

Lugar de celebración: Coimbra, Portugal

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** XXVI Congresso Ibero-Americano de Catálise. Año: 2018; Capítulo: 18; Páginas: 2681-2687. Editorial: Sociedad Portuguesa de Química (Portugal). ISBN: 978-989-8124-23-4

11- Participación en Congreso Nacional Séptima Edición del Encuentro sobre Nanociencia y Nanotecnología de Investigadores y Tecnólogos Andaluces (NANOUCO VII) con:

- Una Comunicación Oral titulada: *“Adsorción de etileno en diferentes MOFs de tipo MIL-88A”*

Autores: Juan Amaro Gahete; Rafael Klee; Daniel Cosano; Dolores Esquivel; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- Cuatro Comunicaciones Póster tituladas:

- 1) *“Síntesis y caracterización de materiales organosilícicos con grupos piridina”*

Autores: Olga Rosado; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; Dolores Esquivel

- 2) *“Síntesis de hidrotalcitas por irradiación con microondas. Aplicaciones en procesos de reducción”*

Autores: Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; Jesús Hidalgo; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

- 3) *“Organosilicas mesoporosas periódicas como catalizadores heterogéneos en reacciones de oxidación”*

Autores: María de los Ángeles Navarro; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; Dolores Esquivel

- 4) *“Nanopartículas periódicas mesoporosas organosilícicas”*

Autores: Raúl Rojas; Juan Amaro Gahete; María Isabel López; César Jiménez Sanchidrián; Francisco José Romero Salguero; Dolores Esquivel

Fecha: 21 y 22-enero-2019

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** NANOUCO VII. Encuentro sobre Nanociencia y Nanotecnología. Año: 2019; Capítulos: 9, 16, 18, 24, 39; Páginas: 34 – 35, 41 – 42, 69 – 70, 75 – 76, 90 – 91. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-09-14458-7

12- Participación en Congreso Nacional VII Congreso Científico de Investigadores en Formación de la Universidad de Córdoba con dos Comunicaciones Orales tituladas:

- 1) *“Síntesis de MOF MIL-88A asistida por ultrasonidos y su aplicación como adsorbente de etileno”*

Autores: Juan Amaro Gahete; Rafael Klee; Daniel Cosano; Dolores Esquivel; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

2) *“Análisis de los morteros de la Torre del Homenaje del Castillo de Priego de Córdoba (Spain)”*

Autores: Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; Francisco José Romero Salguero; César Jiménez Sanchidrián; José Rafael Ruiz.

Fecha: 6 y 7-febrero-2019

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** Creando redes doctorales. Vol. VII: Investiga y Comunica. Año: 2019; Capítulos: 3, 10; Páginas: 251 – 255, 279 – 283. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-341-9

13- Participación en Congreso Internacional XXXVII Reunión Bienal de la Real Sociedad Española de Química 2019 con una Comunicación Póster titulada: *“Biomimetic Models for the Active Site of Hydrogenases on Periodic Mesoporous Organosilicas”*

Autores: Juan Amaro Gahete; Dolores Esquivel; Olga Rosado; Daniel Cosano; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: Del 26 al 30-mayo-2019

Lugar de celebración: San Sebastián, País Vasco, España

14- Participación en Congreso Internacional Reunión BIENAL de la Sociedad Española de Catálisis (SECAT 2019) con

- Una Comunicación Oral titulada: *“Funcionalización de organosílicas periódicas mesoporosas y su aplicación en la reacción de oxidación de estireno”*

Autores: Juan Amaro Gahete; María de los Ángeles Navarro; Daniel Cosano; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero; Dolores Esquivel

- Cuatro Comunicaciones Póster tituladas:

- 1) *“Versatilidad del MOF MIL-88A para su aplicación en catálisis heterogénea y almacenamiento de energía en baterías”*

Autores: Juan Amaro Gahete; Almudena Benítez; Álvaro Caballero; Dolores Esquivel; Francisco José Romero Salguero; César Jiménez Sanchidrián; Julián Morales

- 2) *“Diseño de materiales periódicos mesoporosos bifuncionales para catálisis cooperativa”*

Autores: Dolores Esquivel; Juan Amaro Gahete; Noelia Caballero Casero; Soledad Rubio; José Rafael Ruiz; Francisco José Romero Salguero

- 3) *“Síntesis y caracterización de nanopartículas periódicas mesoporosas organosilícicas (PMO-NPs)”*

Autores: Raúl Rojas; Dolores Esquivel; Juan Amaro Gahete; Daniel Cosano; Francisco José Romero Salguero; José Rafael Ruiz; César Jiménez Sanchidrián

- 4) *“Adsorción de terpenos empleando ciclodextrina intercalada en hidrotalcitas”*

Autores: Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; Francisco José Romero Salguero; César Jiménez Sanchidrián; José Rafael Ruiz

Fecha: Del 24 al 26-junio-2019

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro**: Catálisis para el futuro. Avances en estructuras, procesos y aplicaciones. Año: 2019; Capítulos: 16, 18, 62, 80; Páginas: 209 – 210, 372 – 373, 376 – 377, 462 – 463, 496 – 497. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-454-6

15- Participación en Congreso Nacional IV Encuentro de Jóvenes Investigadores de la SECAT 2020 con:

- Dos Comunicaciones Orales tituladas:

- 1) *“Síntesis de materiales híbridos orgánico-inorgánicos para la producción de hidrógeno mediante la descomposición de ácido fórmico”*

Autores: Raúl Rojas; Daniel Cosano; Dolores Esquivel; María de los Ángeles Navarro; Juan Amaro Gahete; José Rafael Ruiz; Francisco José Romero Salguero; César Jiménez Sanchidrián

- 2) *“Síntesis de organosílices periódicas mesoporosas con centros metálicos tipo cobaloxima para la obtención de hidrógeno”*

Autores: María de los Ángeles Navarro; Daniel Cosano; Dolores Esquivel; Juan Amaro Gahete; Raúl Rojas; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

- Una Comunicación Póster titulada:

- 1) *“Adsorción de nonilfenol empleando desoxicolato intercalado en hidróxidos dobles laminares”*

Autores: Daniel Cosano; Dolores Esquivel; María de los Ángeles Navarro; Raúl Rojas; Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero; José Rafael Ruiz

Fecha: Del 21 al 23-septiembre-2020

Lugar de celebración: Bilbao, País Vasco, España

16- Participación en Congreso Nacional IX Congreso Científico de Investigadores en Formación de la Universidad de Córdoba con una Comunicación Oral titulada: “Síntesis y caracterización de un modelo biomimético [FeFe]-hidrogenasa para producción fotocatalítica de hidrógeno”

Autores: Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: Del 3 y 6-mayo-2021

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** IX Congreso de Investigadores en Formación de la Universidad de Córdoba: Nuevos Desafíos, Nuevas Oportunidades. Año: 2021; Páginas: 177 – 180. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-640-3

17- Participación en **Congreso Nacional de Divulgación Científica I Congreso Divulga NextGen 2021** con una Comunicación Oral titulada: “*Materiales híbridos orgánico-inorgánicos: Diseño y aplicaciones*”

Autores: Juan Amaro Gahete; Dolores Esquivel; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: Del 26 y 28-mayo-2021

Lugar de celebración: Córdoba (Congreso Online), Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** I Edición Divulga NextGen: Una nueva forma de divulgar. Año: 2021; Páginas: 177 – 180. Entidad organizadora: Kunvoca. Editorial: Repositorio de acceso abierto Zenodo. DOI: 10.5281/zenodo.4738432

18- Participación en **Congreso Nacional X Congreso Científico de Investigadores en Formación de la Universidad de Córdoba** con una Comunicación Video-póster titulada: “*Formación de centros activos de tipo FeN_4 en los bordes de grafeno multiláminas funcionalizado y su aplicación en electrocatálisis bifuncional*”

Autores: Juan Amaro Gahete; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: Del 3 y 6-mayo-2022

Lugar de celebración: Córdoba, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** X Congreso de Investigadores en Formación de la Universidad de

Córdoba: El arte de investigar. Año: 2022; Páginas: 161 – 165. Editorial: UCOPress. Ediciones Universidad de Córdoba. Campus Universitario de Rabanales. Carretera Nacional IV, km. 396. 14071, Córdoba, España. ISBN: 978-84-9927-640-3

19- Participación en Congreso Internacional XXXVIII Reunión Bienal de la Real Sociedad Española de Química 2022 con una Comunicación Póster titulada: “*Controlled design of FeN₄ active sites on functionalized multilayer graphene for efficient bifunctional electrocatalysis*”

Autores: Juan Amaro Gahete; Dolores Esquivel; Olga Rosado; Daniel Cosano; José Rafael Ruiz; César Jiménez Sanchidrián; Francisco José Romero Salguero

Fecha: Del 27 al 30-junio-2022

Lugar de celebración: Granada, Andalucía, España

De este congreso se ha obtenido una **Publicación en un Capítulo de un Libro:** XXXVIII Reunión Bienal de la Real Sociedad Española de Química. Año: 2022; Página: 392. Editorial: Grupo Pacífico. The Power of Meeting. ISBN: 978-84-09-42159-6

20- Participación en Congreso Nacional V Encuentro de Jóvenes Investigadores de la SECAT 2022 con una Comunicación Oral titulada: “*Síntesis de un modelo biomimético [FeFe]-hidrogenasa para producción fotocatalítica de hidrógeno: optimización de variables y heterogeneización sobre organosílice periódica mesoporosa (PMO)*”

Autores: Juan Amaro Gahete; Dolores Esquivel; Mariia V. Pavliuk; José Rafael Ruiz; César Jiménez Sanchidrián; Haining Tian; Sascha Ott; Francisco José Romero Salguero

Fecha: Del 11 y 13-julio-2022

Lugar de celebración: Alicante, Comunidad Valenciana, España

I.IV. Cursos, jornadas y seminarios de Formación Científica

A continuación, se exponen los diferentes cursos, jornadas y seminarios en los que ha participado el doctorando que han contribuido a la consecución de su Plan de Formación de Tesis Doctoral:

1- Título de la formación: Curso: Live-Demo with Raman Imaging

Entidad de titulación: Irida. Advance Solution for Science. ThermoScience

Tipo de entidad: Entidad Empresarial

Fecha de finalización: 16/03/2016

Duración en horas: 3 horas

2- Título de la formación: Seminario LEICA: Sistema Confocal e Interferométrico DCM-8

Entidad de titulación: LEICA. SCAI. Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 23/09/2016

Duración en horas: 3 horas

3- Título de la formación: Seminario: Separación y caracterización de nanomateriales mediante la técnica AF4 (Asymmetric Flow Field Flow Fractionation), impartido por los profesores Dña. Yolanda Madrid y D. Jon Sanz-Landaluze de la Universidad Complutense de Madrid

Entidad de titulación: Instituto Universitario de Investigación en Química Fina y Nanoquímica. Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 23/11/2016

Duración en horas: 3 horas

4- Título de la formación: Seminario: Caracterización de nanomateriales mediante la técnica XPS (X-Ray Photoelectron Spectroscopy), impartido por D. Enrique Rodríguez Castellón, Catedrático de Química Inorgánica de la Universidad de Málaga

Entidad de titulación: Instituto Universitario de Investigación en Química Fina y Nanoquímica. Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 12/12/2016

Duración en horas: 3 horas

5- Título de la formación: Curso: Prevención frente a la exposición a agentes químicos y biológicos

Entidad de titulación: Servicio de Prevención de Riesgos Laborales. Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 28/09/2017

Duración en horas: 3 horas

6- Título de la formación: Seminario: Espectroscopia EPR: fundamentos y algunos ejemplos de aplicación en catálisis heterogénea, impartido por la Catedrática Dña. Teresa Blasco, Científica titular del CSIF en el Instituto de Tecnología Química de Valencia

Entidad de titulación: Instituto Universitario de Investigación en Química Fina y Nanoquímica. Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 22/11/2017

Duración en horas: 3 horas

7- Título de la formación: Seminario: Aplicaciones de la espectroscopia EPR en Química y Materiales, impartido por el Catedrático D. Luis Lezama Diago de la Facultad de Ciencias y Tecnología de la UPV/EHU

Entidad de titulación: Instituto Universitario de Investigación en Química Fina y Nanoquímica. Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 01/12/2017

Duración en horas: 3 horas

8- Título de la formación: Curso teórico-básico de Espectroscopia de Fluorescencia de Rayos X (XRF), impartido por: El Técnico Especialista D. Luis Spencer Lima (Portugal) de la empresa Paralab

Entidad de titulación: Instituto Universitario de Investigación en Química Fina y Nanoquímica. Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 10/05/2018

Duración en horas: 3 horas

9- Título de la formación: I Seminario Teórico-Práctico de Microscopía Electrónica de Barrido aplicada a la caracterización de materiales. Impartido por Personal de Izasa/Jeol (expertos del equipo JEOL JSM 7800F) y por el Prof. D. Jesús Canales Vázquez, Profesor Titular de la Universidad de Castilla la Mancha

Entidad de titulación: Instituto Universitario de Investigación en Química Fina y Nanoquímica. Servicio Central de Apoyo a la Investigación (SCAI). Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 16/01/2019

Duración en horas: 20 horas

10- Título de la formación: Curso: Two visions in the bio-inorganic chemistry field: from the primordial broth to physiology and anticancer therapy. Impartido por la Dra. Chiara Nardon (Lecturer, Department of Chemical Sciences, University of Padova, Italy)

Entidad de titulación: Facultad de Ciencias en colaboración con el Instituto Maimónides de Investigación Biomédica (IMIBIC) y el Instituto Universitario de Nanoquímica (IUNAN). Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 17/05/2019

Duración en horas: 12 horas

11- Título de la formación: Curso de postgrado del CSIC. Caracterización químico-física de la superficie de adsorbentes y catalizadores, celebrado en Jarandilla de la Vera (Cáceres, España)

Entidad de titulación: Grupo Especializado de Adsorción de las Reales Sociedades Españolas de Física y de Química

Tipo de entidad: Organismo Público de Investigación

Fecha de finalización: 14/06/2019

Duración en horas: 20 horas

12- Título de la formación: Seminario: Electrodeposition of Doped Manganese Octahedral Sieves (MOS) as a Functionalisation Tool for Practical Applications, impartido por el profesor D. Heorhii Sokolskyi, National Technical University, Igor Sikorsky Polytechnical Institute, Kyiv (Ukraine)

Entidad de titulación: Facultad de Ciencias. Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 19/06/2019

Duración en horas: 4 horas

13- Título de la formación: Escuela de Verano SECAT 19: Avances en Catálisis Orgánica

Entidad de titulación: Sociedad Española de Catálisis (SECAT)

Tipo de entidad: Organismo Público de Investigación

Fecha de finalización: 28/06/2019

Duración en horas: 12 horas

14- Título de la formación: Seminario de Introducción a la Espectroscopía Raman

Entidad de titulación: JASCO ANALITICA SPAIN en colaboración con el Servicio Central de Apoyo a la Investigación (SCAI) de la Universidad de Córdoba.

Tipo de entidad: Entidad Empresarial

Fecha de finalización: 24/09/2019

Duración en horas: 3 horas

15- Título de la formación: Jornada Técnica de Nano-seguridad y Salud laboral: Retos y avances

Entidad de titulación: Universidad de Córdoba. Servicio de Prevención y Protección. Prevención de Riesgos y Protección Radiológica

Tipo de entidad: Universidad

Fecha de finalización: 15/10/2019

Duración en horas: 4 horas

16- Título de la formación: Jornada Formativa: El doctorado en la Universidad de Córdoba, marco normativo, procesos y procedimientos

Entidad de titulación: Escuelas de Doctorado de la Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 13/12/2019

Duración en horas: 4 horas

17- Título de la formación: Webinars:

- 1) Raman spectroscopy - Overcoming difficulties presented by challenging samples
- 2) Total Workflow for Multi-Class, Multi-Residue Analysis of Pesticides in Fatty Food Matrices
- 3) New insight into dietary behavior using NMR profiling
- 4) What every pharmaceutical scientist should know about particle size analysis
- 5) Low-field NMR of polymer materials - An introduction to characterizing multicomponent polymer systems
- 6) The Importance of UHPLC in LC-MS Based Equine Drug Screening
- 7) Raman microscopy - Comprehensive characterization of polymers
- 8) Advances in gas chromatography for challenging separations in environmental and food industries
- 9) Micro-XRF & Raman Microscopy - A winning combo for your elemental and chemical analyses
- 10) Bioanalytical methods for bacteria and protein characterization
- 11) Raman Microscopy - A must for pharmaceutical product analysis, from formulation studies to QC

Entidad de titulación: SelectScience 1998-2020. Company Registration No. 3597730. Science House, Church Farm Business Park, Corston, Bath, BA2 9AP UK

Tipo de entidad: Entidad Empresarial

Fecha: Del 08/07/2020 al 01/12/2020

Duración en horas: 11 horas

18- Título de la formación: Course: How to write a Literature review

Entidad de titulación: Charlesworth Author Services

Tipo de entidad: Entidad Empresarial

Fecha de finalización: 07/08/2020

Duración en horas: 2 horas

19- Título de la formación: Webinars:

- 1) Sustainable development through Green Chemistry
- 2) Surface Engineering of Polymer Membrane

Entidad de titulación: Centre of Chemistry and Chemical Excelent (CCCE)

Tipo de entidad: Entidad Empresarial

Fecha de finalización: 22/09/2020

Duración en horas: 2 horas

20- Título de la formación: II Jornada para doctorandos del CSIC

Entidad de titulación: Departamento de Posgrado y Especialización del CSIC

Tipo de entidad: Agencia Estatal

Fecha de finalización: 16/10/2020

Duración en horas: 6 horas

21- Título de la formación: I Jornadas de Difusión Científica. La tecnología electroquímica al servicio de la Sociedad: aplicaciones en medio ambiente y energía

Entidad de titulación: Red de Excelencia en Aplicaciones Energéticas y Medioambientales de la Tecnología Electroquímica (CTQ2017-90659-REDT)

Tipo de entidad: Agencia Estatal

Fecha de finalización: 27/10/2020

Duración en horas: 14 horas

22- Título de la formación: Seminario: Conceptos básicos y aplicaciones del vacío - Análisis de gases. Impartido por D. César Atienza Atienza, Experto en Aplicaciones y Procesos en Vacío con sede en Écija (Sevilla)

Entidad de titulación: Programa de Doctorado de Química Fina de la Universidad de Córdoba. Instituto Universitario de Nanoquímica (IUNAN)

Tipo de entidad: Universidad

Fecha de finalización: 29/10/2020

Duración en horas: 10 horas

23- Título de la formación: Conferencia científico-formativa: Sensores luminiscentes para aplicaciones biomédicas. Impartido por el profesor D. Ángel Orte Gutiérrez, Catedrático de la Universidad de Granada

Entidad de titulación: Programa de Doctorado de Química Fina de la Universidad de Córdoba. Instituto Universitario de Nanoquímica (IUNAN)

Tipo de entidad: Universidad

Fecha de finalización: 17/11/2020

Duración en horas: 2 horas

24- Título de la formación: Conferencia científico-formativa: Enzymes as Models for the Design of Solid Catalysts. Impartido por el profesor D. Avelino Corma, Catedrático del Instituto de Tecnología Química de Valencia (CSIC-UPV)

Entidad de titulación: Real Sociedad Española de Química

Tipo de entidad: Institución Científica

Fecha de finalización: 19/11/2020

Duración en horas: 3 horas

25- Título de la formación: Jornada formativa sobre el doctorado en la Universidad de Córdoba: Nueva Normativa 2020

Entidad de titulación: Escuelas de Doctorado de la Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 15/12/2020

Duración en horas: 5 horas

26- Título de la formación: Curso: Introducción básica en el uso de Materials Studio (para IUNAN)

Entidad de titulación: Addlink Software Científico, S.L.

Tipo de entidad: Entidad Empresarial

Fecha de finalización: 13/04/2021

Duración en horas: 4 horas

27- Título de la formación: Curso: FT-IR: Técnicas de muestreo y aplicaciones

Entidad de titulación: Perkin Elmer Hispania, S.A.

Tipo de entidad: Entidad Empresarial

Fecha de finalización: 05/05/2021

Duración en horas: 1 horas

28- Título de la formación: Curso: Espectroelectroquímica. Impartido por: Dra. Aranzazu Heras Vidaurre, Catedrática de Química Analítica de la Universidad de Burgos

Entidad de titulación: Enseñanza de Posgrado de la Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 26/11/2021

Duración en horas: 8 horas

29- Título de la formación: Curso: Síntesis, caracterización y propiedades electrocatalíticas de nanopartículas metálicas. Impartido por: Dr. José Solla Gullón, Profesor de la Universidad de Alicante

Entidad de titulación: Enseñanza de Posgrado de la Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 03/12/2021

Duración en horas: 8 horas

30- Título de la formación: Jornada formativa sobre el doctorado en la Universidad de Córdoba 2021

Entidad de titulación: Escuelas de Doctorado de la Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 15/12/2021

Duración en horas: 3 horas

31- Título de la formación: Seminario: Futuras tecnologías habilitadoras para la descarbonización de la industria de procesos, impartido por el Dr. José Manuel Serra (Instituto de Tecnología Química de Valencia, Universidad Politécnica de Valencia – Consejo Superior de Investigaciones Científicas)

Entidad de titulación: Instituto Universitario de Nanoquímica (IUNAN) de la Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 16/03/2022

Duración en horas: 2 horas

32- Título de la formación: Seminario: Making Fuels from Sunlight and Water: The Holy Grail of Artificial Photosynthesis, impartido por el Dra. Murielle Chavarot-Kerlidou (CNRS Researcher and Deputy Director of the French Solar Fuels Network-Laboratory of Chemistry and Biology of Metals (LCBM) de Grenoble-Francia)

Entidad de titulación: Instituto Universitario de Nanoquímica (IUNAN) de la Universidad de Córdoba

Tipo de entidad: Instituto Universitario de Investigación

Fecha de finalización: 12/05/2022

Duración en horas: 2 horas

33- Título de la formación: Curso: Gestión y Minimización de Residuos Peligrosos en la Universidad de Córdoba

Entidad de titulación: Servicio de Prevención y Protección. Área de Protección Ambiental de la Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de finalización: 12/05/2022

Duración en horas: 1 horas

I.V. Gestión y participación en Comités Científico

El doctorando ha formado parte del **Comité Organizador** en el **VII Congreso Científico de Investigadores en Formación de la Universidad de Córdoba** desarrollado en el Rectorado de la Universidad de Córdoba (Córdoba, Andalucía, España) en las fechas del 6 y 7 de febrero de 2019 contando con un número total de asistentes de 211.

I.VI. Participación en Proyectos de Investigación

A continuación, se citan los Proyectos de Investigación Nacionales en los que ha participado la doctoranda durante el periodo pre-doctoral:

1- Referencia del proyecto: MAT2013-44463-R

Denominación del proyecto: Construcción de superficies homoquirales estereoespecíficas sobre materiales híbridos orgánicos-inorgánicos y poliméricos estructurados

Investigadores responsables: Francisco José Romero Salguero y José Rafael Ruiz Arrebola (Universidad de Córdoba)

Nombre del programa: Convocatoria 2013 - Proyectos I+D+i - Programa Estatal de Investigación, Desarrollo e Innovación Orientada a los Retos de la Sociedad

Entidad Financiadora: Ministerio de Economía, Industria y Competitividad

Periodo de ejecución: 01/12/2014 - 31/12/2016 (3 años)

2- Referencia del proyecto: MAT2017-89568-R

Denominación del proyecto: Transcripción quiral en catálisis heterogénea

Investigadores responsables: Francisco José Romero Salguero y José Rafael Ruiz Arrebola (Universidad de Córdoba)

Nombre del programa: Extensión anual del proyecto MAT2013-44463-R. Convocatoria 2013 - Proyectos I+D+i - Programa Estatal de Investigación, Desarrollo e Innovación Orientada a los Retos de la Sociedad

Entidad Financiadora: Ministerio de Economía, Industria y Competitividad

Periodo de ejecución: 01/01/2017 - 31/12/2017 (1 año)

3- Referencia del proyecto: RAMON ARECES 16

Denominación del proyecto: Catalizadores biomiméticos heterogéneos basados en arquitecturas híbridas orgánico-inorgánicas funcionalizadas para producción de hidrógeno

Investigadores responsables: Dolores Esquivel (Universidad de Córdoba)

Nombre del programa: XVIII Concurso Nacional para la Adjudicación de Ayudas a la Investigación en Ciencias de la Vida y de la Materia. Energía renovable: materiales y procesos

Entidad Financiadora: Fundación Ramón Areces

Periodo de ejecución: 02/03/2017 - 02/03/2020 (3 años)

4- Referencia del proyecto: RTI2018-101611-B-I00

Denominación del proyecto: Transformación fotocatalítica de CO₂ en combustibles solares utilizando nanocomposites basados en hidróxidos dobles laminares y grafenos

Investigadores responsables: Francisco José Romero Salguero y José Rafael Ruiz Arrebola (Universidad de Córdoba)

Nombre del programa: Convocatoria 2018 - Proyectos de I+D+i «Retos Investigación» - Programa Estatal de I+D+i orientada a los Retos de la Sociedad, en el Marco del Plan Estatal de Investigación Científica y Técnica y de Innovación 2017 -2020

Entidad Financiadora: Ministerio de Ciencia, Innovación y Universidades

Periodo de ejecución: 01/12/2018 - 31/12/2021 (3 años)

I.VII. Cursos y seminarios de perfeccionamiento, innovación y mejora docente

Seguidamente, se describen los cursos y seminarios relacionados con el ámbito docente en los que ha participado la doctoranda durante el periodo pre-doctoral:

1- Título del curso/seminario: Curso de formación docente: Innovación Docente en Física y Química

Entidad organizadora: Universidad de Córdoba y Robokids

Tipo de entidad: Universidad

Fecha de inicio-fin: 25/02/2019 - 05/03/2019

Duración en horas: 16 horas

2- Título del curso/seminario: Jornadas DIM-EDU. 6º Encuentro de Centros Innovadores de Andalucía

Entidad organizadora: Universidad de Córdoba y Red Educativa de Centros Innovadores DIM-EDU

Tipo de entidad: Universidad

Fecha de celebración: 02/10/2019

Duración en horas: 10 horas

3- Título del curso/seminario: Curso de formación docente: Robótica educativa y gamificación en el aula

Entidad organizadora: Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de inicio-fin: 07/10/2019 - 22/10/2019

Duración en horas: 100 horas

4- Título del curso/seminario: Jornada Informativa: Cómo puede contribuir el profesorado a los Objetivos de Desarrollo Sostenible. Docencia universitaria en el marco de la Agenda 2030

Entidad organizadora: Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de celebración: 19/11/2019

Duración en horas: 2 horas

5- Título del curso/seminario: Curso de formación docente: Sostenibilización Curricular. Introducción de la sostenibilidad en la Docencia Universitaria

Entidad organizadora: Programa de Formación en Competencias Transversales. Formación del Profesorado Universitario. Universidad de Córdoba

Tipo de entidad: Universidad

Fecha de inicio-fin: 26/01/2021 - 07/02/2021

Duración en horas: 25 horas

I.VIII. Actividad docente

La docencia impartida en títulos de Grado oficiales de la Universidad de Córdoba durante el período pre-doctoral bajo la financiación del contrato FPU (FPU17/03981) ha sido la siguiente:

Título Oficial	Curso académico	Créditos ECTS
Grado en Bioquímica	2018/2019	1.8
Grado en Ingeniería Mecánica	2018/2019	3.6
Síntesis Orgánica	2019/2020	5.4
Síntesis Orgánica	2020/2021	5.4
Síntesis Orgánica	2021/2022	5.4

I.IX. Actividades de divulgación científica

A continuación, se recogen las actividades de divulgación científica en las que el doctorando ha participado durante el periodo pre-doctoral:

1- Participación como ponente del Stand del Departamento de Química Orgánica en el evento de divulgación científica La Noche Europea de los Investigadores 2016

Entidad organizadora: Fundación Descubre

Fecha: 30-septiembre-2016

Lugar de celebración: Córdoba, Andalucía, España

2- Participación en las X Jornadas de Introducción al Laboratorio Experimental de Química 2017 dentro del 3º Plan Anual de Captación de Estudiantes (PACE)

Entidad organizadora: Universidad de Córdoba

Fecha: 12-enero-2017

Lugar de celebración: Córdoba, Andalucía, España

3- Participación en las XI Jornadas de Introducción al Laboratorio Experimental de Química 2018 dentro del 4º Plan Anual de Captación de Estudiantes (PACE)

Entidad organizadora: Universidad de Córdoba

Fecha: 10-enero-2018

Lugar de celebración: Córdoba, Andalucía, España

4- Participación como ponente del Stand informativo del Instituto Universitario de Investigación en Química Fina y Nanoquímica Orgánica

en el evento de divulgación científica **XIII Edición Paseos por la Ciencia 2018**

Entidad organizadora: Asociación de Profesorado de Córdoba por la Cultura Científica (APCCC). Facultad de Ciencias. Instituto Universitario de Investigación en Química Fina y Nanoquímica. Universidad de Córdoba

Fecha: 14-abril-2018

Lugar de celebración: Córdoba, Andalucía, España

5- Participación como conferenciante en el evento **II Feria de Posgrado 2018 de la Universidad de Córdoba** llevando a cabo una exposición titulada: *“Mi experiencia en el Máster Interuniversitario de Química en la UCO”*

Entidad organizadora: Universidad de Córdoba

Fecha: 24-abril-2018

Lugar de celebración: Córdoba, Andalucía, España

6- Participación en las **XII Jornadas de Introducción al Laboratorio Experimental de Química 2019 dentro del 5º Plan Anual de Captación de Estudiantes (PACE)**

Entidad organizadora: Universidad de Córdoba

Fecha: 30-enero-2019

Lugar de celebración: Córdoba, Andalucía, España

7- Participación como ponente del Stand informativo del Instituto Universitario de Nanoquímica (IUNAN) en el evento de divulgación científica **XIV Edición Paseos por la Ciencia 2019: Los Elementos Químicos: Ladrillos de la Materia**

Entidad organizadora: Asociación de Profesorado de Córdoba por la Cultura Científica (APCCC). Facultad de Ciencias. Instituto Universitario de Investigación en Química Fina y Nanoquímica. Universidad de Córdoba

Fecha: 6-abril-2019

Lugar de celebración: Córdoba, Andalucía, España

8- Participación en las IX Jornadas de Divulgación Científica de la UCO: UCODivulga. Más allá de los papers

Entidad organizadora: Unidad de Cultura Científica y de la Innovación de la Universidad de Córdoba

Fecha: 24-mayo-2021

Lugar de celebración: Córdoba, Andalucía, España

9- Participación como ponente del Stand informativo del Instituto Universitario de Investigación en Química Fina y Nanoquímica de la Universidad de Córdoba en los evento de divulgación científica XV Edición Paseos por la Ciencia 2021 (1º Virtual) y XVI Edición de Paseos Por la Ciencia 2022 (2º Virtual)

Entidad organizadora: Asociación de Profesorado de Córdoba por la Cultura Científica (APCCC) y Fundación Descubre. Facultad de Ciencias. Instituto Universitario de Investigación en Química Fina y Nanoquímica. Universidad de Córdoba

Fecha: 10/05/2021 - 12/05/2021. 16/05/2022 - 22/05/2022

Lugar de celebración: Córdoba, Andalucía, España

10- Participación como ponente del Stand del Departamento de Química Orgánica en el evento de divulgación científica La Noche Europea de los Investigadores 2022

Entidad organizadora: Fundación Descubre

Fecha: 30-septiembre-2022

Lugar de celebración: Córdoba, Andalucía, España

I.X. Estancias de Investigación en el extranjero

El doctorando ha llevado a cabo dos estancias de investigación internacionales cumpliendo con el periodo máximo de 9 meses establecido por Programa de Doctorado de Química Fina de la Universidad de Córdoba y el contrato de formación de profesorado universitario (FPU) financiado por el Ministerio de Universidades del Gobierno de España para realizar estancias en centros extranjeros durante la Tesis Doctoral:

Entidad de realización	Uppsala University
Tipo de entidad	Universidad
Facultad, instituto, centro	Department of Chemistry - Ångström Laboratory
Ciudad entidad realización	Uppsala, Stockholm, Suecia
Fecha de inicio-fin:	01/12/2019 - 31/05/2020
Duración	6 meses
Objetivos de la estancia	Mención Internacional de Tesis Doctoral
Proyecto de investigación	Photocatalytic hydrogen production from [FeFe]-hydrogenase biomimetic models
Supervisor	Dr. Sascha Ott, Full Professor in Synthetic Molecular Chemistry at Uppsala University

Entidad de realización	Lisbon University
Tipo de entidad	Universidad
Facultad, instituto, centro	Instituto Superior Técnico (IST)
Ciudad entidad realización	Lisbon, Lisbon, Portugal
Fecha de inicio-fin:	01/07/2021 - 30/09/2021
Duración	3 meses
Objetivos de la estancia	Ampliación de la formación investigadora del doctorando durante el desarrollo de su Tesis Doctoral
Proyecto de investigación	Synthesis and characterization of hybrid photoactive silica-based nanoparticles for photochemical applications
Supervisor	Dr. Carlos Baleizão, Assistant Professor in Instituto Superior Técnico at Lisbon University

I.XI. Becas

A continuación, se exponen las becas de investigación obtenidas por el doctorando durante el periodo pre-doctoral:

1- Nombre de la ayuda: Beca Iniciación a la investigación UCO 2014-2016 (VII Convocatoria de Becas Iniciación a la investigación)

Entidad concesionaria: Universidad de Córdoba

Fecha de concesión/finalización: 01/12/2014 - 31/07/2016

Entidad de realización: Universidad de Córdoba

2- Nombre de la ayuda: Beca SECAT de Introducción a la Investigación en Catálisis. BECAS INTRO-2016

Entidad concesionaria: Sociedad Española de Catálisis

Fecha de concesión/finalización: 01/06/2016 - 31/10/2016

Entidad de realización: Universidad de Córdoba

3- Nombre de la ayuda: Beca de Colaboración de estudiantes en departamentos universitarios para el curso académico 2016-2017

Entidad concesionaria: Ministerio de Educación, Ciencia y Deporte

Fecha de concesión/finalización: 01/12/2016 - 31/07/2017

Entidad de realización: Universidad de Córdoba

4- Nombre de la ayuda: Beca SECAT para realización de Proyectos Fin de Máster en Catálisis 2017

Entidad concesionaria: Sociedad Española de Catálisis

Fecha de concesión/finalización: 01/06/2017 - 31/12/2017

Entidad de realización: Universidad de Córdoba

5- Nombre de la ayuda: Beca de movilidad otorgada por la Universidad de Córdoba (UCO) en la Convocatoria Extraordinaria de “Ayudas Movilidad Internacional” 2018/2019 para obtener la Mención Internacional en la Tesis Doctoral

Entidad concesionaria: Universidad de Córdoba

Fecha de concesión/finalización: 01/12/2019 - 28/02/2020

Entidad de realización: Ångström Laboratory, Uppsala University, Sweden

6- Nombre de la ayuda: Beca de movilidad otorgada por el ceiA3 en la Convocatoria de ayudas a la Movilidad Erasmus+ para estudiantes de DOCTORADO hacia Países del Programa para el curso académico 2019/2020, en el marco del Programa Erasmus+ KA103 de la Comisión Europea

Entidad concesionaria: Campus de Excelencia Internacional Agroalimentario (ceiA3)

Fecha de concesión/finalización: 01/03/2020 - 31/05/2020

Entidad de realización: Ångström Laboratory, Uppsala University, Sweden

7- Nombre de la ayuda: Beca de movilidad otorgada por el Ministerio de Universidades en la Convocatoria de ayudas complementarias destinadas a beneficiarios de ayudas de Formación del Profesorado Universitario del Subprograma Estatal de Formación en I+D+i para la realización de estancias breves y traslados temporales en 2021 (Orden 24 de noviembre de 2020)

Entidad concesionaria: Ministerio de Ciencia e Innovación.
Universidades

Fecha de concesión/finalización: 01/07/2021 - 30/09/2021

Entidad de realización: Instituto Superior Técnico (IST), Lisbon
University, Portugal

8- Nombre de la ayuda: Beca de Formación de Profesorado Universitario
(FPU17/03981)

Entidad concesionaria: Ministerio de Ciencia e Innovación.
Universidades

Fecha de concesión/finalización: 22/10/2018 - 16/12/2022

Entidad de realización: Universidad de Córdoba

I.XII. Premios

Durante la etapa predoctoral, el doctorando ha sido galardonado con los siguientes premios:

1- Premio al colectivo de jóvenes participantes en el I Congreso Científico de investigadores noveles

Entidad concesionaria: Delegación de Gobierno de la Junta de Andalucía

Tipo de entidad: Organismo Público de Investigación

Ciudad entidad concesionaria: Córdoba, Andalucía, España

Fecha de concesión: 20/03/2017

2- Premio Extraordinario Fin de Máster del Máster Universitario de Química. Curso 2016/2017

Entidad concesionaria: Universidad de Córdoba

Tipo de entidad: Universidad

Ciudad entidad concesionaria: Córdoba, Andalucía, España

Fecha de concesión: 29/10/2018

3- Premio en la II Convocatoria de Premios a la excelencia para Investigadores/as noveles de la UCO

Entidad concesionaria: Universidad de Córdoba

Tipo de entidad: Universidad

Ciudad entidad concesionaria: Córdoba, Andalucía, España

Fecha de concesión: 19/11/2018

4- Premio en el VII Congreso Científico de Investigadores en Formación de la Universidad de Córdoba a la mejor Comunicación Oral en el área de Ciencias

Entidad concesionaria: Universidad de Córdoba

Tipo de entidad: Universidad

Ciudad entidad concesionaria: Córdoba, Andalucía, España

Fecha de concesión: 07/02/2019

5- Premio Extraordinario del Máster Universitario en Profesorado de Enseñanza Secundaria Obligatoria y Bachillerato, Formación Profesional y Enseñanza de Idiomas. Especialidad: Física y Química. Curso 2018/2019

Entidad concesionaria: Universidad de Córdoba

Tipo de entidad: Universidad

Ciudad entidad concesionaria: Córdoba, Andalucía, España

Fecha de concesión: 27/11/2020

Anexo 2

Compendio de publicaciones

**II.I. Sección 1: Polímeros de
coordinación-Metal
Organic Frameworks
(MOFs)**



Zirconium coordination polymers based on tartaric and malic acids as catalysts for cyanosilylation reactions

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ARTICLE INFO

Keywords:

Coordination polymers
Zr(IV) complexes
Chiral linkers
Cyanosilylation reaction
Enantioselectivity
Heterogeneous catalysis

ABSTRACT

The synthesis of chiral materials is a great challenge. This work describes the synthesis of Zr-based coordination polymers composed of chiral ligands derived from natural products. L-tartaric acid, dibenzoyl-L-tartaric acid and L-malic acid were selected as ligands from the chiral pool. Their reaction with zirconium oxychloride gave rise to several materials that were characterized by different techniques, such as XRD, Raman spectroscopy, ¹³C MAS NMR, TGA and N₂ adsorption/desorption isotherms. Significant structural and textural properties have been observed depending on the ligand, the synthesis procedure and the metal to ligand ratio. These polymers were used for the first time as catalysts in the cyanosilylation of benzaldehyde with trimethylsilyl cyanide and their activity was compared with that of UiO-66. Different reaction parameters and reusability were studied for this asymmetric reaction. Some of the reported materials were very active in this reaction and provided a remarkable enantioselectivity depending on the reaction conditions.

1. Introduction

Coordination polymers are hybrid materials composed of organic linkers and metal nodes. [1,2] Among different organic ligands used for the preparation of coordination polymers, malic and tartaric acids are promising linkers because they are readily abundant natural products and, besides two carboxylate groups, contains hydroxyl groups which can provide multiple coordination modes. In addition, both acids and their derivatives are simple and inexpensive chiral sources [3,4].

Numerous coordination polymers and metal organic frameworks composed of malic and tartaric acids have been synthesized in the last years. Thus, for example, Williams et al. [5] reported two new indium tartrates, one of them with a microporous 3D framework with a channel size of ca. 6 Å and Del Castillo et al. [6] described cadmium tartrates with open frameworks. Metal tartrates exhibit interesting applications such as antiferromagnetic coupling by manganese coordination polymers [3], photoluminescence by some rare-earth MOFs (La, Sm, Eu, Tb and Dy) [4] and ferroelectricity by cerium coordination polymers [7], among others. Metal malates of a variety of metal ions have also been synthesized [8]. For instance, the crystal structure of several chiral and achiral malates of Sr(II), Cu(II), Pb(II), Co(II), Ni(II), Mg(II), Zn(II) and Cd(II) have been reported in the last years [9–12].

Zirconium coordination polymers are particularly attractive because they generally exhibit a high stability due to the significant strength of Zr-O bonds. An example is UiO-66, which is a Zr-terephthalate based MOF, a versatile material for catalytic applications [13]. Both Lewis and Brønsted sites present in this material can act complementary to each other, making it very attractive for catalysis [14]. Even, the strength of the Lewis acid sites can be modulated changing the electronic character of groups bound to the linker [15]. Also, the important role of the accessibility of substrates to internal active sites was revealed by comparison of the catalytic activity of UiO-66 and UiO-67, the latter containing biphenyl-4,4'-dicarboxylate ligands [16]. Other Zr-based MOFs have been used as catalysts, i.e. a bimetallic Zr(Ti)-naphthalenedicarboxylate MOFs [17], which was active in Lewis acid catalyzed reactions, such as Meerwein-Ponndorf-Verley and isomerization of α -pinene oxide, among others.

The first example of chiral catalysis with a MOF was reported by Kim et al. [18] This material was synthesized from a pyridyl derivative of tartaric acid and Zn(II). The enantiomeric excess in the transesterification of 2,4-dinitrophenyl acetate with 1-phenyl-2-propanol was 8%. Later, the coordination polymer Ni(L-asp)bipy_{0.5}, with L-asp = L-aspartate and bipy = 4,4'-dipyridyl, provided enantiomeric excess between +17% and -6% in the methanolysis of *cis*-2,3-epoxybutane [19].

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<https://doi.org/10.1016/j.apcata.2019.117190>

Received 7 May 2019; Received in revised form 17 July 2019; Accepted 4 August 2019

Available online 08 August 2019

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Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Fast ultrasound-assisted synthesis of highly crystalline MIL-88A particles and their application as ethylene adsorbents



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ARTICLE INFO

Keywords:
MOF
MIL-88A particles
Ultrasound irradiation
Ethylene adsorption

ABSTRACT

Highly crystalline MIL-88A particles have been successfully synthesized via fast ultrasound-assisted processes. The influence of the sonication generator and synthesis time on the structure, crystallinity, morphology and surface area of the materials were studied in detail. Under this modified ultrasonic method, X-ray diffraction patterns of MIL-88A particles showed highly crystalline structures in contrast to those reported in literature. Significant differences on surface areas and microporosity were appreciated under ultrasound conditions employed. Specific surface areas in the range between 179 and 359 m² g⁻¹ were obtained. That material synthesized under ultrasound batch conditions during 1 h had the highest surface area and microporous character. Different particle sizes and morphologies were obtained depending on the synthesis procedure. In general, probe sonicators led to smaller particle sizes. Moreover, a comparative study of the ethylene adsorption of the MIL-88A particles and several common MOFs in the ethylene adsorption was investigated. The results suggest that the modified ultrasound-assisted procedure for the synthesis of MIL-88A is effective to obtain highly crystalline particles, which are very efficient to adsorb ethylene molecules.

1. Introduction

Metal Organic Frameworks (MOFs) have been increasingly studied [1,2] due to their feasibility in applications such as gas storage [3] and separation [4], catalysis, and drug delivery [5], among others. These compounds consist in metal ions coordinated to organic ligands. The combination of these two components in a MOF provides limitless opportunities to tailor different materials with a chosen purpose. One of the most used synthetic routes for MOF particles involves the use of solvothermal conditions [6]. Even though this route exhibits a reasonable good performance in the quality of the obtained product, it requires relative long periods of heating and high temperatures. So, it is still challenging to precisely set the conditions -timing, temperature, solvent, modulating agent- during synthesis to keep the structural integrity of the framework.

Ultrasonic syntheses have been scarcely used for the preparation of MOFs [7,8]. This is an interesting method in which ultrasonic waves interact with the liquid solution generating small bubbles that provoke pressure and temperature alterations. This promotes effective collisions between particles and simplifies the reaction mechanism by helping the

product crystallization. This route also enables the coordination reaction, improving surface morphology by facilitating the percolation of the reagents solution into the porous structure of the initial formed crystals, thus aiding a faster and more homogeneous crystal growth [9]. Different MOF materials such as UiO-66, HKUST-1, TMU-34 have been synthesized by ultrasound irradiation showing important effects on the morphology and growth process of their particles [10–13]. Recently, the ultrasound-assisted synthesis of DUT-32 and other Zn(II)-based MOFs have been carried out and their application as drug and pollutant adsorbents have been reported [14–17].

Also, structured coordination polymers have been successfully synthesized by sonochemical routes, validating it as a very attractive method for the preparation of particles with diverse shapes, sizes and morphologies [18]. In addition, the ultrasound-assisted synthesis of composites of MOFs, specifically HKUST-1, with activated carbon or molecularly imprinted polymers, useful as adsorbents, have been reported [19,20].

Iron (III) MOFs have been previously studied by different groups and they have shown their innocuous character in human health for drug delivery [21]. Although Fe-MIL-88 serial MOFs have been

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<https://doi.org/10.1016/j.ultsonch.2018.08.027>

Received 31 May 2018; Received in revised form 1 August 2018; Accepted 27 August 2018

Available online 27 August 2018

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Article

MIL-88A Metal-Organic Framework as a Stable Sulfur-Host Cathode for Long-Cycle Li-S Batteries

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Received: 20 January 2020; Accepted: 24 February 2020; Published: 28 February 2020



Abstract: Lithium-sulfur (Li-S) batteries have received enormous interest as a promising energy storage system to compete against limited, non-renewable, energy sources due to their high energy density, sustainability, and low cost. Among the main challenges of this technology, researchers are concentrating on reducing the well-known “shuttle effect” that generates the loss and corrosion of the active material during cycling. To tackle this issue, metal-organic frameworks (MOF) are considered excellent sulfur host materials to be part of the cathode in Li-S batteries, showing efficient confinement of undesirable polysulfides. In this study, MIL-88A, based on iron fumarate, was synthesised by a simple and fast ultrasonic-assisted probe method. Techniques such as X-ray diffraction (XRD), Raman spectroscopy, Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and N₂ adsorption/desorption isotherms were used to characterise structural, morphological, and textural properties. The synthesis process led to MIL-88A particles with a central prismatic portion and pyramidal terminal portions, which exhibited a dual micro-mesoporous MOF system. The composite MIL-88A@S was prepared, by a typical melt-diffusion method at 155 °C, as a cathodic material for Li-S cells. MIL-88A@S electrodes were tested under several rates, exhibiting stable specific capacity values above 400 mAh g⁻¹ at 0.1 C (1C = 1675 mA g⁻¹). This polyhedral and porous MIL-88A was found to be an effective cathode material for long cycling in Li-S cells, retaining a reversible capacity above 300 mAh g⁻¹ at 0.5 C for more than 1000 cycles, and exhibiting excellent coulombic efficiency.

Keywords: Li-S battery; metal-organic framework; sulfur composite; polysulfides confinement

1. Introduction

The current energy economy based on the demand for non-renewable sources, such as fossil fuels and oil, continues to be a high-risk social problem. The increase in CO₂ emissions, global warming, and dramatic climate change, are some of the main problems that are taking place and seriously worrying the future of world society [1–3]. Therefore, it is vitally important to replace these energy generation systems with others based on cleaner and more environmentally sustainable sources of renewable energy [4,5]. In this area, batteries are currently considered a fundamental energy storage system due to their high efficiency and lifetime, and are being postulated as the key to future development of power system applications [6–8].

Lithium-sulfur (Li-S) and lithium-oxygen (Li-O₂) batteries were proposed as promising high-energy rechargeable systems for emerging applications. Despite the various problems that still present, these

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MIL-88A Metal-Organic Framework as a Stable Sulfur-Host Cathode for Long-Cycle Li-S Batteries

Authored by:

Almudena Benítez; Juan Amaro-Gahete; Dolores Esquivel; Francisco José Romero-Salguero; Julián Morales; Álvaro Caballero

Published in:

Nanomaterials **2020**, Volume 10, Issue 3, 424



Basel, April 2020

**II.II. Sección 2: Materiales
híbridos orgánico-
inorgánicos basados en
sílice-Periodic
Mesoporous
Organosilicas (PMOs)**



Review

Catalytic systems mimicking the [FeFe]-hydrogenase active site for visible-light-driven hydrogen production



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ARTICLE INFO

Article history:

Received 18 May 2021

Accepted 16 August 2021

Keywords:

Photochemistry

Biomimetic chemistry

Artificial photosynthesis

Light-driven hydrogen evolution

Bioinorganic chemistry

ABSTRACT

A global hydrogen economy could ensure environmentally sustainable, safe and cost-efficient renewable energy for the 21st century. Solar hydrogen production through artificial photosynthesis is a key strategy, and the activity of natural hydrogenase metalloenzymes an inspiration for the design of synthetic catalytic systems.

[FeFe]-hydrogenase enzymes, present in anaerobic bacteria and green algae, are the most efficient class of biological catalysts for hydrogen evolution. The enzymes operate in an aqueous environment, utilizing electrons that ultimately stem from photosynthesis as the only energy source. Functional synthetic models of the [FeFe]-hydrogenase enzyme active site have garnered intense interest as potential catalysts for the reduction of protons to molecular hydrogen.

Herein, we take an extensive journey through the field of biomimetic hydrogenase chemistry for light-driven hydrogen production. We open with a brief presentation of the structure and redox mechanism of the natural enzyme. Synthetic methodologies, structural characteristics, and hydrogen generation metrics relevant to the synthetic diiron catalysts ([2Fe2S]) are discussed. We first examine multi-component photocatalysis systems with the [2Fe2S] cluster, followed by photosensitizer-[2Fe2S] dyads and molecular triads. Finally, strategies for the incorporation of [2Fe2S] complexes into supramolecular assemblies, semiconductor supports, and hybrid heterogeneous platforms are laid out. We analyze the individual properties, scope, and limitations of the components present in the photocatalytic reactions. This review illuminates the most useful aspects to rationally design a wide variety of biomimetic catalysts inspired by the diiron subsite of [FeFe]-hydrogenases, and establishes design features shared by the most stable and efficient hydrogen producing photosystems.

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<https://doi.org/10.1016/j.ccr.2021.214172>

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Article

Hydroxyl-Decorated Diiron Complex as a [FeFe]-Hydrogenase Active Site Model Complex: Light-Driven Photocatalytic Activity and Heterogenization on Ethylene-Bridged Periodic Mesoporous Organosilica

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Citation: Amaro-Gahete, J.; Esquivel, D.; Pavliuk, M.V.; Jiménez-Sanchidrián, C.; Tian, H.; Ott, S.; Romero-Salguero, F.J. Hydroxyl-Decorated Diiron Complex as a [FeFe]-Hydrogenase Active Site Model Complex: Light-Driven Photocatalytic Activity and Heterogenization on Ethylene-Bridged Periodic Mesoporous Organosilica. *Catalysts* **2022**, *12*, 254. <https://doi.org/10.3390/catal12030254>

Academic Editor: Omer Yéchezkel

Received: 21 December 2021

Accepted: 22 February 2022

Published: 23 February 2022

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Abstract: A biomimetic model complex of the [FeFe]-hydrogenase active site (FeFeOH) with an ethylene bridge and a pendant hydroxyl group has been synthesized, characterized and evaluated as catalyst for the light-driven hydrogen production. The interaction of the hydroxyl group present in the complex with 3-isocyanopropyltriethoxysilane provided a carbamate triethoxysilane bearing a diiron dithiolate complex (NCOFeFe), thus becoming a potentially promising candidate for anchoring on heterogeneous supports. As a proof of concept, the NCOFeFe precursor was anchored by a grafting procedure into a periodic mesoporous organosilica with ethane bridges (EthanePMO@NCOFeFe). Both molecular and heterogenized complexes were tested as catalysts for light-driven hydrogen generation in aqueous solutions. The photocatalytic conditions were optimized for the homogenous complex by varying the reaction time, pH, amount of the catalyst or photosensitizer, photon flux, and the type of light source (light-emitting diode (LED) and Xe lamp). It was shown that the molecular FeFeOH diiron complex achieved a decent turnover number (TON) of 70 after 6 h, while NCOFeFe and EthanePMO@NCOFeFe had slightly lower activities showing TONs of 37 and 5 at 6 h, respectively.

Keywords: [FeFe]-hydrogenase; periodic mesoporous organosilica; biomimetic chemistry; artificial photosynthesis; light-driven hydrogen evolution

1. Introduction

The current energy crisis produced by the imminent depletion of non-renewable energy sources has prompted the scientific community to carry out numerous investigations with the aim of finding inexhaustible and environmentally friendly alternative energy forms [1–3]. In this area, solar energy applied to the chemical decomposition of an abundant substrate such as water is constantly on the rise as a key strategy for obtaining hydrogen [4–8].

A large part of the energy-sustainable systems of the future is based on hydrogen as a renewable energy carrier due to its high energy density and its combustion free of polluting gases [9,10]. The naturally occurring [FeFe]-hydrogenase enzymes in certain algae and bacteria catalyze the reduction of protons to hydrogen with a very high efficiency [11–13]. Due to the low availability of natural hydrogenases, a large number of investigations have been reported in the search for biomimetic catalysts reproducing the biological activity carried out by these enzymes, with the aim of designing an artificial photocatalytic system capable of providing light-driven hydrogen production [14,15].

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Haining Tian; Sascha Ott;
Francisco J. Romero-Salgiero

Published in:

Catalysts **2022**, Volume 12, Issue 3, 254



Basel, April 2022

II.III. Sección 3: Materiales híbridos basados en grafeno



Article

A Comparative Study of Particle Size Distribution of Graphene Nanosheets Synthesized by an Ultrasound-Assisted Method

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Received: 24 December 2018; Accepted: 23 January 2019; Published: 26 January 2019



Abstract: Graphene-based materials are highly interesting in virtue of their excellent chemical, physical and mechanical properties that make them extremely useful as privileged materials in different industrial applications. Sonochemical methods allow the production of low-defect graphene materials, which are preferred for certain uses. Graphene nanosheets (GNS) have been prepared by exfoliation of a commercial micrographite (MG) using an ultrasound probe. Both materials were characterized by common techniques such as X-ray diffraction (XRD), Transmission Electronic Microscopy (TEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). All of them revealed the formation of exfoliated graphene nanosheets with similar surface characteristics to the pristine graphite but with a decreased crystallite size and number of layers. An exhaustive study of the particle size distribution was carried out by different analytical techniques such as dynamic light scattering (DLS), nanoparticle tracking analysis (NTA) and asymmetric flow field flow fractionation (AF4). The results provided by these techniques have been compared. NTA and AF4 gave higher resolution than DLS. AF4 has shown to be a precise analytical technique for the separation of GNS of different sizes.

Keywords: graphene nanosheets; exfoliation; particle size distribution; nanoparticle tracking analysis; asymmetric flow field flow fractionation

1. Introduction

Particle size analysis is a key element because many properties of nanomaterials are size dependent [1]. This parameter is essential since the synthesis at a small scale must be monitored for subsequent bulk production and for the control of nanotechnological products in the market. The control of size during the synthesis of nanomaterials is decisive in various industrial sectors such as nanomedicine, nanofood, nanoenergy or nanocosmetics [2–6].

It is well known that graphene has excellent properties that provide a multitude of technological applications in different fields. It is formed by a pattern of hexagonal rings of carbon atoms constituting a huge flat molecule [7]. Some of its most important properties are its high thermal and electrical

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Published in:

Nanomaterials 2019, Volume 9, Issue 2, 152



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Luminescent Graphene-Based Materials via Europium Complexation on Dipyriddyridazine-Functionalized Graphene Sheets

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Dedicated to Professor Jean-Marie Lehn on the occasion of his 80th birthday

Abstract: Graphene-based materials exhibit outstanding physical properties and so are potentially applicable in a great variety of fields. Unlike their corresponding oxides, graphite and graphene are not prone to functionalization. Diels–Alder reactions are among the scarce reactions that they can occur without disrupting their conjugated sp^2 systems. Herein, the reaction between graphite and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine under different conditions affords several graphene-based materials consisting of dipyriddyri-

dazine-functionalized few-layer graphene, multilayer graphene and graphite, the sheets of which act as ligands for the grafting of a europium complex. These three materials show strong red emission under 365 nm UV radiation. Their emitting particles can be visualized by confocal microscopy. The rich coordination chemistry of dipyriddyridazine ligands has potential novel properties for similarly functionalized graphene-based materials grafted with other metal complexes.

Introduction

Graphene-based materials will have an outstanding technological impact in the future by virtue of their availability and excellent mechanical, thermal, electrical and electronic properties. The possibility to impart them with photonic properties is challenging and will be of high interest. Emitting nanomaterials have potential applications in many areas, including sensing, bioimaging and photocatalysis, among others.^[1] However, graphene is a zero band gap semiconductor and so practically it does not exhibit any luminescence.^[2]

At present there are two general strategies to produce luminescent graphene-based materials.^[3] The first one involves the existence of sp^2 isolated islands without π connections, as occurs in some reduced graphene oxides. The second one originates from the presence of defects, as occurs in carbon

quantum dots. These nanomaterials exhibit emissions that are concentrated in the blue and green regions.

Previous strategies are basically based on the introduction of defects in the graphene sheets and so unavoidably will lead to materials with depleted properties.

3,6-Di(2-pyridyl)pyridazine units have received great attention as ligands for coordination and supramolecular chemistry.^[4] These ligands can be synthesized by an inverse electron demand Diels–Alder reaction between the corresponding 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (as diene) and alkynes or alkenes (as dienophiles).^[5]

Hybrid materials have also been functionalized through hetero-Diels–Alder reactions. Thus, in recent years, the emission properties of different organosilicas by their functionalization with lanthanide complexes via surface dipyriddyridazine ligands have been explored. These surface adducts were generated by Diels–Alder reaction between C=C double bonds in the organosilica (dienophile) and 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (diene). In particular, these surface adducts were proven to be suitable sensitizing ligands for europium ions,^[6] provided hybrid near-infrared (NIR) emitting materials upon complexation with NIR emitting lanthanide ions (Nd^{3+} , Er^{3+} , Yb^{3+})^[7] and a luminescent optical thermometer when grafted with Eu^{3+} / Tb^{3+} ions.^[8]

Nitrogen-doped graphenes can be obtained by two general strategies, that is, direct synthesis and posttreatment. Regardless of the doping procedure, different nitrogen types at different locations are generated and so specific sites for metal coordination are ill-defined.^[9]

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<https://doi.org/10.1002/chem.201900512>

measurements were recorded using a 60 W pulsed Xe lamp operating at a frequency of 100 Hz (for visible emitting lanthanides). The very short decay times of the ungrafted dipyriddypridazine graphene-based materials were measured using a Supercontinuum white light laser for TCSPC (time correlated single photon counting). A Hamamatsu R928P photomultiplier tube was used to detect the emission signals in the near UV to visible range. All luminescence measurements were recorded at room temperature. Crystals were put between quartz plates (Stama cuvettes for powder samples, type 20/C/Q/0.2). For all of the compounds the luminescence decay curves were measured when excited into the broad ligand band (at different wavelengths) and monitored at the strongest europium transition. All of the decay curves could be well fitted using either a single exponential function or biexponential function [Eq. (1), (2)]:

$$I = A \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

$$I = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

where I represents the luminescence intensity and A , A_1 and A_2 are constants, t is time and τ , τ_1 and τ_2 are the luminescence lifetimes. All steady state and decay time measurements were performed with slit sizes of 1 nm (both excitation and emission) and a step size of 1 nm. The absolute overall quantum yields of the materials were measured by using an integrated sphere with a BENFLEC coating provided by Edinburgh Instruments as follows [Eq. (3)]:

$$\eta = \frac{\int E_{\text{emission}}}{\int E_{\text{blank}} - \int E_{\text{sample}}}$$

where E_{emission} is the integrated value of the emission spectrum, and E_{blank} and E_{sample} are the integrated values of the "excitation" band of the blank and the excitation band of the sample (since the sample absorbs part of the light, this value is smaller than E_{blank}), respectively.

Acknowledgements

The authors wish to acknowledge the financial support from Ramon Areces Foundation (Spain), Andalusian Regional Government (FQM-346 group), Spanish Ministry of Science, Innovation and Universities for an FPU teaching and research fellowship (FPU17/03981), Feder Funds and the technical staff from the Instituto Universitario de Investigación en Química Finas y Nanoquímica (IUNAN) and Servicio Central de Apoyo a la Investigación (SCAI). A.M.K. acknowledges Ghent University for funding and thanks Prof. Riv Van Deun for access to the Edinburgh Instruments Spectrofluorometer in his laboratory.

Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloaddition · graphene · lanthanides · luminescence · N ligands

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Manuscript received: February 1, 2019

Accepted manuscript online: March 18, 2019

Version of record online: April 26, 2019

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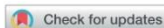
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Cite this: *Sustainable Energy Fuels*,
2022, 6, 1603

Surface Diels–Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN₄ sites for ORR and OER electrocatalysis†

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The assembly of atomically dispersed iron–nitrogen (FeN₄) sites into graphitic structures is a promising approach for sustainable production of bifunctional electrocatalysts for the oxygen electroreduction (ORR) and oxygen evolution (OER) reactions. In addition, single-atom FeN₄ sites at the edges of carbon substrates provide higher electrocatalytic performance than those in plane. Unfortunately, the conventional high-temperature pyrolysis method does not allow the generation of edge-enriched FeN₄ single-atom sites. Herein, a novel low-temperature and solvent-free mechanochemical synthesis based on the use of dipyrrolypyridazine (dppz) functionalized multilayer graphene as a starting material is proposed for precisely engineered location of these FeN₄ active sites at the edges. After careful characterization of these dppz-based materials, the ORR and OER electrocatalytic performance was investigated, demonstrating the efficient formation of FeN₄ sites at the edges as well as their excellent bifunctional behavior for the ORR and OER. This work paves the way for the development of sustainable approaches for the generation of edge-enriched FeN₄ single atom sites on multilayer graphene structures.

Received 2nd January 2022
Accepted 14th February 2022

DOI: 10.1039/d2se00004k

rsc.li/sustainable-energy

Introduction

The growing demand for renewable, clean and sustainable energy to counteract the depletion of fossil fuels and reduce CO₂ emissions as well as mitigate global warming has led the scientific community to focus great attention on the development of low-cost and efficient alternative energy resources and energy storage systems. The abundance of hydrogen in the universe and the relatively easy H₂ gas production from water by

electrolysis make it an ideal energy carrier. However, the use of electricity from renewable energy sources (such as solar or wind power) to split water into hydrogen, which is subsequently employed in fuel cells, requires the development of efficient and low-cost electrocatalyst materials.^{1–3} For these reasons, the design of non-noble-metal or metal-free catalysts showing enhanced performance towards the critical reactions involved in these electrocatalytic processes is crucial for the rapid advancement of the hydrogen economy.^{4,5} In this sense, highly active bifunctional electrocatalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) are of increasing interest due to their extensive applicability in a wide variety of renewable energy technologies such as rechargeable metal–air batteries, water splitting or reversible fuel cells.^{6–10} To date, Pt- and Ru/Ir-based catalysts have generally been regarded as the benchmark commercial catalysts for the ORR and OER, respectively.¹¹

Carbon-based electrocatalysts are promising materials for the above-mentioned electrocatalytic processes, due to their good stability, high surface area, excellent electrical conductivity, and flexibility for the introduction of dopants.^{12,13} Accordingly, a hot topic in electrocatalysis is focused on the appropriate doping of carbon-based materials with heteroatoms (e.g. N, S, P) and transition metals (e.g. Fe or Co) to obtain

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d2se00004k

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