

Preparation of graphene-based nanomaterials by pulsed RF discharges on liquid organic compounds

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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

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 twenty five 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.

2. Experimental section

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 gases of the discharges in both chambers due to its inert and easy ionizable character.

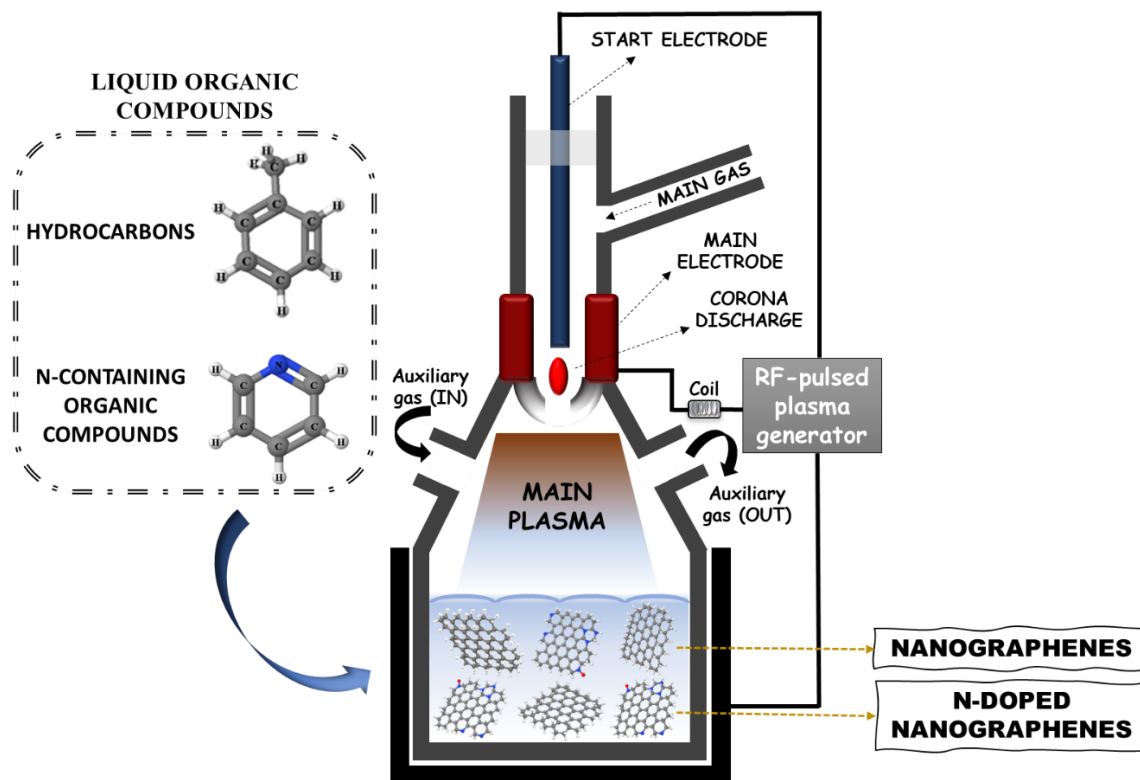


Figure 1. Configuration of the pulsed plasma reactor

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.

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 μ L 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 α 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 cm² and analyzed under ultra-high vacuum conditions.

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).

Three fundamental bands can be distinguished: (i) the G band, associated to splitting of the E_{2g} stretching mode, confirming sp² hybridized carbon atoms in the graphitic structure; (ii) the D band characteristic of C-C single bonds

with sp³-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 sp² hybridization [19].

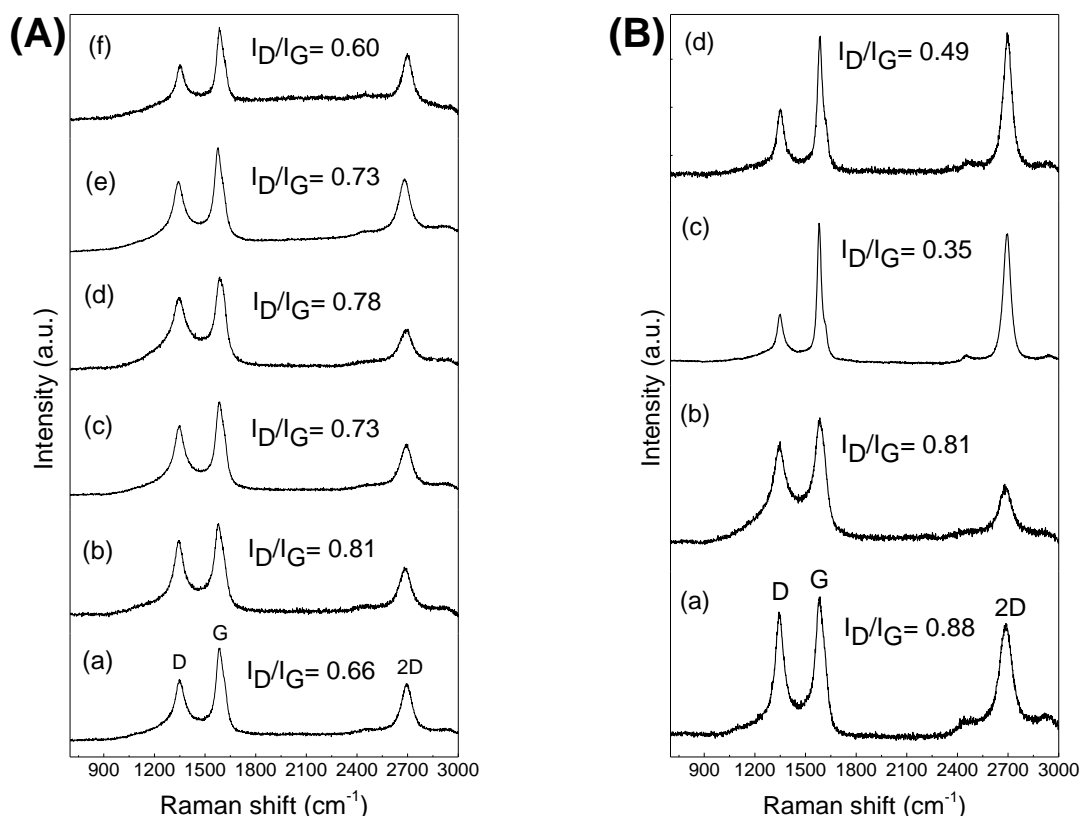


Figure 2. Raman spectra of graphene-based materials obtained from hydrocarbons (A): cyclohexane (a), cyclohexene (b), heptane (c), hexane (d), pentane (e) and toluene (f); and from N-containing compounds (B): cyclohexylamine (a), pyridine (b), dipropylamine (c) and triethylamine (d).

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: $I_{G/2D} = 0.14 + n/10$, 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].

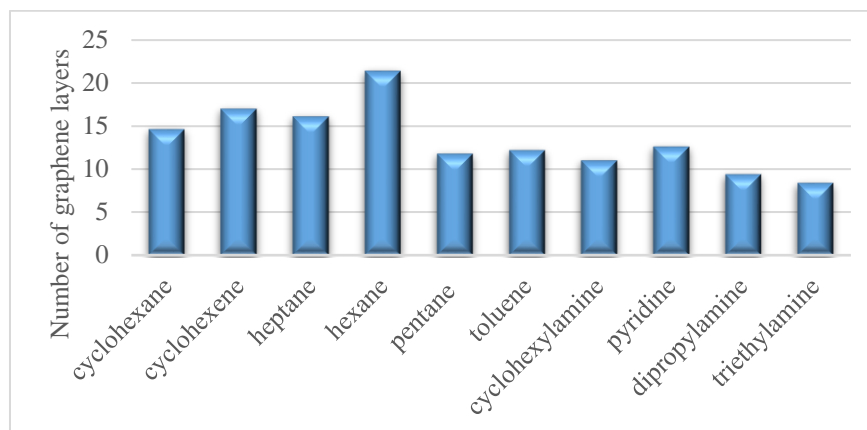


Figure 3. Number of layers in nanographenes obtained by pulsed plasma discharges on different organic compounds.

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.

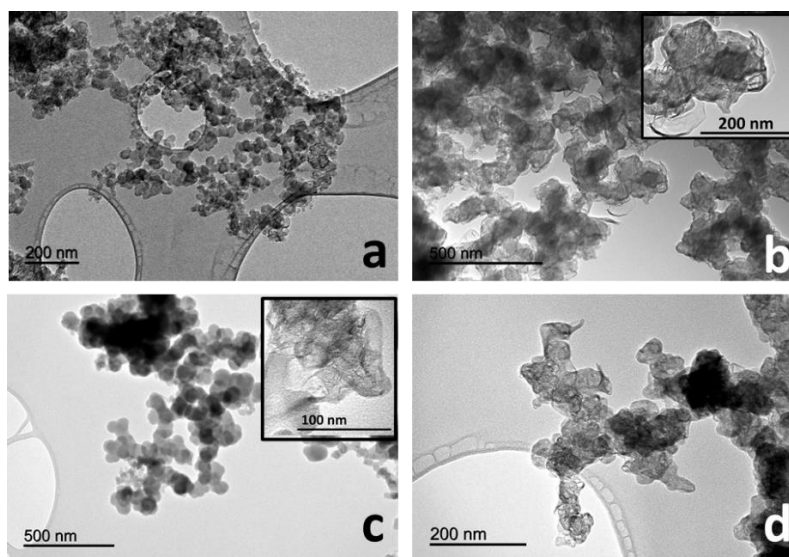


Figure 4. Representative TEM images of nanographenes obtained from cyclohexene (a), hexane (b), toluene (c) and pyridine (d).

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].

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.

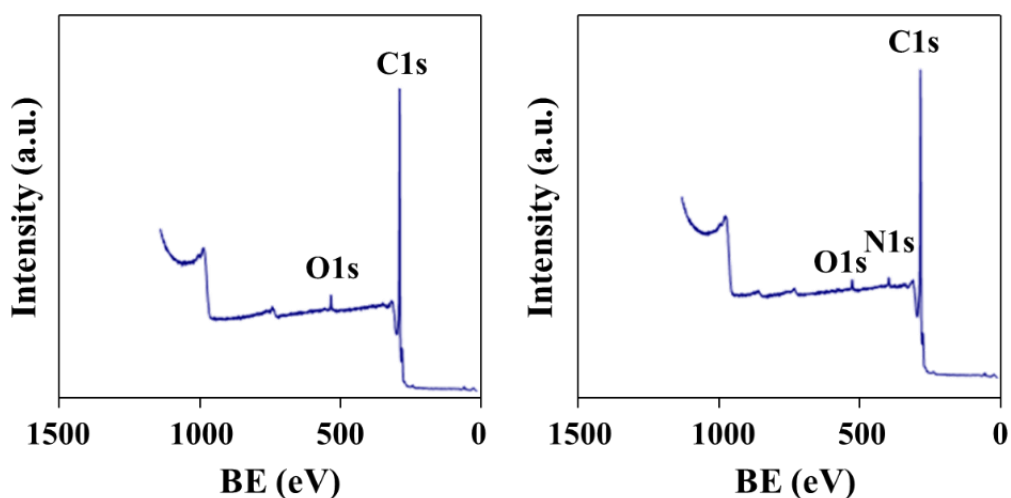


Figure 5. XPS survey for nanographenes obtained from toluene (right) and pyridine (left)

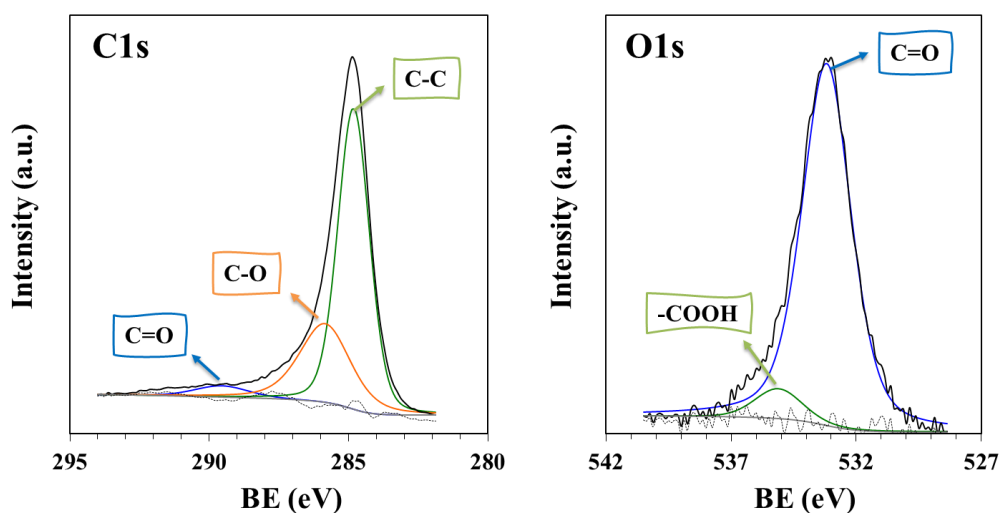


Figure 6. XPS spectra for the C1s and O1s photoemission peaks of nanographenes obtained from toluene

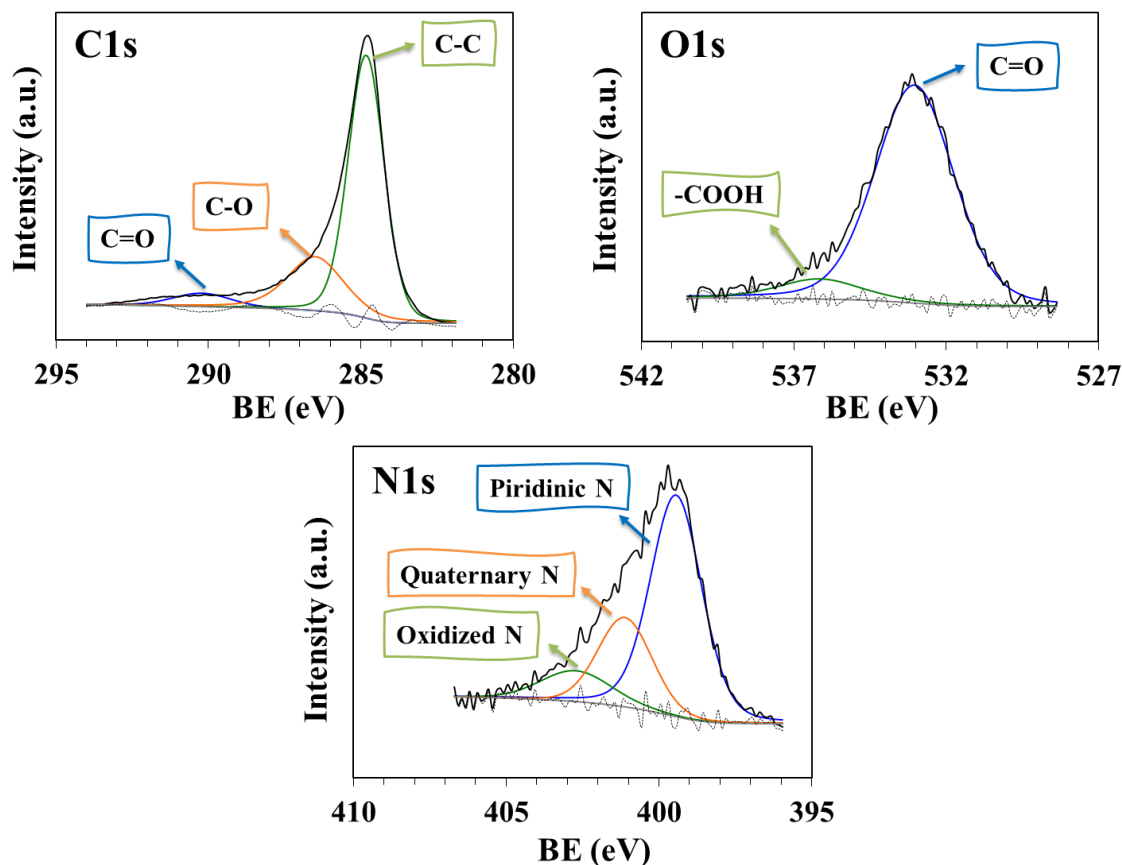


Figure 7. XPS spectra for the C1s, O1s and N1s photoemission peaks of nanographenes obtained from pyridine.

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.

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.

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