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Microwave-assisted preparation of Ag/Ag₂S carbon hybrid structures from pig bristles as efficient HER catalysts

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Ag/Ag₂S hybrid structures have recently attracted significant interest due to their high chemical and thermal stability, in addition to their unique optical and electrical properties. However, their standard synthetic protocols have important drawbacks including long term and harsh reaction conditions and the utilization of highly toxic sulfur precursors. Herein, an innovative, simple one-pot green approach for the synthesis of Ag/Ag₂S carbon hybrid structures is reported. The procedure involved a one-step microwave-assisted step using ethylene glycol as solvent and reducing agent, pig bristles as sulphur and carbon source and silver nitrate as metal precursor. Different amounts of silver nitrate were employed in order to investigate the synthetic mechanism for the formation of zerovalent silver over silver sulphide nanoparticles, producing three different samples. Materials were characterized by XRD, SEM, EDX, N₂ physisorption and XPS spectroscopy. Aiming to prove the efficiency of the as-synthesized compounds, their electrocatalytic activities were explored in the hydrogen evolution reaction (HER) performing linear sweep voltammetries.

Introduction

Environmental and economic metrics are becoming increasingly and equally important in the design of new materials. Currently, most industrially available compounds are derived from non-renewable sources, following the so-defined as linear economy. However, the rising costs of gas and crude oil and more importantly the drive towards a more sustainable future utilisation of low toxicity reagents is pushing research on the valorisation of renewable sources through sustainable synthetic processes.¹ In this context, meeting the principles of green chemistry can be considered as key in the sustainable design of innovative materials.²⁻⁴

In the last decades, different metal chalcogenides have attracted interest because of their unique physical and chemical properties that make them suitable in diverse areas ranging from electronics to biomedicine. These materials include copper sulphide (Cu₂S), silver sulphide (Ag₂S), nickel sulphide (NiS), lead sulphide (PbS), cadmium sulphide (CdS) and mercury sulphide (HgS).⁵⁻⁷ Silver sulphide emerged as

excellent material for the preparation of metal-semiconductor heterostructures.^{8, 9} These heterostructures may exhibit a behaviour not limited to the combination of the properties of the separated components, but also a synergetic effects of the two constituents.¹⁰ For example, Ag/Ag₂S heterostructures have attracted special attention as antibacterial agent, biosensing probes and photocatalysts.^{11, 12} Ag/Ag₂S heterostructures have been also proposed as efficient catalyst for the hydrogen evolution reaction (HER).^{13, 14} Hydrogen is in fact a promising candidate as alternative green energy source that can be produced *via* water splitting. Consequently, the development of suitable, low cost, high performance catalyst for hydrogen evolution reactions (HER) is of high importance and practical needs. However, despite the reported scope for the production of green hydrogen as alternative energy source, the synthesis of Ag/Ag₂S materials entails some sustainability restrictions. All reported synthetic protocols for these materials are normally time and energy consuming.¹² Most importantly, these syntheses involve the utilization of expensive and toxic sulphur sources including highly hazardous compounds such as H₂S, thiols or Na₂S as well as less aggressive (but still toxic) silver thiol salts.^{8, 15, 16}

Based on recent endeavours from our group in microwave chemistry and biomass valorisation, herein we report a sustainable and innovative one-step synthesis of pig bristles-derived Ag/Ag₂S carbon hybrid structures *via* a microwave-assisted reaction.¹⁷⁻¹⁹ The synthesized material exhibited a high performance as catalyst for the hydrogen evolution reaction (HER). In this way, the designed nanohybrid

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Electronic Supplementary Information (ESI) available: SEM mapping of the samples; complete list of XRD peaks; N₂ absorption-desorption isotherm of sample 1.4Ag/Ag₂S; LSV curves of the samples and Pt/C normalized by the electrochemical surface area. See DOI: 10.1039/x0xx00000x

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material follows the principles of circular economy, being derived from a biowaste (pig bristles), also being used as a catalyst for the sustainable production of hydrogen. Pig bristles are indeed an unexploited waste source of sulphur and carbon. Every year ~225k tons of wasted pig bristles are produced only in EU slaughterhouses. However, few reports available about pig bristles valorisation are limited to their utilization as food fodder supplements and material for brushes.^{20,21}

The preparation of Ag/Ag₂S involved a simple microwave assisted reaction. Microwave synthetic protocols show several advantages compared to conventional heating procedures. For example, they allow reactions in fast time, obtaining higher yields with potentially switchable selectivities.²²⁻²⁴ Ethylene glycol (common solvent used as antifreeze agent in the automotive industry) was additionally employed as solvent and reducing agent. Wasted pig bristles were used as carbon and sulphur source while silver sulphide was employed as metal precursor. In order to investigate the formation of silver (0) over silver (I) sulphide, the reaction was carried out using different quantities of silver precursor and a fixed amount of pig bristles, resulting in a sequence of three materials with varying Ag/Ag₂S ratios. The hybrid nanostructures were characterized by XRD, N₂ physisorption, SEM, EDX and XPS spectroscopy.

The materials were tested as catalyst for the hydrogen evolution reaction (HER). Recently Ren *et al.*, reported HER activity of porous Ag₂S/CuS generating 10 mA/cm² by supplying ~0.2 V in 0.5 M H₂SO₄.²⁵ Using the same electrolyte solution, Basu *et al.* reported HER activity of Ag/Ag₂S nanostructures with a current density of 10 mA/cm² upon application of -0.199 V potential.¹⁴

Herein, the best sample allowed the production of 10 mA/cm² operating at -0.190 V potential, one of the lowest applied potential reported in literature for these type of heterostructures.

Experimental

Materials

Ethylene glycol (HOCH₂CH₂OH, 99.9%), silver nitrate (AgNO₃), acetone (CH₃COCH₃), sulfuric acid (H₂SO₄, 95-97%) and ethanol (CH₃CH₂OH, 99.5%) were purchased from Sigma-Aldrich Inc., St. Louis, MO, USA. All reagents were used without any further purification.

Synthesis of Ag/Ag₂S

A sequence of three different Ag/Ag₂S carbon hybrid structures with different Ag(0)/Ag(I) ratio was synthesized. The materials were prepared modifying a methodology recently developed in our group for the synthesis of Cu₂S.¹⁸ In a typical procedure, the correct amount of silver nitrate (340-2040 mg, 2-12 mmol) was dissolved in 20 mL of ethylene glycol in a 50 mL Teflon microwave tube under vigorous stirring. Sequentially, 1.5 g of pig bristles (cut in pieces of ~0.5 cm)

were added. The mixture was kept at room temperature under magnetic stirring (700 rpm) for 10 minutes. Successively, the Teflon tube was closed and inserted into a Milestone Ethos D microwave reactor (Milestone Srl, Italy). The tube was subjected to microwave irradiation at 500 W for 4 minutes. In order to avoid any unwanted decomposition of ethylene glycol, the reaction time never exceeded 4 minutes, and the microwave reactor was set at 200 °C as maximum external temperature (Infra-Red temperature control) and 60 °C as maximum internal temperature (a fiber optic cable was inserted into the reference tube) and all tubes were equipped with pressure safe valves. After reaction, the mixture was cooled down to room temperature for ~2 hours. The homogeneous dark precipitate was filtrated and washed several times with distilled water, ethanol and acetone. The material was finally oven-dried at 100 °C for 24 hours.

Material characterization

Ag/Ag₂S carbon hybrid composites were characterized by Scanning electron microscopy (SEM), Powder X-ray diffraction (XRD) and X-ray photoelectronic spectroscopy (XPS).

Scanning electron microscopy images were recorded in a JEOL JSM-6300 scanning microscope (JEOL Ltd., Peabody, MA, USA) equipped with Energy-dispersive X-ray spectroscopy (EDX) at 15 kV at the Research Support Service Center (SCAI) from University of Cordoba.

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 DISCOVER A25 diffractometer (PanAnalytic/Philips, Lelyweg, Almelo, The Netherlands) using CuKα (λ=1.5418Å) radiation. Wide angle scanning patterns were collected over a 2θ range from 10° to 80° with a step size of 0.018° and counting time of 5 s per step.

Textural properties of the materials were determined by N₂ physisorption using a Micromeritics ASAP 2020 automated system (Micromeritics Instrument Corporation, Norcross, GA, USA) with the Brunauer-Emmet-Teller (BET) and the Barret-Joyner-Halenda (BJH) methods. Prior to analysis, samples were outgassed for 24 h at 100 °C under vacuum (P₀ = 10⁻² Pa) and subsequently analysed.

XPS studies were performed at the Central Service of Research Support (SCAI) of the University of Cordoba, using an ultrahigh vacuum (UHV) multipurpose surface analysis system SpecsTM. The experiments were carried out at pressures <10⁻¹⁰ mbar, using a conventional X-ray source (XR-50, Specs, Mg-Kα, hv = 1253.6 eV, 1 eV = 1.603 × 10⁻¹⁹ J) in a "stop and go" mode. The samples were deposited on a sample holder using a double sided adhesive tape, and afterwards evacuated overnight under vacuum (<10⁻⁶ mbar). Spectra were collected at room temperature (pass energy: 25 and 10 eV, step size: 1 and 0.1 eV) with a Phoibos 150-MCD energy detector. The deconvolutions of the obtained curves and element quantification were carried out using XPS CASA program.

Preparation of the electrodes

Prior to coating, 10x10 mm ITO glasses were washed following a standard procedure. Firstly, the glasses were washed with

distilled water and soap. Sequentially, the electrodes were washed in an US bath with deionized water, ethanol and acetone. Ag/Ag₂S/ITO electrodes were prepared by dispersing 1 mg of each different sample into 1 ml of ethanol and by drop casting the mixture (90 μ L) over ITO surfaces. The geometric area of the electrode and the electrochemical active surface area (ECSA) were 0.80 cm² and 2 cm² respectively. Electrochemical active surface area was determined by measuring the non-Faradaic capacitive current with double-layer charging at a potential of 0.2 V, where non electrocatalytic contributions were observed.²⁶

Electrochemical measurement

Linear-sweep voltammetry measurements were performed in a three-electrode electrochemical cell Potentiostat/Galvanostat Autolab (Solartron1286). 50 mL of a 0.5 M aqueous solution of H₂SO₄ was employed as electrolyte. Ag/AgCl was used as the reference electrode; a Pt substrate was used as counter electrode and the different Ag/Ag₂S/ITO electrodes as working electrodes. It should be point out that the area of the Pt substrate was at least ten times higher than the geometrical WE areas with the objective to avoid the deposition of Pt nanodots on the Ag/Ag₂S carbon hybrid structures through the formation of large energy barrier.²⁷ All electrochemical experiments were performed applying a potential range from 0.2 V to -0.64 V vs Ag/AgCl at a scan rate of 2 mV/s.

Results and discussion

Synthesis of Ag/Ag₂S

The synthetic protocol for the production of Ag/Ag₂S carbon hybrid composites allowed the exploitation of wasted pig bristles as a non-toxic and renewable source of sulphur and carbon as opposed to toxic and hazardous thiols, hydrogen and sodium sulphides^{28,29, 30} as shown in Fig.1. The synthetic procedure involved two different reaction pathways. On one hand, silver ions were reduced to zerovalent silver. On the other hand, silver ions reacted with sulphur (released from pig bristles) in order to form Ag₂S. For the reduction of silver ions, we resorted to the oxidation of ethylene glycol. This redox reaction is in fact widely known and has been proved to be a highly efficient procedure for the reduction of silver.³¹ As shown in the upper arrow in Fig.1, the proposed reaction mechanism involved the reduction of Ag (I) to Ag (0) and the oxidation of ethylene glycol to glycolaldehyde (2-hydroxyacetaldehyde). Additional details about the reaction mechanism and GC-MS analysis can be found in a precedent work where ethylene glycol was used to reduce Ni²⁺ to metallic Nickel in a similar microwave-assisted approach.¹⁷ At the same time, silver ions underwent a competitive reaction for the formation of silver sulphide. This reaction involved the rapid degradation of pig bristles via microwave heating and the release of sulphur. Pig bristles are in fact sulphur-rich derived from keratin-containing aminoacids (e.g. methionine,

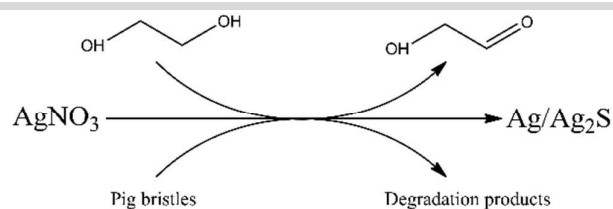


Fig. 1 Schematic illustration of the synthesis of Ag/Ag₂S.

cysteine and cysteic acid).³⁰ The total amount of sulphur in pig bristles has been previously quantified to be ca. 5% wt. in average.^{20, 31} The rapid microwave heating and the quick increase of pressure in the reaction tube favoured the fast decomposition of the aminoacids and the release of sulphur. Sequentially, silver sulphide was formed due to the reaction between Ag(I) and S₂. In this step, particles self-aggregated to minimize the surface energy, binding together with pig bristles residual carbon, as shown in SEM images and as confirmed by XPS analysis.

As summarized in Table 1, three different samples were prepared, using the same amount of pig bristles, and varying silver nitrate concentration. The hybrid materials were denoted 1.4Ag/Ag₂S, 0.5Ag/Ag₂S and 0.2Ag/Ag₂S, indicating the wt. ratio between AgNO₃ and pig bristle in the starting mixture. The weight ratio limit of 1.4 between AgNO₃ and pig bristles was determined by a practical reason. In fact, all the samples produced with increased amounts of silver nitrate were found to be considerably inhomogeneous, therefore useless for HER reactions.

Table 1 Pig bristles and silver nitrate used for the three different samples

Sample	Pig bristles / g	AgNO ₃ / g	AgNO ₃ / pig bristles
0.2Ag/Ag ₂ S	1.5	0.34	0.2
0.5Ag/Ag ₂ S	1.5	0.75	0.5
1.4Ag/Ag ₂ S	1.5	2.04	1.4

In order to determine the influence of microwave heating in the formation of Ag/Ag₂S, different trials using conventional heating were carried out in open vessel for safety issues.³² In fact, due to possible degradation of ethylene glycol after long heating times, the utilization of an autoclave was avoided. In all experiments, the formation of pure silver was completed before the degradation of pig bristles took place, resulting in a visibly heterogeneous precipitate, not suitable for an electrochemical cell.

Materials characterization

The morphology of Ag/Ag₂S carbon hybrid structures was investigated by SEM and EDX analyses. Fig.2 shows SEM images for the three samples. All samples exhibited a coral-like homogeneous morphology where carbon derived from pig bristles is aggregated with Ag/Ag₂S. Fig.3 shows cross-sectional images of SEM for 1.4Ag/Ag₂S.

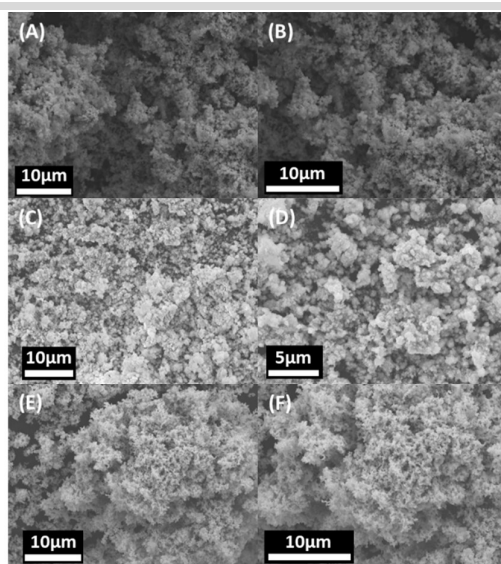


Fig. 2 SEM images of the three different Ag/Ag₂S carbon heterostructures. (A) and (B) 1.4Ag/Ag₂S; (C) and (D) 0.5Ag/Ag₂S; (E) and (F) 0.2Ag/Ag₂S.

Remarkably, silver, sulphur and carbon were found to be nicely distributed in the material, confirming the homogeneous conditions of the synthesis (please see Fig.S.1 for 0.5Ag/Ag₂S and 0.2Ag/Ag₂S mapping).

EDX-mapping micrographs detected the presence of carbon, sulphur and silver. The atomic percentage of S, Ag and C of the three different samples are shown in Table 2. Except oxygen, found in the atomic percentage of ~ 8% in all samples, and most likely absorbed as CO₂, no other elements were detected in EDX analysis, indicating the high purity of the samples.

The phase purity and crystallinity of synthesized Ag/Ag₂S carbon hybrid composites were subsequently investigated by XRD analysis. As shown in Fig.4, XRD patterns for all different samples show the presence of both Ag₂S and Ag crystals. All diffraction peaks nicely match with the lattice planes of Ag₂S along with cubic Ag crystals. Most intense diffraction peaks of sample 1.4Ag/Ag₂S could be observed at 2θ values of 37.65°, 43.95°, 64.04° and 77.15°, correspondingly indexed to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of silver with cubic structure (JCPDS 01-087-0597).³³ Peaks of the same sample at 2θ values of 28.49°, 31.07°, 33.14°, 34.25°, 36.19°, 40.31°, 52.87° and 63.85° could be indexed to (0 2 1), (-3 1 1), (1 2 1), (2 2 0), (0 2 2), (-1 3 0), (0 0 4) and (-6 0 1) planes of silver sulphide (JCPDS 00-009-0422).³⁴ No other impurity peaks detected through XRD also suggested high purity of the materials (for a complete list of the peaks and the assigned planes of all the samples, please see Table S.1).

Brunauer–Emmett–Teller (BET) physisorption was carried out in order to determine the specific surface area of the materials by nitrogen adsorption–desorption measurements. BET surface areas were found to be ~20 m²/g for all samples, with isotherms clearly pointing to the formation of non-porous

Table 2 EDX data of the three different samples

Sample	S / Atomic %	Ag / Atomic %	C / Atomic %
0.2Ag/Ag ₂ S	28.7	33.8	29.4
0.5Ag/Ag ₂ S	12.9	40.2	37.4
1.4Ag/Ag ₂ S	6.4	53.6	32.1

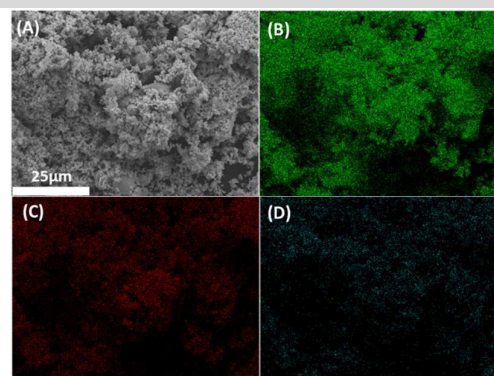


Fig.3 SEM images with mapping analysis of (a) 1.4Ag/Ag₂S carbon hybrid structure. (b) Silver; (c) Carbon; (d) Sulphur.

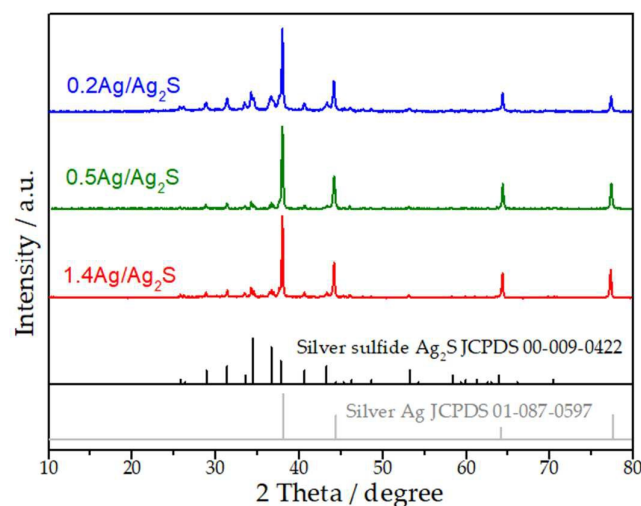


Fig.4 XRD pattern of Ag/Ag₂S hybrid materials.

materials, confirming SEM analysis (please see Fig.S.2 for the isotherm of sample 1.4Ag/Ag₂S).

In order to obtain additional information of the surface for the composite samples, XPS analysis of C 1s, Ag 3d and NNM as well as S 2p were carried out. C 1s shows no difference in C species through the series, with a reference peak at the same position (please see Fig.5 (A) for the analysis of C 1s) used for calibration ca. 284.6 eV (C-C). Ag 3d_{5/2} and Ag 3d_{3/2} contributions were analysed considering both Ag(0) and Ag(I), as presented in Fig.5(B) and Table 3. Literature shows certain ambiguity over the binding energy value of Ag(0) and Ag(I) ions due to the very similar peaks position detected. In fact, several references have been reported Ag 3d_{5/2} in the range of 367.9–368.4 eV and 367.6–368.5 eV for Ag(0) and Ag(I),

respectively.³⁵⁻³⁹ The clear shift through the series and the analysis of Ag MNN level allowed the following assignment. The contribution at *ca.* 367.9 (Ag 3d_{5/2}) and 373.8 (Ag 3d_{3/2}) eV may be assigned to Ag(0) species,^{40, 41} while peaks at *ca.* 368.6 and 374.7 eV may be attributed to those of Ag 3d_{5/2} and Ag 3d_{3/2} of Ag(I) ions in Ag₂S.^{35, 40} These hypotheses are also confirmed by the S 2p XPS region (Fig.5(C)). The values of *ca.* 161.5 eV and 163.0 eV are in agreement with S 2p_{3/2} and S 2p_{1/2} for Ag₂S of previous reports (Table 3).^{35, 40} As it can be seen in Table 3 and Fig.5 (B and C), the signal enhancement for sulphur can be unambiguously associated with a higher S concentration and consequently with a higher concentration of Ag₂S. In addition, quantitative analysis confirmed the dominant presence of metallic silver for 1.4Ag/Ag₂S while a higher superficial concentration of Ag₂S was obtained in samples 0.5Ag/Ag₂S and 0.2Ag/Ag₂S, in good agreement with

XRD results (Table 3). The ratio between the two Ag species varies along the series. Interestingly, Ag(0)/Ag(I) showed a roughly linear trend suggesting the possibility to control and fine-tune Ag(0)/Ag(I) ratios in the novel synthetic protocol (Fig.5(D) and (E)). Finally, as it is represented in Fig.5(E), the ratio Ag/S as function of the pig bristle (pb)/Ag precursor ratio (wt.) showed similar values in comparison to the obtained by EDX (Table 1) while, as expected, Ag(I)/S ratio presented a relative constant value (*ca.* 2) for all samples (see Table 3 for details).

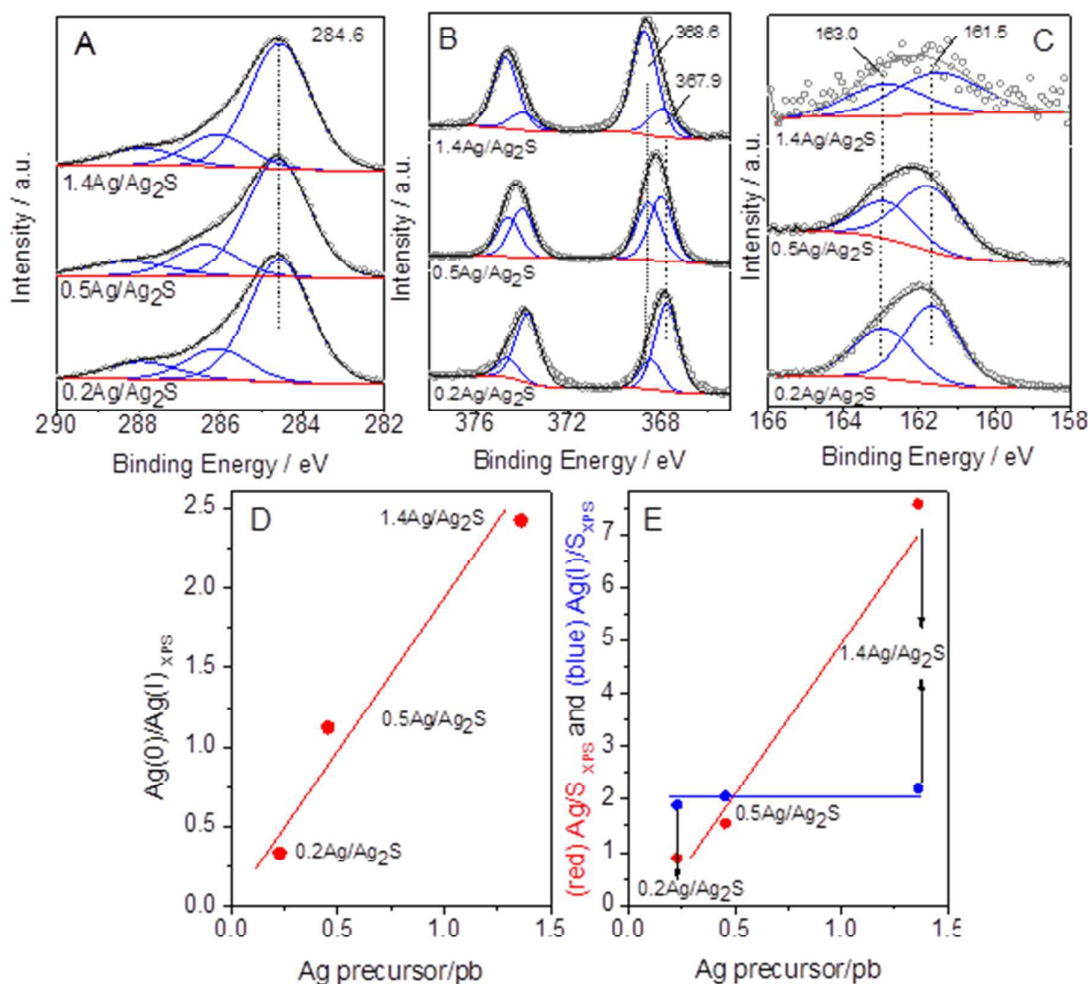


Fig. 5 (A) C 1s, (B) Ag 3d, (C) S 2p of the xAg/Ag₂S samples; (D-E) XPS ratios obtained by XPS vs. pig bristle (pb)/Ag precursor ratio (wt. ratio).

Table 3 XPS Data for Ag/Ag₂S samples

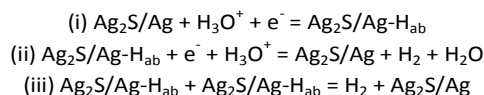
Sample	Position / eV						
	Ag3d _{5/2}		S 2p _{2/3}	C 1s	Ag(0)/Ag(I)	Ag/S	Ag(I)/S
	Ag(0)	Ag(I)					
0.2Ag/Ag ₂ S	367.9	368.5	161.5	284.6	0.3	0.9	1.9
0.5Ag/Ag ₂ S	367.9	368.6	161.6	284.6	1.0	1.5	2.1
1.4Ag/Ag ₂ S	367.9	368.7	161.5	284.6	2.4	7.6	2.2

Electrochemical hydrogen evolution

Ag/Ag₂S/ITO electrodes were subsequently prepared and tested for electrochemical activity in the hydrogen evolution reaction (HER) using linear sweep voltammetry (LSV) experiments in 0.5 M of H₂SO₄ at a scan rate of 2 mV/s. Potentials were measured vs Ag/AgCl electrode and reported against the reversible hydrogen electrode (RHE). Fig.6(A) shows the electrocatalytic performances towards hydrogen evolution in acid media of 0.2Ag/Ag₂S, 0.5Ag/Ag₂S and 1.4Ag/Ag₂S composites respectively. Notably, 0.5Ag/Ag₂S and 1.4Ag/Ag₂S hybrid materials can generate a current density of ca. 37 mA/cm² and ca. 110 mA/cm² at -0.6 V respectively, while 0.2Ag/Ag₂S sample shows a negligible electrocatalytic response. It should be pointed out that the current densities of the Fig.6(A) and (B) were calculated from the geometric area of the electrodes. Additional plots of the current density normalized to the electrochemical surface area of the catalyst are provided in the ESI (Fig.S.3). Importantly, at a scan rate of 2mV/s, sample 0.5Ag/Ag₂S required an overpotential of 370 mV to produce a current density of 10 mA/cm² whereas sample 1.4 Ag/Ag₂S could successfully generate 10 mA/cm² at a -190 mV potential. This value surpassed the electrocatalytic activity of the Ag₂S/CuS which exhibited, at the best of our knowledge, among the hybrid catalysts constructed from Ag, the best activity with demand of overpotential to deliver 10 mA/cm² (193 mV).²⁵ Therefore, aforementioned findings constitute, to date, one of the lowest applied potentials reported in literature for these type of materials.^{13, 14, 25, 42} Interestingly, the increase of the current density followed a pronounce linear trend with respect to the Ag(0)/Ag(I) ratio (Fig.6(D)), suggesting that the content of Ag(0) at the heterostructure surfaces controls the electrocatalytic yields of the hydrogen evolution process. Recently, the improvement of the electrocatalytic performances of Ag/Ag₂S heterostructures towards hydrogen production has been ascribed to differences in microstructures. Indeed, these differences can in turn modulate the number of hydrogen anions adsorbed at the composites surfaces and therefore the current densities involved in the electrocatalytic processes.¹⁴ All synthesized samples have a similar microstructure and surface area. Considering that the anchorage of the hydrogen anions on the metallic silver surfaces is the first step of the HER process (see mechanism below), is conceivable to think that increasing silver contents, therefore of metallic silver surface, provide

more catalytic active sites, effectively improving hydrogen production.

The evaluation of the Tafel slopes is a useful tool to get insights on mechanistic pathways for HER processes. Fig.6(C) depicts the Tafel slopes for 0.5Ag/Ag₂S and 1.4Ag/Ag₂S composites. The Tafel slope obtained for 1.4Ag/Ag₂S (150mV/dec) exhibits a comparatively lower value to that obtained for 0.5Ag/Ag₂S (240 mV/dec), indicating a remarkable enhancement in the kinetics of the catalytic process for 1.4Ag/Ag₂S as electrocatalyst. These results strongly confirm the superior catalytic performance of 1.4Ag/Ag₂S towards HER. The proposed mechanism for HER processes in acidic medium consist of two steps (i) the Volmer step, (ii) the desorption step or Heyrovsky process and (iii) the recombination step or Tafel step.⁴³



It is worth to point out that the rate-determining step of HER for 1.4Ag/Ag₂S is the Volmer step due to its Tafel slope being closer to 120 mV/dec rather than 40mV/dec.

Importantly, since the rate-limiting step of 1.4Ag/Ag₂S for HER is the anchorage of hydrogen anions onto the catalytically active metallic Ag sites, larger amounts of metallic Ag in the composites surfaces consequently improve the electrocatalytic efficiency in terms of hydrogen production. In addition, the high content of carbon in all the samples most likely improved the catalytic activity. Indeed, carbon itself is inert carbon itself is inert for hydrogen evolution reaction. However, as reported by Zhou et al. and by Zhang et al., the catalytic activity of carbon can be improved by the introduction of transition metal nanoparticles in order to modify the electronic properties of carbon and create new active sites for HER.^{44, 45} Considering that, as reported in EDX analysis (Please see Table 2) all the materials showed a similar content of carbon (~30 atomic %), the effect of carbon was comparable in all the HER reactions.

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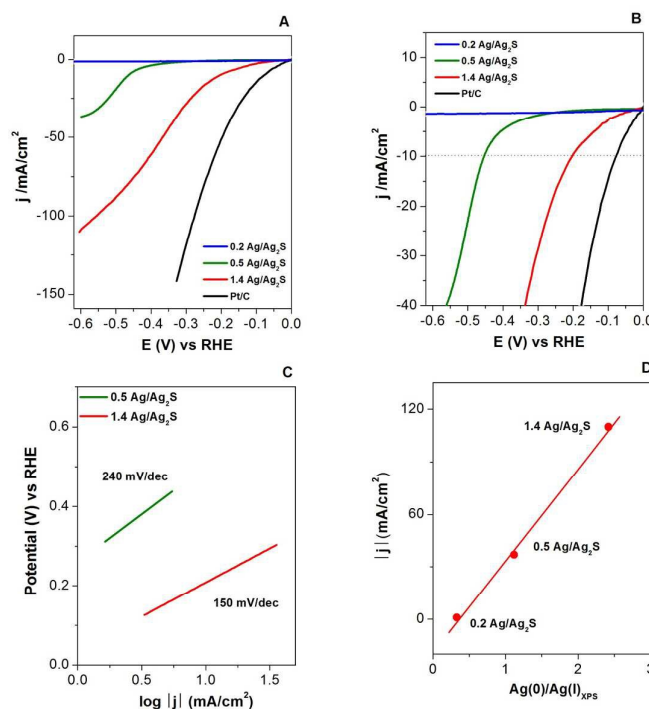


Fig.6 (A,B) LSV curves for 0.2Ag/Ag₂S, 0.5Ag/Ag₂S, 1.4Ag/Ag₂S and commercial Pt/C with a scan rate of 2 mV/s for HER; (C) Tafel plots for 0.5Ag/Ag₂S and 1.4Ag/Ag₂S carbon-hybrid composites respectively; (D) Current densities vs Ag(0)/Ag(I) ratio determined by XPS.

Conclusions

A sequence of Ag/Ag₂S carbon hybrid composites were synthesized using pig bristles as source of sulphur and silver nitrate under microwave irradiation. The presence of both phases, metallic silver and silver sulphide, was demonstrated by XRD analysis, which clearly showed diffraction peaks relative to Ag and Ag₂S. A ratio between the concentration on the surface of the two different oxidation states of Ag (i.e. Ag(0) and Ag(I)) could be found from XPS. This Ag(0)/Ag(I) ratio shows a linear dependence as function of the pig bristle/silver precursor. Materials were tested in the electrocatalytic hydrogen evolution reaction, with the most active sample (1.4 Ag/Ag₂S), allowing the production of 10 mA/cm² operating at -0.190 V potential. Such value is one of the lowest applied potential reported in literature for Ag/Ag₂S hybrid compounds in HER. Importantly, the synthetic protocol is simple, sustainable and allows the valorisation of a waste feedstock (pig bristle) for the design of highly active electrocatalytic materials. The catalytic activity of the materials was found to linearly depend on the ratio between Ag(0) and Ag(I) which

can be easily fine-tuned in the microwave-assisted methodology, pointing to a potentially tunable synthetic protocol depending on target applications (i.e. electrosynthesis of biomass-derived molecules) that will be additionally reported in due course.

Conflicts of interest

There are no conflicts to declare.

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