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Additional Information

Innovative Preparation of MoS₂-Graphene Heterostructures Based on Alginate Containing (NH₄)₂MoS₄ and their Photocatalytic Activity for H₂ Generation

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Abstract

Films and particles of MoS₂ on graphene (G) showing synergy for photocatalytic H₂ evolution due to the strong interaction between the two layered components have been obtained by pyrolysis at 900 °C under argon flow of ammonium alginate, films or powders, containing variable proportions of (NH₄)₂MoS₄. X-ray diffraction shows that under these conditions (NH₄)₂MoS₄ decomposes to MoS₂, while simultaneously alginate forms few layers G or graphitic carbon residues. Sonication of MoS₂-G powders in water produces exfoliation of the material leading to few-layers platelets of MoS₂-G heterostructures. MoS₂ is considered as an alternative of noble metals for H₂ evolution in dye-sensitized photocatalytic systems. In the present case, MoS₂-G heterostructures exhibit more than double photocatalytic activity for H₂ generation than pristine MoS₂ particles.

1. Introduction

Molybdenum disulfide (MoS₂) is a layered material constituted by individual MoS₂ layers in which Mo⁺⁴ cations are sandwiched between two layers of hexagonally packed S⁻² anions.(1)The interlayer forces between MoS₂ layers are mostly van der Waals interactions, being possible to exfoliate bulk MoS₂ powders to obtain single layer MoS₂ sheets.(2) This exfoliation has been reported that can be accomplished either mechanically, using adhesive tape, or by sonication of bulk MoS₂ powder in non-volatile organic solvents such as N-methyl- or N-cyclohexylpyrrolidone.(3-5) Other exfoliation methods include chemical treatments such as intercalation of Li atoms followed by addition of water and sonication.(6)

Exfoliated MoS₂ exhibits unique properties, such as the appearance of photoluminescence with apparent quantum yield increasing as the number of layers decreases and the increase in the band gap energy due to 2D quantum confinement.(7-9)

Single layer or few layers MoS₂ find application in microelectronics and photonics as well as can be used as electrocatalysts for the H₂ evolution reaction in replacement of costly Pt electrodes.(10-12) Exfoliated MoS₂ has also been applied in photocatalysis as co-catalyst in H₂ generation.(13, 14) While it has been found that single or few layers MoS₂ do not exhibit itself photocatalytic activity for H₂ generation in the absence of a semiconductor or photosensitizer, MoS₂ can be an efficient co-catalyst to enhance H₂ generation replacing expensive noble metals such as Pt, Pd or Rh.(13, 14)

Due to the 2D morphology there is an increasing interest in the synthesis of heterostructures of single layer MoS₂ and graphene (G).(15-17) MoS₂-G heterostructures can exhibit synergy and enhanced properties due to the strong interaction between these two components. These hybrid layered MoS₂-G heterostructures can find application as H₂ evolution reaction electrocatalysts and also as photocatalysts.(18-21) It has been proposed that the synergy observed for hybrid MoS₂-G materials in these processes derives from the electron migration from G to MoS₂. In this hybrid system, due to its large electron conductivity, G favors charge separation, while MoS₂, due to its ability to act as cocatalyst, increases the rate of H₂ evolution. The photocatalytic system is generally completed by a soluble dye, acting as light harvester, and a sacrificial electron donor to quench the generated holes. As light harvester, Eosin Y and metal polypyridine complexes have been widely used.(22, 23) However, the main problem is the preparation of MoS₂-G heterostructures. The most widely used procedure consists in mixing pre-synthesized graphene oxide (GO) with molybdate salts that are hydrotreated in autoclave in the presence of a sulfur containing compound, typically thiourea.(20, 23) In this treatment, formation of MoS₂ from sulfuration of molybdate should take place in some degree concomitantly with the reduction of GO and assembly of the

heterostructure. In the present manuscript we report an innovative procedure for the synthesis of MoS₂-G heterostructure either as powder or thin films on arbitrary substrates, in a single step that constitutes a notable example of biomass wastes valorisation.

2. Results and Discussion

The process is based on the use and properties of a natural biopolymer, namely, alginate that acts as G precursor and also as matrix to absorb molybdate precursor. Recent precedents in the literature have shown that pyrolysis of alginate and other natural polysaccharides, such as chitosan, at temperatures above 800 °C can form G films on arbitrary substrates or can generate graphitic carbon residues that subsequently can be easily and efficiently exfoliated in water or other volatile organic solvents.(24-26) Also, we and others have used alginate containing transition metals to form heterostructures based on G and metal nanoparticles or metal oxides, metal carbides or metal phosphides.(27, 28) The process followed in the present study is shown in **Fig1**.

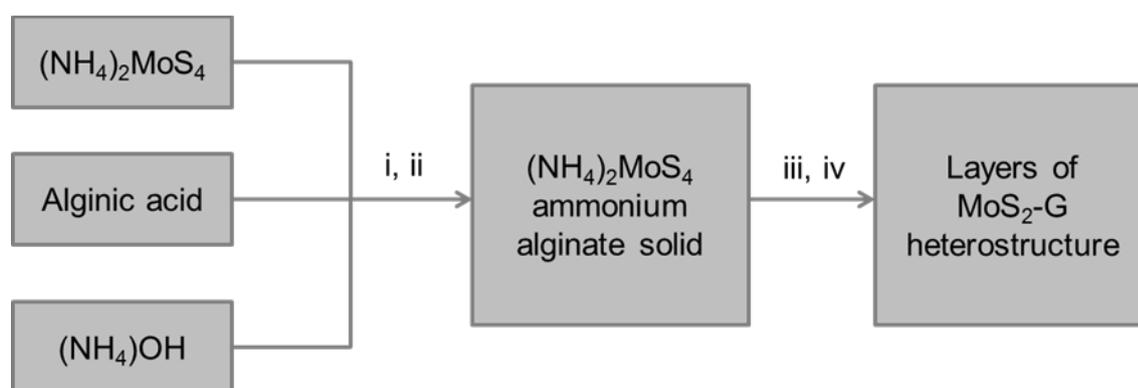


Fig.1. Steps followed in the present work for the preparation of few layers MoS₂-G heterostructure: i) dissolution in water, ii) cast on a substrate or water removal, iii) pyrolysis under Ar flow at 900 °C, and iv) sonication of powder residues in water to obtain suspensions.

Basically, the procedure consists in the intimate mixing in aqueous phase of an ammonium alginate solution with tetrathiomolybdate. After mixing, water is removed under reduced pressure and the resulting solid is submitted to pyrolysis under inert atmosphere at 900 °C. Alternatively, the aqueous solution can be used to spin coat a substrate such as quartz and the resulting film can be pyrolyzed under the same conditions (see **fig.2**).

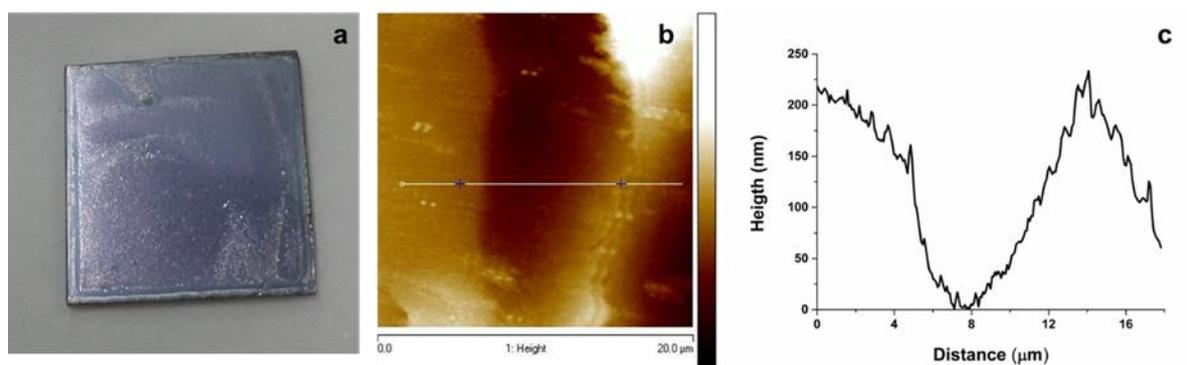
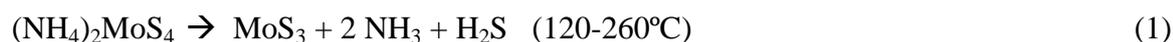


Fig. 2. Nanometric film of MoS₂-G material: a) photograph of the MoS₂-G film onto a quartz substrate, b) Atomic force microscopy (AFM) image of a cut of the film (the dark part in the middle shows the quartz substrate) and c) section profile of image b).

It has been reported in the literature that at temperatures between 120 and 260 °C the ammonium tetrathiomolybdate decomposes to MoS₃, ammonia and sulphydric acid (Equation 1).(29) At temperatures above 800 °C, MoS₃ also decomposes to MoS₂ and elemental sulphur that sublimates at these temperatures (Equation 2).



We anticipated that Equations 1 and 2 would also take place in the case of (NH₄)₂MoS₄ embedded in alginic acid during pyrolysis. During pyrolysis, alginic acid will form G, as it

has been reported,(30, 31) and the two phases MoS₂ and G would segregate spontaneously, becoming in intimate contact.

After pyrolysis, the resulting material was characterized by chemical analysis, X-ray diffraction (XRD), Raman spectroscopy and electron microscopy. A blank control using (NH₄)₂MoS₄ pyrolysed at 900 °C followed by combustion chemical analysis reveals the absence of N element, in accordance with Equation 1. In addition, this material has a sulphur content of 40.3 % that agrees with a MoS₂ stoichiometry. For the powdered MoS₂-G materials prepared in this study, C and S were observed. A series of materials in which the amount of (NH₄)₂MoS₄ was varied between 0-100 % was prepared. Table 1 summarizes the series of MoS₂-G heterostructures prepared as powder and the corresponding chemical analysis. XRD was in accordance with the formation of MoS₂ upon the pyrolysis of (NH₄)₂MoS₄ embedded in alginate. Fig. 2a presents the recorded XRD for MoS₂-G10 showing the indexation of the peaks in agreement with the success in the formation of MoS₂ (JCPDS 77-1716).

Table 1. Combustion chemical analysis after pyrolysis of (NH₄)₂MoS₄ (MoS₂), alginic acid (G), and mixtures of (NH₄)₂MoS₄ and ammonium alginate (MoS₂-Gx). The percentage of G in the heterostructure (x) is calculated from their carbon content.

Material	C	S	N	H
MoS ₂	0 ^{a)}	40.3	0	0
MoS ₂ -G1	1.1	40.1	0.1	0.1
MoS ₂ -G4	3.9	38.2	0.2	0.1
MoS ₂ -G10	8.7	33.9	0.7	0.1
MoS ₂ -G22	20	28.7	1.2	0.2
MoS ₂ -G35	31.9	22.7	1.4	0.4
G	88	0	0.15	0.4

^{a)}(all values in %wt)

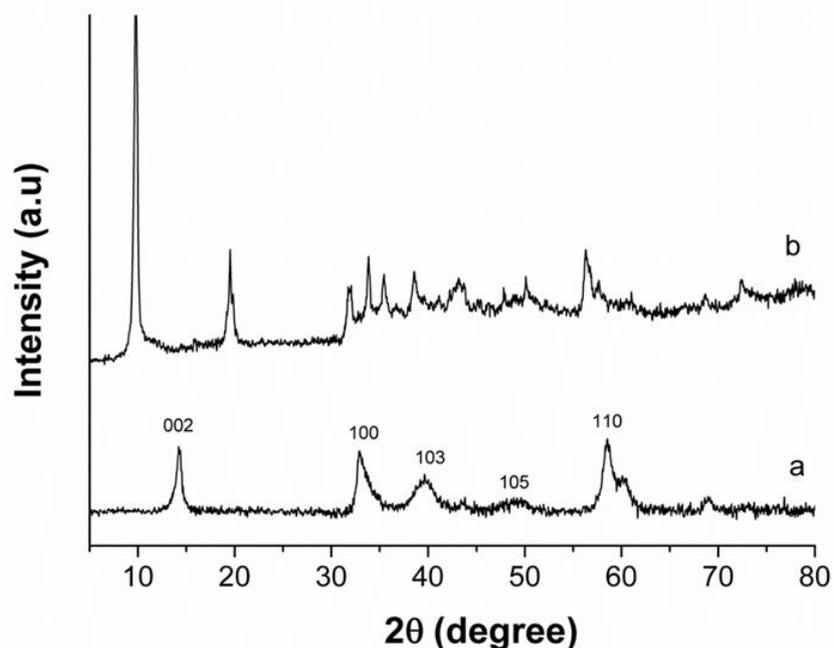


Fig. 3. XRD pattern for a) MoS₂-G10 and b) the material prepared under the same conditions but using sodium alginate instead of ammonium alginate that corresponds to NaMoS₂ according to Sergent and Prigent.(32) Peaks in plot a) have been indexed for convenience.

It is worth commenting at this stage that the use of alternative precursors for G or MoS₂ can lead to a different result or to the formation of MoS₂ accompanied by other molybdenum compounds. Specifically, the use of sodium alginate in the process shown in Scheme 1 results in the formation of NaMoS₂ as indicated by the observation in XRD of the peaks corresponding to this solid (**Fig. 3b**).⁽³²⁾ Also, the use as MoS₂ precursor of ammonium molybdate in combination with a sulfur containing compound (Na₂SO₄) results again in the preferential formation of NaMoS₂. For this reason the process indicated in Scheme 1 was among the various possibilities the one adequate for the preparation of the MoS₂-G heterostructure.

The presence of G after pyrolysis of alginate containing (NH₄)₂MoS₄ was established by Raman spectroscopy. The expected 2D, G and D peaks of graphitic materials appearing at 2892, 1596 and 1358 cm⁻¹, respectively, were observed. It has been reported that the presence

of the D peak is associated to a residual percentage of oxygenated functional groups in G. In addition to these intense bands, Raman spectroscopy also shows two additional peaks at 403 and 377 cm^{-1} corresponding to the A_{1g} and E_{2g} vibration modes reported for MoS_2 .(33) As an example, **Fig. 4** shows the Raman spectra for MoS_2 -G10 material.

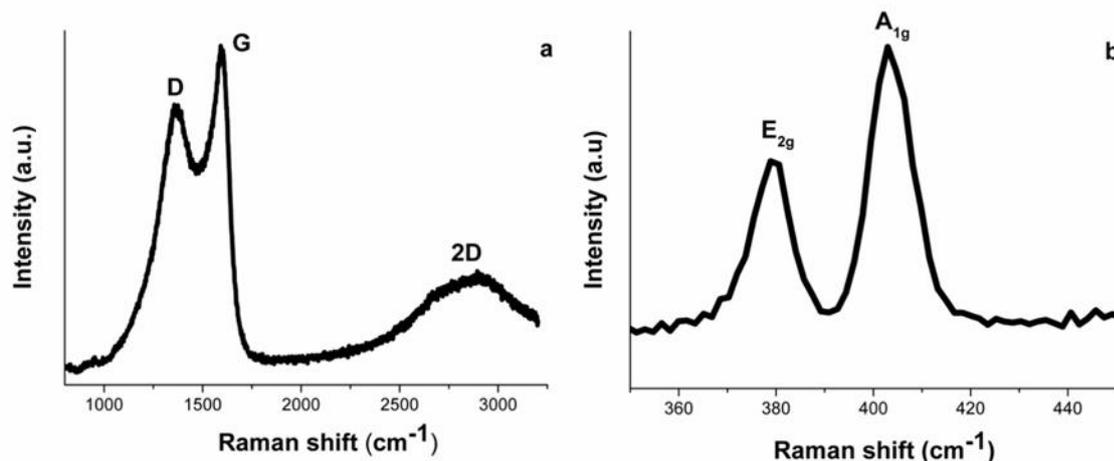


Fig. 4. Raman spectra of MoS_2 -G10 material showing the expected bands for the a) G component and b) MoS_2 .

The material after pyrolysis of ammonium alginate containing $(\text{NH}_4)_2\text{MoS}_4$ was also characterized by electron microscopy. Field emission scanning electron microscopy (FESEM) images show particles of 7 μm average size corresponding to the graphitic carbon residue. On top of these particles the presence of smaller MoS_2 particles was observed, either in bright or dark field (**Fig. 5a and 5b**, respectively). Energy dispersive X-Ray spectroscopy (EDS) analysis shows that these carbon residues contain S and Mo in the expected 2:1 atomic ratio.

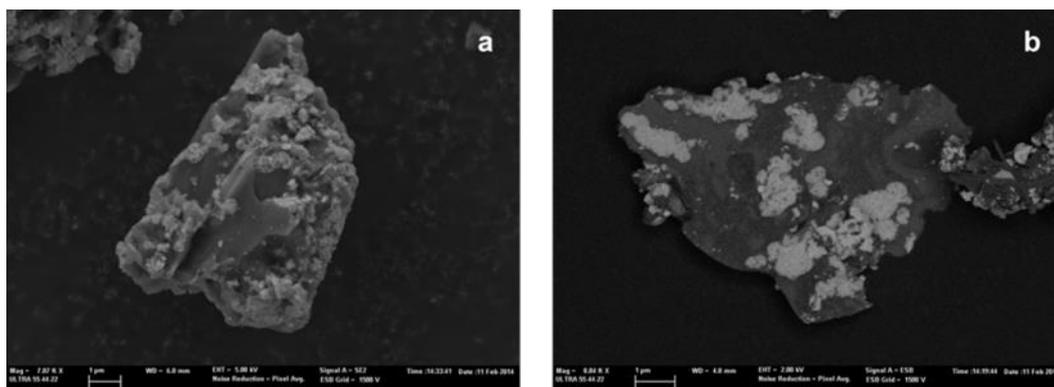


Fig. 5. FESEM images of MoS₂-G10 material before exfoliation in a) bright and b) dark field showing the graphitic and MoS₂ components of the heterostructure.

Fig. 6 shows selected high resolution transmission electron microscopy (HRTEM) views of the MoS₂-G10 heterostructure after exfoliation in water. The morphology of the MoS₂-G heterostructure after exfoliation shows the characteristic images of materials constituted by sheets (**Fig. 6a**). The interlayer distance determined by HRTEM in some parts was 0.62 nm corresponding to the expected value for 002 interlayer distance in MoS₂ (**Fig. 6c and 6d**). The layered morphology of MoS₂-G10 material exfoliated in water was also observed by atomic force microscopy (AFM) (**Fig. 7**). This AFM image corresponds to a layered material (G) of around 0.3 μm in length with some layered particles (MoS₂) on top, similar to the images seen by HRTEM (**Fig. 6a**).

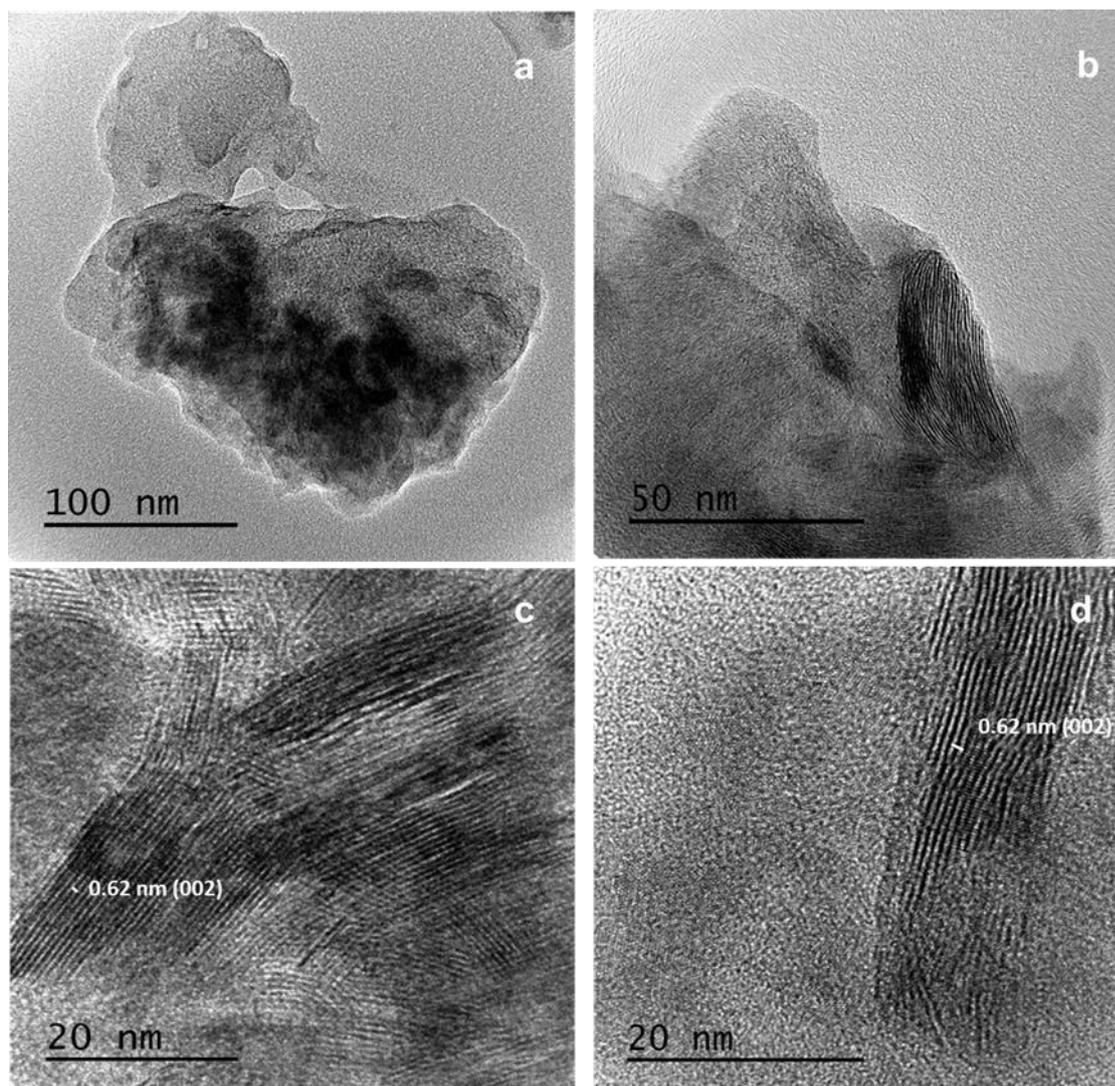


Fig. 6. HRTEM images of MoS₂-G10 heterostructure exfoliated in water: a) G layers on top of which a heavier material (MoS₂) is observed, b) magnification of image a) showing the carbonaceous and MoS₂ components of the heterostructure, c) and d) magnification of the sample showing the 002 interplanar distance of MoS₂.

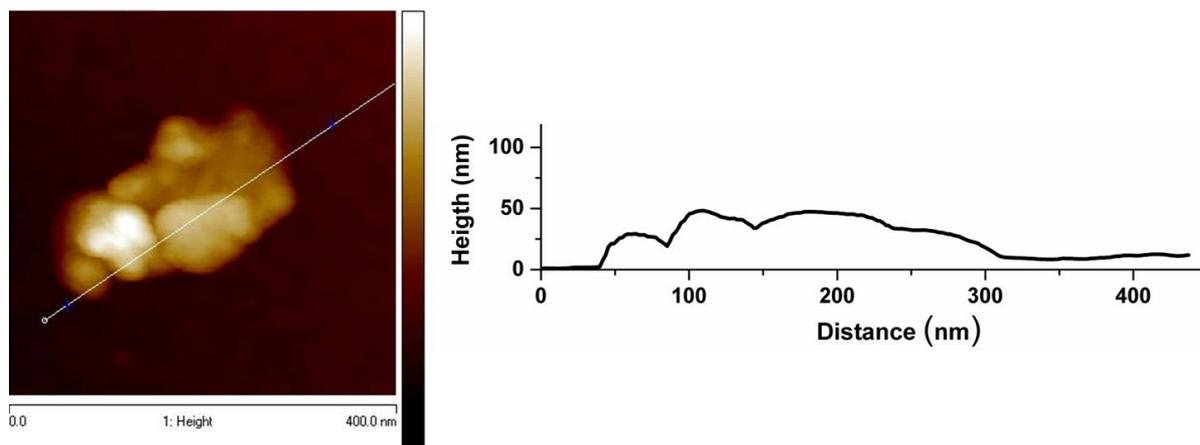


Fig. 7. AFM image of a particle of exfoliated MoS₂-G10 material (left) and its section profile (right).

Exfoliation of the MoS₂-G heterostructure was also confirmed by the stability of the suspension (no precipitation occurred for several weeks) and also by UV-vis spectroscopy, where the four characteristic absorption peaks located at 600-700 nm and 400-450 nm regions reported for few layers MoS₂ dispersions were observed (Fig. 8).(34)

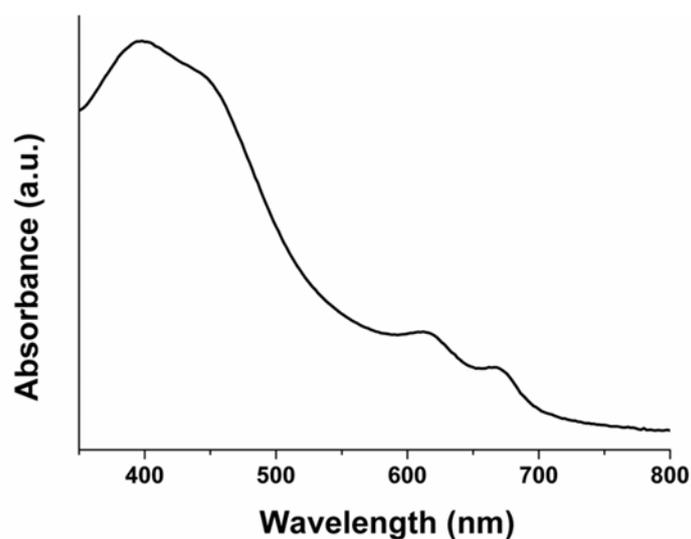


Fig. 8. UV-vis spectra of MoS₂-G10 material exfoliated in water.

Photocatalytic experiments for H₂ generation were carried out using a xenon lamp whose light was filtered with a 390 nm cut-off filter. The aqueous solution contained 15 mM Eosin Y dye (EY) as photosensitizer and 15 % triethanolamine (TEOA) as electron donor. The results obtained on the H₂ evolution rate are presented in **Fig. 9**.

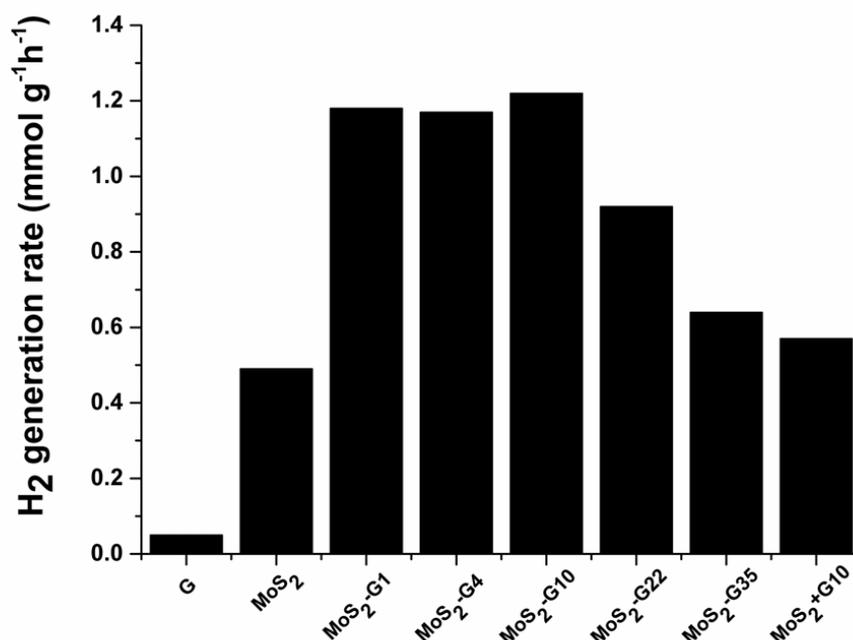


Fig. 9. Photocatalytic H₂ generation rate for G, MoS₂ and MoS₂-G heterostructures.

MoS₂+G10 corresponds to the physical mixture of MoS₂ and G, the latter in 10 % loading.

As it can be seen in this figure, the rate of H₂ evolution is similar for experiments carried out using MoS₂-G heterostructures with G weight percentage between 1-10%. In the absence of G the photocatalytic activity is 2.4 times lower than the maximum H₂ evolution rate. On the other hand, G weight percentages higher than 10 % also reduce the H₂ evolution rate with respect to the optimal value. Particularly notable is the photocatalytic activity of G in the absence of MoS₂ that was more than one order of magnitude lower than the sample containing the optimal proportion of MoS₂. The photocatalytic activity of a physical mixture constituted

by 90 % MoS₂ and 10 % of G (MoS₂+G10) was also measured. However, the activity for H₂ evolution is half than that for MoS₂-G10, which indicates that when the two components of the heterostructure are in intimate contact the system is clearly improved.

The most reasonable mechanism for the photocatalytic H₂ generation from water containing TEOA as electron donor is presented in **Fig. 10**.

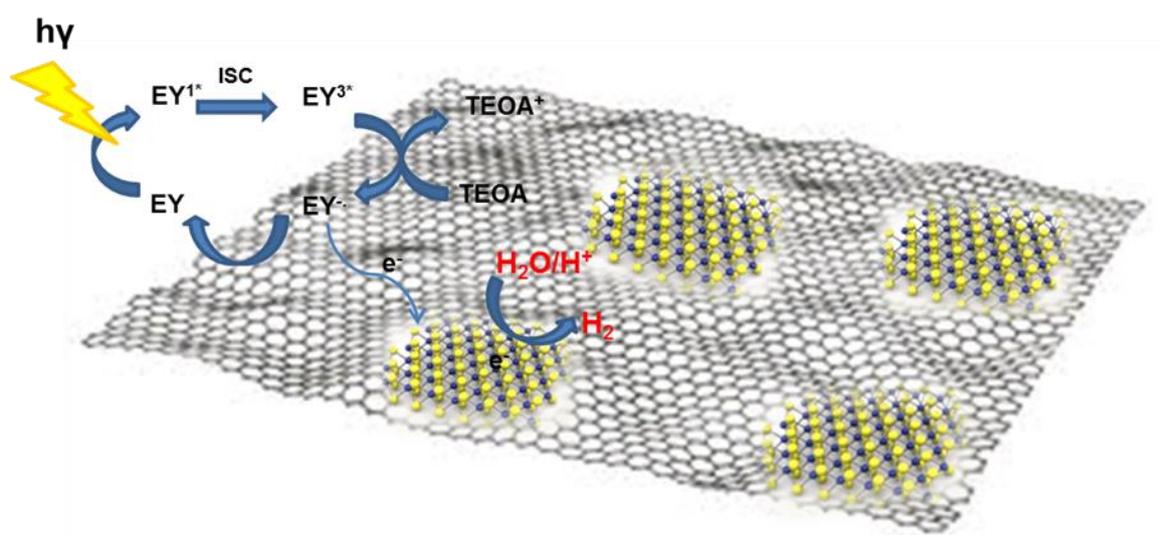


Figure 10. Photocatalytic mechanism proposed for the system used in the present study.

According to this proposal EY will absorb visible light being promoted to the singlet excited state. Intersystem crossing (ISC) will generate the triplet excited state of the EY dye. This triplet excited state will be quenched by TEAO forming TEOA⁺ radical ion and EY^{-•}. The radical anion of the dye will transfer one electron to G, regenerating the dye in the ground state. The electron in G will be highly mobile reaching MoS₂ that will be the H₂ evolution center. The important point is that as reported in the literature the combination of MoS₂ and G increases the photocatalytic activity for H₂ generation with respect to the individual components.(20)

3. Conclusion

In the present manuscript we have shown a very convenient procedure for the reliable synthesis of MoS₂-G heterostructures that can be applied either for the preparation of powders or films and only requires affordable starting materials and an oven. These hybrid materials are able to show the expected synergy between MoS₂ and G indicating the interaction between the two components in the heterostructure. Considering that alginate is a biomass waste, the present results constitute a remarkable example of biomass valorization leading to the formation of high added value materials with applications in microelectronics and photocatalysis.

4. Experimental section

4.1. Preparation of G, MoS₂ and MoS₂-G heterostructures

MoS₂-G1, MoS₂-G4, MoS₂-G10, MoS₂-G22 and MoS₂-G35 were prepared by mixing in 50 mL of milli_Q water 33.7, 67.5, 125, 250 and 500 mg of alginic acid and 0.33, 0.67, 1.25, 2.5 and 5 mL of (NH₄)OH 25% solution, respectively, with 0.35 g of (NH₄)₂MoS₄. After mixing, water is removed under reduced pressure and the resulting solid is submitted to pyrolysis under argon flow at 250 °C for 2 h and, then, at 900 °C for 2 h (5 °C min⁻¹ ramp rate). MoS₂ and G were prepared under the same pyrolysis conditions but using 100 % (NH₄)₂MoS₄ or alginic acid, respectively. After pyrolysis, the powder is grinded and exfoliated in water using a 750 W Sonics Vibracell high intensity ultrasonic liquid processor for 1.5 h. In order to prepare the films of the MoS₂-G material the aqueous solutions of (NH₄)₂MoS₄, alginic acid and (NH₄)OH are spin coated (2000 rpm for 60 s) onto a quartz substrate, dried at 80 °C and the resulting film pyrolyzed under the same conditions.

4.2. Photocatalytic H₂ production tests

The photocatalytic solution (30 mL) was composed of an aqueous solution containing 15 % of TEOA as a sacrificial electron donor, 15 mM of EY as photosensitizer and 0.2 g L⁻¹ of heterostructure as photocatalyst. It was irradiated in a cylindrical pyrex vessel (50 mL) with a Hamamatsu filtered xenon lamp ($\lambda > 390$ nm) with a focused intensity of 1.3 W m⁻². The system was purged with an argon flow for at least 30 min before irradiation to ensure the absence of oxygen in the system and it was continuously magnetically stirred and refrigerated at 20 °C during irradiation. The hydrogen evolved in the photoreactor during the irradiation was determined by gas chromatography (GS-MOL 15 meters column ID 0.55 mm TCD from J&W Scientific).

4.3. Characterization techniques

The Raman measurements (Renishaw Via Raman Microscope) were carried out at room temperature with the 514.5 nm line of an Ar ion laser as excitation source. XRD patterns were obtained in a Philips X'Pert diffractometer using the copper radiation (Cu-K α = 1.541178 Å). AFM images were made with a Multimode Nanoscope 3A equipment working in tapping mode, using mica as substrate. FESEM images were taken with an ULTRA 55 ZEISS Oxford instrument and HRTEM images with a JEM 2100F JEOL 200kV electronic microscope.

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