Sulfur-doped Graphene / Transition Metal Dichalcogenide Heterostructured Hybrids with Electrocatalytic Activity Toward the Hydrogen Evolution Reaction

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ABSTRACT. A facile route for the preparation of molybdenum disulfide (MoS$_2$) and tungsten disulfide (WS$_2$), uniformly deposited onto sulfur-doped graphene (SG), is reported. The realization of the SG/MoS$_2$ and SG/WS$_2$ heterostructured hybrids was accomplished by employing microwave irradiation for the thermal decomposition of ammonium tetrathiomolybdate and tetrathiotungstate, respectively, in the presence of SG. Two different weight ratios between the SG and the inorganic species were used, namely 3:1 and 1:1, yielding SG/MoS$_2$ (3:1), SG/MoS$_2$ (1:1), SG/WS$_2$ (3:1) and SG/WS$_2$ (1:1). The SG and all newly developed hybrid materials were characterized by ATR-IR and Raman spectroscopy, TGA and HR-TEM and EELS. The electrocatalytic activity of the SG/MoS$_2$ and SG/WS$_2$ heterostructured hybrids was examined against the hydrogen evolutions reaction (HER) and found that the presence of SG not only significantly improved the catalytic activity of MoS$_2$ and WS$_2$ but also made it comparable to the one due to commercial Pt/C. Specifically, hybrids containing higher amount of SG, namely SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1), exhibited extremely low onset overpotentials of 26 and 140 mV vs RHE, respectively. The latter result highlighted the beneficial role of SG as substrate for immobilizing MoS$_2$ and WS$_2$ and stressed out its significance for achieving optimum electrocatalytic performance toward HER. Finally, examination of the Tafel slopes as extracted from the electrocatalytic polarization curves, manifested the adsorption of hydrogen as the rate-limiting step for SG/MoS$_2$ (3:1), while for SG/WS$_2$ (3:1) the electrochemical desorption of adsorbed hydrogen atoms to generate hydrogen was revealed to be the rate-limiting step.

Introduction

Hydrogen is an environment friendly fuel for motive and stationary power generation and is expected to replace the non-renewable fossil fuels in future times. In order to satisfy the growing energy demands, ecological approaches should be employed to achieve hydrogen production, since there are no widely accessible hydrogen natural resources. In this frame, the electrochemical reduction of water provides an easy and cheap method to generate

\[ \text{H}_2 \]
hydrogen and has drawn great attention in recent years. Up to now, Pt-based electrocatalysts are most effective towards the electrochemical water splitting, however, their high cost and low natural abundance prevent their large-scale use. Hence, the increase of the catalytic activity of non Pt-based, inexpensive and abundant catalysts is an extremely important, yet challenging issue. In recent years, research has focused on non-noble electrocatalysts for the Hydrogen Evolution Reaction (HER), with transition metal dichalcogenides (TMDs) rapidly evolving as promising materials with low cost and high chemical stability.

In general, TMDs are two-dimensional layered materials composed of stackings of atomic metal layers sandwiched by chalcogen layers, in which the individual chalcogen-metal-chalcogen layers weakly interact each other. These materials are considered to be the inorganic analogues of graphene, as the weak van der Waals forces between the layers can be easily overcome when exfoliated from the bulk, leading to few or even monolayered sheets. Molybdenum and tungsten disulfide, MoS$_2$ and WS$_2$, respectively, as typical examples of TMDs, have been exfoliated from the bulk by diverse wet chemistry approaches, mainly assisted by sonication, via a top-down approach. The exfoliated TMDs exhibit dramatically different properties from the bulk material, and their novel physical and electronic properties make them suitable to energy related applications.

Recently, TMDs started to appear as effective materials for the HER, owed to their appealing electrocatalytic properties and based on the improvement of energy conversion efficiency through harvesting a higher current density at a lower overpotential. The HER activity for TMDs is directly related with exposed edges, contrasting the catalytically inert basal planes. Hence, in order to improve the electrocatalytic performance of TMDs, the density of active edges should be increased. The latter can be achieved by edge and/or defect engineering, based on unsaturated chalcogen atoms at the edges and/or by promoting the electron transport efficiency between the electrode and the electrocatalyst. Furthermore, the population of defect sites can be adjusted by adopting the synthetic bottom-up approach of TMDs coupled with the presence of an additional component playing the role of electrocatalyst substrate. Specifically, incorporating TMDs on supports with high surface area can provide more active edge sites for electrocatalysis, while by employing highly conducting supports, such as graphene, fast electron transport is guaranteed.

Graphene, attributed to its large surface area, excellent electrical conductivity and high chemical stability, has been widely employed as supporting material for electrocatalysts in general and for TMDs in particular. In the same context, introduction of heteroatoms within the sp$^2$ hybridized carbon network of graphene alters its electrical properties, resulting in enhanced electrocatalytic activity. The origin of the enhanced catalytic activity
of graphene-doped materials is attributed to the electronegativity difference between carbon and the doping element, which polarizes the adjacent carbon atoms in the graphene lattice, hence, potentially facilitating HER. For example, this was true when N-doped graphene/MoS$_2$ nanocomposites were prepared and found to exhibit high catalytic activity for HER.$^{33, 34}$ However, beyond N-doped graphene and the aforementioned results, the electrocatalytic properties examination of other heteroatom-doped graphene as substrate for TMDs has yet to be realized. Particularly focusing on sulfur-doped graphene (SG), with sulfur being more electron rich than carbon, an n-type doping effect in graphene, analogous to that of nitrogen doping, is provided.$^{35}$ However, contrasting other n-type dopants, the difference in electronegativity between S and C as compared to N and C is small, entailing that a different mechanism for improved electrocatalytic activity is prevalent in SG.$^{36}$ Briefly, incorporation of sulfur within the skeleton of graphene modifies the electronic structure of the material by inducing a non-uniform spin density distribution, which derives from the mismatch of the outermost orbitals of sulfur and carbon atoms, being responsible, along with the charge density, for the SG intrinsic electrocatalytic activity.$^{37}$ Considering all the above points, it is absolutely timely and surely deserves examination the development of hybrid heterostructures, incorporating sulfur-doped graphene sheets and TMDs, as electrocatalysts.

The current study goes beyond the state-of-the-art, by in-situ growing MoS$_2$ and WS$_2$ onto SG, aiming the development of efficient HER heterostructured electrocatalysts. Herein, based on the microwave-assisted thermal decomposition of the inorganic precursor species of MoS$_2$ and WS$_2$, namely (NH$_4$)$_2$MoS$_4$ and (NH$_4$)$_2$WS$_4$, respectively, in the presence of SG as obtained upon a facile and low-cost route, the preparation of SG/MoS$_2$ and SG/WS$_2$, for two different weight ratios between the inorganic species and the SG, was accomplished. The newly developed heterostructures were characterized by Raman spectroscopy, while transmission electron microscopy (TEM) imaging allowed their morphological evaluation and electron energy loss spectroscopy (EELS) provided necessary information for the elements present on these structures. Furthermore, the SG/MoS$_2$ and SG/WS$_2$ heterostructured hybrids were tested against HER and found that the presence of SG not only significantly improved the catalytic activity of MoS$_2$ and WS$_2$ but also made it comparable to that due to commercial Pt/C catalyst. The exceptional electrocatalytic functioning of SG/MoS$_2$ and SG/WS$_2$ was attributed to the following reasons (a) the electronegativity difference between carbon and sulfur inducing n-type behaviour in S-doped graphene by polarizing the adjacent carbon atoms to sulfur in the graphene lattice and facilitating HER, (b) the enhanced population of defect sites in TMDs, as a result of the
bottom-up approach employed, (c) the intimate contact of SG with TMDs, (d) the uniform immobilization of TMDs onto the SG surface, in the absence of any organic/surfactant species, and (e) the synergetic effect between SG and TMDs.

**Experimental**

**General.** Chemicals, reagents, and solvents were purchased from Sigma-Aldrich and used as received. Infrared (IR) spectra were acquired on a Fourier Transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). Raman measurements were performed with a Renishaw confocal spectrometer at 514 nm. The intensity ratio I_D/I_G was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software. Thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27 instrument by TA in a nitrogen (purity >99.999%) inert atmosphere. Microwave Synthesis was undertaken in 10 mL vials using a CEM Discover SP Microwave System with an Activent technology. During the synthesis, the microwave system was operated in a dynamic mode where the power was automatically adjusted to maintain the set temperature. High-resolution transmission electron microscopy (HR-TEM) and electron energy loss spectroscopy (EELS) were performed using a FEI Titan Cube TEM working at 80 kV and equipped with a Cs image corrector and a Gatan Tridiem spectrometer. The size of the analyzed area was around 200 nm. Convergence and collection angles were 6.3 and 19.7 mrad, respectively. Typical energy resolutions (full-width at half-maximum of the ZLP) of the measurements were better than 0.8 eV. The energy dispersion used was 0.2 eV/channel. The EELS acquisition times were 10 s. The TEM samples were prepared by drop-depositing samples on holey carbon thin films. Scanning electron microscopy (SEM) imaging and energy dispersive X-ray spectroscopy (EDS) were performed using a FE-SEM (model JSM-7610F) equipped with EDAX (X-ACT, Oxford instrument). Electrochemical measurements were carried out at room temperature in N_2-saturated 0.5 M H_2SO_4 in a standard three-compartment electrochemical cell by using an EG&G Princeton Applied Research potentiostat/galvanostat (Model PARSTAT® 2273A). Platinum wire was used as a counter-electrode and as reference a Hg/HgSO_4 (0.5 M K_2SO_4) electrode was placed into a Luggin capillary. Potentials were corrected according to the relationship: E vs RHE = E vs Hg/HgSO_4 + 0.680. The working electrode was a glassy carbon disk with a geometric surface area of 0.071 cm^2. Linear sweep voltammetry measurements were conducted with a scan rate of 5 mV s^{-1}. To prepare the catalyst ink, 4.0 mg of the hybrid catalytic powder were dispersed in a mixture of solvents (1 mL) containing
water, isopropanol, and 5% Nafion (v/v/v=4:1:0.02) and sonicated for 30 min. The working electrode was first cleaned through polishing by 6, 3 and 1mm diamond pastes, rinsed with deionized water, and sonicated in double-distilled water. Then, 3 µL aliquots of the catalyst ink were casted on the electrode surface and dried at room temperature.

**Preparation of SG.** Initially, graphene oxide was prepared from graphite powder by following a modified Hummers method and then SG was produced by employing a solvothermal method. In detail, 40 mg of graphene oxide and 800 mg of Lawesson’s reagent were dispersed in diethyleneglycol methyl ether and sonicated for 30 minutes. Then the solution was refluxed at 90 °C under N₂ atmosphere for 48 hours. After that period, methanol was added and the reaction mixture was centrifuged 5 times with methanol (5 minutes at 4000 rpm). The SG was precipitated, dried at 60 °C overnight and stored in dark.

**Preparation of SG/MoS₂ and SG/WS₂.** All SG/MoS₂ and SG/WS₂ hybrids were synthesized by employing microwave irradiation conditions. To get MoS₂ or WS₂ the reaction mixture was prepared by adding (NH₄)₂MoS₄ or (NH₄)₂WS₄ (12 mg) to DMF (3 mL). For the preparation of the SG/MoS₂ or SG/WS₂ hybrids, SG was added to the reaction mixture. In more detail, 3 mg of SG and 1 mg of (NH₄)₂MoS₄ were dissolved in 3 mL DMF to prepare the SG/MoS₂ (denoted as 3:1, according to the weight ratio of reactants employed), while 30 mg of SG and 10 mg of (NH₄)₂WS₄ were used for the preparation of SG/WS₂ (3:1). The SG/MoS₂ (1:1) and SG/WS₂ (1:1) hybrids were prepared accordingly. All samples were bath sonicated for 30 minutes prior the microwave treatment. The materials were then centrifuged at 4000 rpm for 5 minutes and washed with dimethylformamide, water and methanol for several times, before characterizing and testing them as electrocatalysts.

**Results and discussion**

The preparation of SG was accomplished by treatment of graphene oxide with the Lawesson’s reagent, as illustrated in Figure 1. Under the particular conditions the Lawesson’s reagent acts as both sulfur source and reducing agent, restoring the defected graphene lattice by forming new and/or more graphene domains with continuous sp² hybridization. Next, the SG/MoS₂ and SG/WS₂ heterostructured hybrids were realized upon microwave irradiation by employing two different weight ratios of SG and ammonium tetrathiomolybdate and tetrathiotungstate, namely 3:1 and 1:1, as the inorganic precursor species for MoS₂ and WS₂, respectively. Markedly, microwave irradiation as a green and facile method, enables the preparation of nanostructures with controllable size and morphology with more active sites and therefore more catalytically effective, contrasting expensive, time-consuming and complex methods such as CVD that are commonly employed for preparing MoS₂-based electrocatalysts.
Figure 1. Illustrative preparation of sulfur-doped graphene (SG) with the Lawesson’s reagent and fabrication of SG/MoS$_2$ and SG/WS$_2$ hererostructures via microwave irradiation.

Direct evidence for the realization of SG was obtained by vibrational spectroscopy and thermogravimetric analysis. In more detail, the ATR-IR spectrum of SG shows a broad band at 1080 cm$^{-1}$ corresponding to C-S vibrations (Figure 2a), while bands related to oxygen species owed to the starting material graphene oxide and attributed to carbonyl stretching vibrations of carboxylic acid moieties at 1720 cm$^{-1}$ and to ether groups at 1220 and 1050 cm$^{-1}$ were disappeared and/or significantly reduced. Furthermore, the Raman spectrum of SG was changed as compared to that due to graphene oxide. Evidently, the sp$^2$ related G-band was shifted to lower frequencies by 8 cm$^{-1}$, at 1593 cm$^{-1}$ (Figure 2b), as compared to that attributed to graphene oxide, indicating that incorporation of sulfur within the lattice of graphene results on n-doping for SG. Moreover, the I$_D$/I$_G$ ratio found increased for SG as compared to the one owed to graphene oxide. This is due to the increase of the defectiveness attributed to etching of graphene sheets, with the simultaneous formation of new and/or more graphene domains with continuous sp$^2$ hybridization, as resulted by a reduction process that also takes place along with the sulfur-doping upon treatment with the Lawesson’s reagent. The latter was further confirmed by thermogravimetric analysis (TGA), which revealed a 50% reduction on the mass loss observed for the thermal decomposition of SG as compared to the value registered for graphene oxide. In Figure 2c the TGA graphs of SG and graphene oxide are presented and compared. Evidently, a 10% mass loss was observed in the temperature region 230-420 °C under an inert atmosphere for SG, as opposed to the 20% for graphene oxide in the temperature range 150-260 °C. The shift to higher decomposition temperature for SG as opposed to graphene oxide is justified by considering that the Lawesson’s reagent not only incorporated sulfur species within the graphene lattice but also reduced the oxygenated moieties, restoring to some extent the graphene network by forming islands with continuous sp$^2$
structure. The mass loss occurred above 420 °C is attributed to the thermal decomposition of sp³ defects created at sites nearby where sulfur doping took place.

**Figure 2.** (a) ATR-IR spectra for SG (red) and graphene oxide (black). (b) Raman spectra (514 nm) for SG (red) and graphene oxide (black). (c) Thermogravimetric analysis graphs for SG (red) and graphene oxide (black), obtained under nitrogen.
Focusing on SG/MoS$_2$ and SG/WS$_2$, Raman spectroscopy revealed characteristic modes due to both components, regardless the weight ratio 3:1 or 1:1 between the SG and the inorganic precursor species for MoS$_2$ and WS$_2$ employed for the preparation of the hybrids. This is to say that, for SG/MoS$_2$, bands at 379 and 405 cm$^{-1}$ (Figure 3a), corresponding to the in-plane $E^{12g}$ and out-of-plane $A_{1g}$ vibrational modes of MoS$_2$, respectively,$^{1,40,41}$ and for SG/WS$_2$ at 352 and 415 cm$^{-1}$ (Figure 3b), corresponding to the $E^{12g}$ and $A_{1g}$ modes of WS$_2$, respectively,$^{42}$ were observed, while in both spectra the D and G bands due to SG were present at 1352 and 1593 cm$^{-1}$, respectively. The $I_D/I_G$ ratio for SG/MoS$_2$ and SG/WS$_2$ was found almost unaltered, ca. 1.08 and 1.12 respectively, as compared to that registered for SG, demonstrating that the microwave irradiation conditions employed for the growth and incorporation of MoS$_2$ and WS$_2$ did not create any serious damage on the framework of SG.

![Raman spectra](image)

**Figure 3.** Raman spectra (514 nm) for (a) SG/MoS$_2$ (3:1) and (b) SG/WS$_2$ (3:1) heterostructured hybrid materials.

Thermogravimetric analysis (TGA) assays, performed under nitrogen atmosphere, allowed to estimate the amount of MoS$_2$ and WS$_2$ within the hybrid materials. Specifically, SG/MoS$_2$
(3:1) and SG/MoS$_2$(1:1) found to thermally lose 22 and 26 % of mass, respectively, in the temperature range 200-800 °C (ESI, Figure S1a). Based on the latter observation and considering that SG is also thermally labile, showing around 10 % mass loss in the temperature region 230-420 °C and another 6 % up to 800 °C (Figure 2), while intact MoS$_2$ shows a continuous mass loss to the whole temperature range (ESI, Figure S1a) due to the presence of defect sites, the rough content of MoS$_2$ within SG/MoS$_2$(3:1) and SG/MoS$_2$(1:1) was estimated to be 37 and 66 %, respectively. Similarly, from the TGA profiles for SG/WS$_2$(3:1) and SG/WS$_2$(1:1) (ESI, Figure S1b), while taking into account the overall 16 % mass loss due to SG, the content of WS$_2$ in the two hybrids was estimated to be 35 and 64 %, respectively.

Figure 4 shows HR-TEM images and EEL spectra of intact MoS$_2$ and WS$_2$ as well as of SG/MoS$_2$ and SG/WS$_2$ hybrids for the two different weight ratios 3:1 and 1:1 screened. Intact MoS$_2$ and WS$_2$ showed different nanostructures with different crystallographic orientations, aggregated in clusters with size in tenths of nm. This behavior can be clearly seen in the FFT diffraction pattern of MoS$_2$ (inset of Figure 4a), where several defined spots can be observed. As for the SG/MoS$_2$ and SG/WS$_2$, the TEM analysis showed a variation in contrast, which is believed to be related to the presence of MoS$_2$ and WS$_2$, respectively, on SG – see for example the crumpled structures in Figure 4d. The EELS results, shown in Figure S2a, S2b1 and S2b2 validated the presence of MoS$_2$ and WS$_2$ on SG, which is coherent with the rest of the microscopy and spectroscopic studies performed. In addition, SEM imaging of SG (ESI, Figure S3) together with SEM and EDX analysis for MoS$_2$, SG/MoS$_2$ and SG/WS$_2$ (ESI, Figures S4 and S5) and TEM imaging (ESI, Figure S6) further confirmed the presence of MoS$_2$ and WS$_2$ in all hybrid materials.

Figure 4. HR-TEM images of (a) MoS$_2$ deposited on an amorphous carbon substrate, (b) SG/MoS$_2$(1:1), (c) SG/MoS$_2$(3:1). HR-TEM images of (d) WS$_2$ on an amorphous carbon substrate, (e)
Next, the electrocatalytic activity of SG/MoS$_2$ and SG/WS$_2$ toward HER was examined by performing linear sweep voltammeter measurements with a rotating-disc working glassy carbon electrode in a standard three-electrode glass cell at a scan rate of 5 mV/sec in nitrogen saturated 0.5 M aqueous sulfuric acid. Polarization curves for the SG/MoS$_2$ (3:1) and SG/MoS$_2$ (1:1) hybrids, as accordingly denoted for the different weight ratios of SG and the inorganic precursor species for MoS$_2$ employed for the preparation, together with those for individual MoS$_2$ and SG and along with that for commercially available Pt/C as reference are shown in Figure 5a. Evidently, for a given potential, the cathodic current increased for SG/MoS$_2$ as compared to that for individual MoS$_2$ and SG. The onset overpotential for SG/MoS$_2$ (1:1) was registered at -0.175 V vs RHE, shifted by 0.215 V to more positive potentials as compared to that due to individual MoS$_2$ appearing at -0.390 V vs RHE. Notably, for the electrocatalyst with higher amount of SG, namely SG/MoS$_2$ (3:1), the onset overpotential is similar to that of commercially available Pt/C, appearing at -0.026 V vs RHE (Figure 5a). The same trend was identified for SG/WS$_2$, in which the heterostructured hybrid with the higher amount of SG, namely SG/WS$_2$ (3:1), showed lower overpotential, ca. -0.140 V vs RHE as compared not only with that owed to the individual WS$_2$, ca. -0.460 V, but also with the one due to SG/WS$_2$ (1:1), ca. -0.390 V (Figure 5b). An overall graph showing the onset overpotential for all examined materials is presented in Figure 5c. The aforementioned results, not only highlight the beneficial role of SG as substrate for uniformly immobilizing MoS$_2$ and WS$_2$, but more importantly stress out the importance of the relative amount of SG with regard to MoS$_2$ and WS$_2$ for achieving optimum electrocatalytic performance toward HER. Overall, a synergetic effect attributed to both the conducting nature of SG in intimate contact with MoS$_2$ and WS$_2$, allowing effective charge transport, and the presence of active edge sites in MoS$_2$ and WS$_2$, leads to more active electrocatalytic behavior against HER with comparable performance with that of platinum. Focusing on the best performing hybrids as electrocatalysts for HER, namely SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1), bubbles of hydrogen were visualized to evolve at a cathodic current density of 0.6 and 0.3 mA/cm$^2$, respectively, with enhanced rate at around -0.290 and -0.240 V, respectively. Considering that the amount of cathodic current density is analogous to the amount of hydrogen evolved and since it is very common to compare electrocatalysts for HER against overpotential at a cathodic current density of 10 mA/cm$^2$, ...
the corresponding tabulated graph for all examined materials, shown in Figure 5d, nicely demonstrates the highest activity for SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1), with the former performing best at lower overpotential (cf. Figure 5c).

In order to obtain meaningful insight and characterize the fluent charge transport efficiency and efficacy of the electrocatalytic HER, Tafel slopes for SG/MoS$_2$ (3:1) as well as SG/MoS$_2$ (1:1), and SG/WS$_2$ (3:1) as well as SG/WS$_2$ (1:1) were extracted from the LSV polarization curves and presented in Figure 6a and 6b, respectively. In addition, the tabulated Tafel values are given in Figure 6c. Generally, the Tafel slope is an inherent property of the electrocatalyst that is determined by the rate-limiting step of HER. Hence, analysis of the Tafel plots data aids the elucidation of the HER mechanism and importantly the identification of the rate-limiting step of the reaction. With all these in mind, the dominated mechanism of the hydrogen evolution for the materials tested is interpreted by considering initial adsorption of a proton onto the electrode surface via a reduction process, according to the Volmer adsorption – Equation 1. Next, bonding of the adsorbed hydrogen with a proton and electron transfer from the electrode surface takes place, according to the Heyrovsky desorption – Equation 2. Alternatively, recombination of two hydrogen atoms adsorbed on the electrode surface occurs, according to the Tafel desorption – Equation 3.

\[ \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_{\text{ads}} + \text{H}_2\text{O} \]  
\[ \text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O} \]  
\[ \text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \] 

**Figure 5.** Linear sweep voltammograms (LSV) for HER of (a) SG/MoS$_2$ (3:1) (red), SG/MoS$_2$ (1:1) (green), MoS$_2$ (black), SG (pink) and Pt/C (blue), and (b) SG/WS$_2$ (3:1) (purple), SG/WS$_2$ (1:1) (cyan), WS$_2$ (grey), SG (pink) and Pt/C (blue). The LSV polarization
curves were obtained in a nitrogen saturated aqueous 0.5 M H$_2$SO$_4$ electrolyte, at a rotation speed of 1,600 rpm and scan rate of 5 mV/s. (c) Graph for onset overpotential for all tested materials. (d) Graph for overpotential registered at -10 mA/cm$^2$ current density for all tested materials.

Individual MoS$_2$, WS$_2$ and SG exhibited relatively high Tafel slopes, 271, 246 and 153 mV/dec, respectively. Realization of the SG/MoS$_2$ and SG/WS$_2$ heterostructured hybrids, regardless of the relative amount of SG versus the transition metal precursor employed, i.e. 3:1 and 1:1, caused a drop on the corresponding Tafel value (Figure 6). Since smaller Tafel slope implies that for the generation of an equivalent current only a lower overpotential is required, the electrocatalytic activity of MoS$_2$ and WS$_2$ was improved, particularly for the SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1) systems, which showed Tafel slopes of 152 and 53 mV/dec, respectively. Again, the improvement in charge transport is facilitated by the good electrical contact between SG and TMDs, while the observed Tafel values manifest that the adsorption of hydrogen onto the modified electrode is the rate-limiting step for the SG/MoS$_2$ (3:1) according to Equation 1, while for the SG/WS$_2$ (3:1) the electrochemical desorption of adsorbed hydrogen atoms onto the modified electrode to generate hydrogen is the rate-limiting step, according to Equation 2.
Figure 6. Tafel slope for (a) SG/MoS$_2$ (3:1) (red), SG/MoS$_2$ (1:1) (green), MoS$_2$ (black), SG (pink) and Pt/C (blue), and (b) SG/WS$_2$ (3:1) (purple), SG/WS$_2$ (1:1) (cyan), WS$_2$ (grey), SG (pink) and Pt/C (blue), showing overpotential versus current density. (c) Tabulated values for Tafel slope for all tested materials.

In order to further understand the improved electrocatalytic activity of the SG/MoS$_2$ and SG/WS$_2$ hybrid materials, the electrochemically active surface area (ECSA) was calculated according to the equation ECSA = $C_d/C_s$, where $C_d$ is the electrochemical double-layer capacitance and $C_s$ is the specific capacitance of a flat surface with 1 cm$^2$ of real surface area with a value assumed to be 40 $\mu$F/cm$^2$ for the flat electrode.$^{43}$ To this end, measuring cyclic voltamograms in a non-Faradaic region at different scan rates of 50, 100, 200, 300 400 and 500 mV/sec (ESI, Figure S7), allowed to estimate the ECSA value from the $C_{dl}$ by plotting...
the $\Delta j = (ja - jc)$ at 0.1 V vs RHE as a function of the scan rate according to the equation $C_d = \frac{d(\Delta j)}{dV}$.\textsuperscript{43} Evidently, the ECSA values of SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1) were significantly higher than SG/MoS$_2$ (1:1) and SG/WS$_2$ (1:1) respectively, as shown in Table 1. These higher ECSA values indicate more effective accessibility of the active sites of the SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1) hybrid materials, similarly with recent reports.\textsuperscript{44}

Finally, the long-term stability of the hybrid materials was evaluated. Durability studies as an important factor to assess the electrocatalytic activity of the materials were performed (ESI, Figure S8) and found that all tested materials exhibited high stability after cycled continuously for 1,000 cycles, with negligible loss of the cathodic current. In Table 1, the various HER parameters of all screened materials, before and after 1,000 cycles, are summarized.

<table>
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<th>Catalyst</th>
<th>Onset overpotential (V vs. RHE)</th>
<th>Overpotential (V vs. RHE) at -10 mA/cm$^2$</th>
<th>Tafel slope (mV/dec)</th>
<th>ESCA (cm$^2$)</th>
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<td>SG</td>
<td>0.68</td>
<td>0.85</td>
<td>153</td>
<td>~7.25</td>
</tr>
<tr>
<td>SG$^a$</td>
<td>0.68</td>
<td>0.87</td>
<td>157</td>
<td>-</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.026</td>
<td>0.09</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Pt/C$^a$</td>
<td>0.054</td>
<td>0.096</td>
<td>50</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ After 1,000 cycles.
Conclusions

In summary, the fabrication of SG/MoS$_2$ and SG/WS$_2$ hybrids, with two different weight ratios between the SG and the inorganic species as 3:1 and 1:1, as efficient electrocatalysts for the HER was accomplished. The preparation of the hybrids involved microwave-assisted thermal decomposition of (NH$_4$)$_2$MoS$_4$ and (NH$_4$)$_2$WS$_4$, employed as inorganic precursors for MoS$_2$ and WS$_2$, respectively, in the presence of SG. Complementary spectroscopic characterization based on Raman spectroscopy and HR-TEM coupled with EELS, confirmed the successful formation of SG/MoS$_2$ and SG/WS$_2$. Those heterostructured hybrids were scrutinized against HER and found that the presence of SG not only significantly improved the catalytic activity of MoS$_2$ and WS$_2$ but also made it comparable to that due to commercial Pt/C catalyst. This is in line with recent results based on N-doped graphene employed as substrate for TMDs,$^{33,34}$ highlighting the beneficial role of heteroatom doping on graphene for improving the electrocatalytic activity towards HER. More precisely, based on LSV assays, the best electrocatalytic activity for HER was found for hybrids with higher content of SG, namely SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1). The uniform and robust immobilization of MoS$_2$ and WS$_2$ on the surface of SG, without the involvement of surfactants and any insulating organic moieties, thereby facilitating effective charge-transport processes due to intimate contact, play crucial role on the exceptional electrocatalytic functioning of the SG/MoS$_2$ and SG/WS$_2$ hybrids. In addition, the presence of active edge sites in MoS$_2$ and WS$_2$, in combination with the novel characteristics of SG, possess their own share on the better electrocatalytic behavior of SG/MoS$_2$ and SG/WS$_2$ against HER. The higher ECSA values for the hybrid heterostructured materials with the higher content of SG, namely SG/MoS$_2$ (3:1) and SG/WS$_2$ (3:1), rendered a large functioning surface area of catalytic active sites, excellent hydrogen production ability, hence superior catalytic performance. Furthermore, based on the Tafel plot derived from the corresponding polarization curves, the adsorption of hydrogen as the rate-limiting step for SG/MoS$_2$ (3:1) was revealed, while for SG/WS$_2$ (3:1) the kinetics governed by the electrochemical desorption of adsorbed hydrogen atoms to generate hydrogen. Overall, considering that the particular facile approach for developing SG/MoS$_2$ and SG/WS$_2$ heterostructured hybrids can be extended to fabricate diverse materials, incorporating other transition metals and different chalcogens, we firmly believe that a plethora of viable electrocatalysts can be produced, opening wide avenues in the areas of energy conversion and storage.

Conflicts of interest
There are no conflicts to declare.

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**References**


