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MoS₂-graphene-CuNi₂S₄ Nanocomposite an Efficient Electrocatalyst for the Hydrogen Evolution Reaction

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1. Abstract

We present a facile methodology for the synthesis of a novel 2D-MoS₂, graphene and CuNi₂S₄ (MoS₂-g-CuNi₂S₄) nanocomposite that displays highly efficient electrocatalytic activity towards the production of hydrogen. The intrinsic hydrogen evolution reaction (HER) activity of MoS₂ nanosheets was significantly enhanced by increasing the affinity of the active edge sites towards H⁺ adsorption using transition metal (Cu and Ni₂) dopants, whilst also increasing the edge sites exposure by anchoring them to a graphene framework. Detailed XPS analysis reveals a higher percentage of surface exposed S at 17.04%, of which 48.83% is metal bonded S (sulfide). The resultant MoS₂-g-CuNi₂S₄ nanocomposites are immobilized upon screen-printed electrodes (SPEs) and exhibit a HER onset potential and Tafel slope value of – 0.05 V (*vs.* RHE) and 29.3 mV dec⁻¹, respectively. These values are close to that of the polycrystalline Pt electrode (near zero potential (*vs.* RHE) and 21.0 mV dec⁻¹, respectively) and enhanced over bare/unmodified SPE (– 0.43 V (*vs.* RHE) and 149.1 mV dec⁻¹, respectively). Given the efficient, HER activity displayed by the novel MoS₂-g-CuNi₂S₄/SPE electrochemical platform and the comparatively low associated cost of production for this nanocomposite, it has potential to be a cost-effective alternative to Pt within electrolyser technologies.

Keywords: Molybdenum disulfide (MoS₂), graphene, Hydrogen Evolution Reaction, Energy storage

2. Introduction

A plethora of emergent low polluting energy generation technologies rely upon hydrogen gas as a fuel source[37], which has created an impetus for clean hydrogen generation techniques to be developed. A prominent method for clean hydrogen generation is the Hydrogen Evolution Reaction (HER); ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$), which is the cathodic reaction within an electrolyser.[1] The power necessary to operate an electrolyser could feasibly be drawn from renewable sources, making it a “cleaner” fuel source compared to its fossil fuel (FF) counterparts.[32] A limiting factor to the ubiquitous use of electrolysers to generate hydrogen is the requirement for expensive platinum (Pt) as a catalyst for the HER.[13, 18, 31] Much of the research dedicated to finding an alternative to Pt has focused upon the di-chalcogenides, particularly MoS₂ based materials (see Table 1),[31] as 2D-MoS₂ nanosheets have been shown to be effective at lowering the HER onset potential and increasing the achievable current density, whilst typically being composed of significantly cheaper and more earth abundant elements.[7, 17, 19] For example a study by Ruiz *et al.*[35] utilized a chemical vapor deposition (CVD) technique to grow vertically aligned MoS₂ on a gold foil and demonstrated how the optimized (prepared at 600°C) MoS₂ film, when used as an electrode, achieved a current density of 10 mA cm⁻² by -0.355 V (*vs.* saturated calomel electrode (SCE)). Whilst being *ca.* -0.250 V (*vs.* SCE) more electronegative than the optimal value of Pt, it was significantly less electronegative than the values reported by Rowley-Neale *et al.*[31] for unmodified traditional carbon based electrodes (boron doped diamond, edge-plane pyrolytic graphite, glassy carbon and screen-printed electrodes (SPE)).

There are a wide variety of studies within the literature, which demonstrate the capability of a MoS₂ based material to act as an efficient electrocatalyst towards the HER, however few reports show any form of catalyst that can display equivalent HER activity to Pt based electrocatalysts. In order to narrow the potential gap between the HER onset potentials of MoS₂ and Pt based catalysts, numerous studies have utilized MoS₂ nanosheets as a dopant framework in order to fabricate electrocatalysts that show more comparable HER activity to Pt. One such study by Shi *et al.*[38] found that Zinc (Zn) doped MoS₂ (Zn-MoS₂) when drop-cast onto a GC electrode exhibited greater HER catalysis than undoped MoS₂, with a HER onset potential of -0.13 V (*vs.* reversible hydrogen electrode (RHE)) and a Tafel slope of 51 mV dec⁻¹ compared to -1.4 V (*vs.* RHE) and 101 mV dec⁻¹ for undoped MoS₂ nanosheets. Shi and coworkers.[38] attributed the increased HER activity

to a synergistic electron (energy level matching) and morphological effect (increase in the number of exposed active edge sites) between the Zn and the MoS₂ nanosheets.

HER catalysis is thought to predominately occur at the MoS₂ nanosheets edge sites, in particular the exposed Sulfur atoms, which have an affinity towards H⁺ adsorption due to a density functional theory predicting a binding energy of +0.08 eV.[19] In contrast to this, the basal sites are relatively inert and show little catalytic activity,[47] consequently the bulk of the material can be considered electrocatalytically inert.[6] Efforts to maximize the ratio of edge sites to basal sites of a given MoS₂ based material would therefore yield a more effective HER catalyst. Previous studies have shown that hybridizing an electrocatalyst with a graphitic material (*e.g.* reduced graphene oxide) offers a beneficial morphology (an increased number of exposed active sites) leading to increased catalysis.[21] Hybridization in this manner has the additional benefit of improving charge transfer and conductivity for the entire system and notably, the electrocatalytic sites.[10]

Given the above, there are two major factors that should be considered in research focused on optimizing HER catalysis of MoS₂ containing materials. The first being: increasing the affinity of active sites towards H⁺ adsorption and thus their ability to catalyze the HER. Secondly: maximizing the ratio of exposed active edge sites to inert basal sites, which will increase the density of sites enabling catalysis. In order to tackle both of these challenges we present a novel methodology for doping MoS₂ with transition metals (Cu and Ni) in order to increase the electron density at the electrocatalytically active edge sites and therefore improve their HER activity, whilst increasing the exposure of these sites by anchoring them to a graphene framework. The novel MoS₂-graphene-CuNi₂S₄ (MoS₂-g-CuNi₂S₄) nanocomposite is electrically wired *via* immobilization upon SPEs and experimentally explored towards the HER where it exhibits highly efficient HER catalysis.

3. Experimental

3.1. Chemicals

The MoS₂-g-CuNi₂S₄ nanocomposite precursors utilized in this study were, Cu(NO₃)₂.6H₂O, Ni(NO₃)₂.6H₂O, thiourea, MoS₂, graphite powder (30 μm) and polyvinylpyrrolidone. All of precursors were purchased from Sigma Aldrich, Merck and Sd-fine chemical PVT Ltd, respectively and used without further purification. All solutions were prepared with doubly distilled water (18.2 MΩ cm) and were vigorously degassed prior to electrochemical measurements with high purity, oxygen free, nitrogen. All experiments were performed in 0.5 M H₂SO₄ in order to replicate the conditions found within an acidic proton exchange membrane fuel cell (PEMFC).[34]

3.2. Electrochemical Measurements

Electrochemical measurements were studied using CH-Electrochemical analyzer model CHI 6039E (USA). Measurements were carried out using a typical three electrode system with a nickel wire counter and a reversible hydrogen electrode (RHE) reference electrode. The working electrodes are screen-printed graphite macro electrodes (SPEs) comprising a 3.1 mm diameter working area. The SPEs were fabricated in-house with the appropriate stencils using a DEK 248 screen-printing machine (DEK, Weymouth, U.K.).[9] The fabrication of the SPEs has been extensively described in previous publications,[34] however it is repeated within the supporting information for clarity.

3.3. Synthesis of MoS₂-g-CuNi₂S₄ nanocomposite

The MoS₂-g-CuNi₂S₄ nanocomposites were synthesized by the following protocol. In brief, 120 mg of graphite (<20 μm) and MoS₂ powder were mixed into a solution containing a 1:1 mixture of water/isopropanol. This solution was then ultra-sonicated for 3 hrs. Following this, 1 mM of Cu(NO₃)₂.6H₂O, 2 mM Ni(NO₃)₂.6H₂O, PVP and thiourea were added to 12.5 mL of the graphene/MoS₂ solution at a concentration of 1, 2, 1 and 9 mM, respectively. Next, 1 mL of ammonia was added drop wise to the solution under continuous stirring. The solution mixture was then transferred into a Teflon lined autoclave, sealed and heated, at 180 °C, for 24 h. The obtained black solid product was filtered, washed with water and ethanol several times then left to in a hot

air oven, at 80 °C, for 12 h. For comparative purposes CuNi₂S₄, g-CuNi₂S₄ and MoS₂-CuNi₂S₄ were fabricated in the same manner and electrochemically explored towards the HER.

3.4. Instrumentation

The phase transition, purity and crystal structure of the synthesized compounds were analyzed by a PANalytical X'pert PRO powder X-ray powder diffractometer (XRD) equipped with Ni-filtrated Cu K α radiation (40 kV, 200 mA). The composition and functional groups present in the as prepared catalyst was monitored by Agilent carry-630 Fourier transform infrared (FT-IR) spectroscopy over the range of 400-4000 cm⁻¹. Raman Spectroscopy was performed using a 'Renishaw InVia' spectrometer equipped with a confocal microscope ($\times 50$ objective) and an argon laser (514.3 nm excitation). Measurements were performed at a very low laser power level (0.8 mW) to avoid any heating effects. The optical absorbance spectra of as prepared HER catalyst was monitored by UV-visible absorption spectroscopy (UV-1800, Shimadzu, Japan). The morphology, composition, size and crystallinity of the as prepared HER catalyst was analyzed by scanning electron microscope (SEM) using a JEOL JSM-5600LV model SEM. Transmission electron microscopy (TEM) images were obtained using a 200 kV primary beam under conventional bright-field conditions with an energy dispersive X-ray microanalysis (EDX) package. The MoS₂-g-CuNi₂S₄ sample was dispersed onto a holey-carbon film supported on a 300 mesh Cu TEM grid. X-ray photoelectron (XPS) analysis of the samples was performed using a bespoke ultra-high vacuum system fitted with a Specs GmbH Focus 500 monochromated Al K α X-ray source, Specs GmbH Phoibos 150 mm mean radius hemispherical analyser with 9-channeltron detection, and a Specs GmbH FG20 charge neutralising electron gun. The Al monochromator source was used to generate a survey scan and higher resolution scans over C 1s, O 1s, Cu 2p, Ni, 2p, N 1s, S 2p and, where detected, Mo 3d photoelectron lines. A representative area approximately 1.4 mm in diameter over the center of each sample was analysed.

3.5. Electrode preparation

Following the synthesis of the nanocomposites, their HER activity was electrochemically explored. This was done by dispersing 5 mg of the catalyst and 5 wt% nafion into a solution of water and ethanol, the solution was ultra-sonicated for 30 min to ensure it was homogenous. 5 μ L

of this suspension was then drop-caste (where an aliquot of the given solution is deposited onto the working area of an SPE, using a manual micro-pipette). This resulted in a surface coverage of *ca.* 0.3 mg cm^{-2} MoS₂-g-CuNi₂S₄. The electrode was then air dried for 30 mins to ensure evaporation of the water and ethanol. The prepared electrode was then ready for use.

4. Results and Discussion

4.1. Physicochemical characterization of the nanocomposites

A thorough physicochemical analysis of the novel synthesized MoS₂-g-CuNi₂S₄ nanocomposite, was performed using FT-IR, Raman spectroscopy, SEM, TEM, TGA, EDX, XRD and XPS.

TEM imaging of the MoS₂-g-CuNi₂S₄ nanocomposite is shown in Figure 1 showing that the MoS₂-g-CuNi₂S₄ nanocomposite had an average diameter of *ca.* 50 nm, however there are signs of agglomeration of the new particles. Note that Figure 1(B) has five separate sites identified which are the locations of elemental composition analysis *via* EDX, the results of which are prescribed within in Table S1. Note that the presence of all the expected elementals, and there is a higher than expected percentage of Cu observed, which is likely a result of the use of a Cu supporting grid. EDX mapping of a MoS₂-g-CuNi₂S₄ flake (see ESI Figure S1) showed uniform distribution S, Cu, Ni, Mo and O upon the flakes surface. The FTIR spectrum of the MoS₂-g-CuNi₂S₄ nanocomposite is given in Figure 2(A). The majority of peaks between 1000-4000 cm⁻¹ can be ascribed to graphitic components, for example the peaks at 1609 and 2911 cm⁻¹ are characteristic of sp² hybridized carbon and hydroxyl groups, respectively.[40] Note the peak at 3434 cm⁻¹ is the characteristic band of O-H.[50] The weak observable peak at 479 is likely due to Mo-S vibration.[26] Raman spectroscopy was also performed on the MoS₂-g-CuNi₂S₄ with the obtained spectrum being shown in Figure 2(B). Vibrational bands (VB) at *ca.* 378 and 403 cm⁻¹, which correspond to the E_{1g}² and A_{1g} of MoS₂, can be observed.[20] Additionally VBs at *ca.* 1360 and 1578 cm⁻¹ are observed, these correspond to the D and G bands of a graphitic material.[4, 29] Finally, the presence of a peak at *ca.* 2713 cm⁻¹ (2D band) is also characteristic of graphitic materials,[4, 8] thus confirming the presence of high quality few layer graphene and MoS₂. [16, 28] The XRD profile of the MoS₂-g-CuNi₂S₄ nanocomposite is shown in Figure 2(D). Except for the indexed MoS₂ peaks (corresponding to JCPDS No. 37-1492), all of the other diffraction peaks can be ascribed to the cubic phase of CuNi₂S₄ (JCPDS No. 24-334). For instance, the typical diffraction peaks of (311), (400), (511), and (440) diffraction planes can be clearly indexed at 31.4°, 38.2°, 50.1°, and 55.1°, respectively. No obvious peaks from other phases such as CuS, NiS, or organic compounds related to the precursors were detected. Furthermore, graphene/graphite peak (002) at 26.5°,[28] in the XRD patterns as well as the characteristic (002) peak for MoS₂ at 14.2°.[15] It was important to determine the elemental composition of each of the nanocomposites, therefore XPS analysis was performed on the samples.

A typical survey spectra of the MoS₂-g-CuNi₂S₄ is shown in Figure 2(C), where all the expected elements can be observed as well as low levels of N and Si (the presence of N is likely due to atmospheric contamination, whilst the Si can be attributed to the Si containing adhesive tape used to fix the samples during analysis). The full elemental composition of each composite material is shown within Table 2. Table 3 gives the results of the quantification analysis of all the synthesized nanocomposites and ESI Figure S2 displays high resolution XPS spectra of the Mo, S, C, O, Cu and Ni components for the MoS₂-g-CuNi₂S₄ nanocomposite. Note that further XPS analysis is described later within the manuscript in order to provide insights into the substantial HER activity observed by the MoS₂-g-CuNi₂S₄. Lastly, thermogravimetric analysis assessed the thermal stability of the MoS₂-g-CuNi₂S₄. It is clear from inspection of ESI Figure 3 that the nanocomposite was stable until *ca.* 200°C after which the MoS₂-CuNi₂S₄ exhibited a rapid and uniform decomposition to *ca.* 75% by 900°C. The average working temperature of a proton exchange membrane electrolyser is between 50-80 °C,[11] so MoS₂-g-CuNi₂S₄ could maintain its composition within an operating electrolyser. Given the thorough physicochemical analysis given above the MoS₂-g-CuNi₂S₄ nanocomposite is shown to be of high purity and crystallinity.

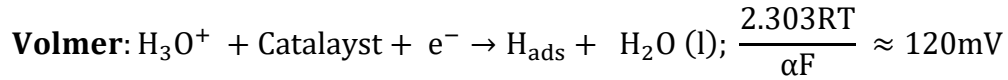
4.2. Application of the MoS₂-g-CuNi₂S₄/SPEs towards the HER

Initially it was important to benchmark the electrochemical behavior of a bare/unmodified SPE and a polystalline platinum (Pt) electrode towards the HER in 0.5 M H₂SO₄. Figure 3(A) shows the linear sweep voltammetry (LSV) obtained for a bare/unmodified SPE and Pt electrode as well as for the CuNi₂S₄/SPE, g-CuNi₂S₄/SPE, MoS₂-CuNi₂S₄/SPE and MoS₂-g-CuNi₂S₄/SPEs. The bare/unmodified SPE had an onset potential of – 0.43 V (*vs.* RHE), as expected this is far more electronegative than the optimal HER onset potential for Pt. Note that within this study the HER onset potential is determined as the potential when the current deviates from the background current by 25 μA cm⁻². From inspection of Figure 3(A) it is clear that upon immobilization of all of the nanocomposites onto an SPE there is a decrease in the electronegativity of the HER onset potential, with the CuNi₂S₄/SPE, g-CuNi₂S₄/SPE, MoS₂-CuNi₂S₄/SPE and MoS₂-g-CuNi₂S₄/SPE exhibiting HER onset potentials of – 0.41, – 0.15, – 0.13 and – 0.05 V (*vs.* RHE), respectively. It is also worth noting there is a corresponding increase in the achievable current densities with the MoS₂-g-CuNi₂S₄/SPEs reaching 10 mA cm⁻² by – 0.12 V (*vs.* RHE). In comparison of the nanocomposites synthesized, the MoS₂-g-CuNi₂S₄/SPE displays the most optimal HER activity

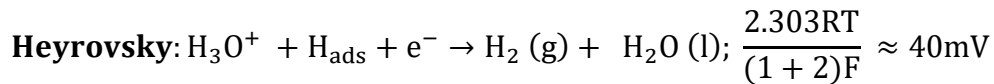
with a HER onset potential close to that of Pt. This is likely a result of MoS₂-g-CuNi₂S₄ having the largest number of exposed active edge sites for H⁺ adsorption as a result of the graphene acting as a framework for optimal exhibition of the sulfur edge sites of MoS₂ and CuNi₂S₄ in addition to the electrocatalytically active functional moieties in graphene. Additionally, the graphene acted to increase the electroconductivity, whilst the interface in MoS₂-g- CuNi₂S₄ facilitates the electron transfer during electrocatalysis.

4.3. Tafel Analysis

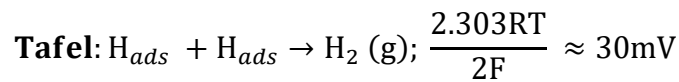
In order to determine whether the increased HER activity observed from an SPE post nanocomposite immobilization was as a result of the catalyst enabling a change in the reaction mechanism, Tafel analysis was performed. The activity of a HER catalyst is related to the kinetic barrier of the rate-determining hydrogen evolution pathway. According to the literature, HER mechanism involves three possible rate limiting steps, those being: (i) initial H⁺ adsorption step, known as the Volmer step,



(ii) Volmer- Heyrosky discharge step:



(iii) Volmer-Tafel discharge step :



where the transfer coefficient (α) is 0.5, F is the Faraday constant, R is the universal gas constant and T is the temperature at which the electrochemical experiment was performed (298 K). Tafel analysis was performed on the Faradaic section of the LSVs shown in Figure 3(A) with the resultant Tafel slopes being given in Figure 3(B). The determined Tafel slopes for the bare/unmodified SPE and Pt electrodes were 149.1 and 21.0 mV dec⁻¹, respectively, these values correspond to those reported in previous literature. The determined Tafel values suggest that the rate limiting step of the HER mechanism on a bare/unmodified SPE is the Volmer step whilst a Pt electrode allows the HER to occur *via* the desirable Volmer-Tafel mechanism. The Tafel slope

values obtained for the CuNi₂S₄/SPE, g-CuNi₂S₄/SPE, MoS₂-CuNi₂S₄/SPE and MoS₂-g-CuNi₂S₄/SPEs were 147.3, 111.8, 44.7 and 29.3 mV dec⁻¹ respectively. Interpretation of these Tafel values, reveals that for the CuNi₂S₄/SPE and g-CuNi₂S₄/SPE there is not an alteration in the reaction mechanism with the Volmer adsorption step still being the rate limiting step. However, for the MoS₂-CuNi₂S₄/SPE and MoS₂-g-CuNi₂S₄/SPEs there is a significant increase in the current density resulting in the Tafel discharge step becoming the rate limiting step. The smallest Tafel value was recorded for the MoS₂-g-CuNi₂S₄/SPE, this suggests that MoS₂-g-CuNi₂S₄ substantially enhances the HER capability of the SPE platform to close to that of a Pt electrode. The data presented above clearly shows that hybridization of MoS₂ with graphene and CuNi₂S₄ significantly improves HER catalysis. The literature suggests that it is the exposed sulfur atoms located at the MoS₂ nanosheets edge sites that produce HER activity, it was therefore vital that we investigate the chemical changes responsible for the reported increase in catalysis. A detailed quantitative XPS analysis of the S components for each of the nanocomposites was performed. The obtained high resolution S 2p spectra (See ESI Figure S2) were complex in shape, exhibiting good evidence for 4 separate chemical environments. S 2p peaks were fitted with multiple sets of 2p_{3/2}-2p_{1/2} doublets. In each case, the two components of the doublet had to be constrained to the same width and line shape, the area ratio is constrained so that the 2p_{1/2} component is 50% of the intensity of the 2p_{3/2} component (as expected from orbital occupancies), and the two components are constrained to be separated by 1.13 eV. The 4 separate chemical environments for S were: Metal-bonded S *e.g.* metal sulfide bonds such as Cu-S, Ni-S, Mo-S, typically 161 – 162 eV, Metal bonded to organic S, typically 162.5 – 163 eV, organic (carbon bonded) sulfur, typically 164.4 – 164.6 eV, and oxidized S *e.g.* as sulfate, typically 168.4 – 168.5 eV. The relative percentage quantity of each of these components with the four nanocomposites is summarized in Table 3. It is evident that there is a strong positive correlation between atomic percentage of S (especially metal bonded S) and electrocatalytic activity towards the HER for the MoS₂-g-CuNi₂S₄, MoS₂- CuNi₂S₄ and g-CuNi₂S₄. As shown by analysis of the MoS₂-g-CuNi₂S₄, which displayed the greatest HER catalysis and had the highest atomic percentage of S at 17.04%, of which 48.83% was metal bonded S (*the highest percentage recorded for any of the nanocomposites*). Note that CuNi₂S₄ has the highest atomic percentage of S of all four nanocomposites and a higher % of metal bonded S than MoS₂- CuNi₂S₄ or g-CuNi₂S₄, however it displays the least amount of HER catalytic activity. We summarize this to the lack of Mo, and therefore the lack of Mo-S sulfides, within the CuNi₂S₄.

So whilst there is a relatively high % of metal-S bonds these are likely Cu-S and Ni-S, therefore suggesting that the S present is not in a chemical environment complimentary to HER catalysis.

The as prepared materials CuNi_2S_4 , $\text{g-CuNi}_2\text{S}_4$, $\text{MoS}_2\text{-CuNi}_2\text{S}_4$ and $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$ were further examined using electrochemical impedance spectroscopy (EIS) in order to determine the impedance of the interface system. EIS is a useful technique to characterize interface reactions and electrode kinetics in HER. ESI Figure S4 shows the Nyquist plots recorded for all of the nanocomposite modified SPEs using an overpotential of 150 mV (vs. RHE). The $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$ exhibited the smallest R_{ct} at 10.08 $\text{k}\Omega$ compared to 44.35, 39.27 $\text{k}\Omega$ and 112.0 $\text{k}\Omega$ for the CuNi_2S_4 , $\text{g-CuNi}_2\text{S}_4$ and $\text{MoS}_2\text{-CuNi}_2\text{S}_4$, respectively. The EIS data presented above supports the prior inference that $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$ is the most effective electrocatalyst for the HER as it displayed the fastest rate of reaction. Lastly it was essential to assess the stability, of the $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$, at catalyzing the HER, as longevity and durability are important considerations if catalyst is to be implemented in an industrial application.[23, 39, 44] The stability of the $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4/\text{SPEs}$ towards HER has been tested by performing 1000 repeat cycling voltammograms (See Figure 3(C)). A slight decrease in catalytic activity of $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4/\text{SPE}$ is observed over the course of the 1000 scans, with the current density at -0.10 V decreasing from -134 μA for the first scan to 98 μA for the 1000th scan. The observed decrease in HER catalysis over for the course of 1000 CVs is likely a result of the $\text{MoS}_2\text{-g-CuNi}_2\text{S}_4$ delaminating from the supporting SPEs surface due to hydrogen bubbling from the surface as the HER occurs.[3]

5. Conclusions

The synthesis of a novel MoS₂-g-CuNi₂S₄ nanocomposite that displays remarkable HER catalysis upon immobilization to a SPE, has been reported. The intrinsic HER activity of MoS₂ was improved by increasing the affinity of the active edge sites, of the MoS₂ nanosheets, for H⁺ adsorption using transition metal (Cu and Ni) dopants, whilst also increasing the edge sites exposure by anchoring them to a graphene framework. Through a detailed XPS analysis, we demonstrated that the synthesis process, in particular hybridizing the MoS₂ with graphene, increases the percentage of electrocatalytic surface exposed S as well as the proportion of metal bonded S from 15.95% and 40.02%, respectively for the MoS₂-CuNi₂S₄ nanocomposite to 17.04% and 48.83%, respectively for the MoS₂-g-CuNi₂S₄ nanocomposite. The optimized MoS₂-g-CuNi₂S₄ electrocatalyst when immobilized upon SPEs display near Pt HER activity with a HER onset potential and Tafel slope value of -0.05 V (*vs.* RHE) and 29.3 mV dec⁻¹, respectively. These values are far greater than those of a bare/unmodified SPE (-0.43 V (*vs.* RHE) and 149.1 mV dec⁻¹), and the equivalent masses of the other synthesized nanocomposites upon an SPE ((CuNi₂S (-0.41 V (*vs.* RHE) and 147.3 mV dec⁻¹), g-CuNi₂S₄ (-0.15 V (*vs.* RHE) and 111.8 mV dec⁻¹) and MoS₂-CuNi₂S₄ (-0.13 V (*vs.* RHE) and 44.7 mV dec⁻¹)). We have provided insights into the synthesis of a novel HER catalyst (MoS₂-g-CuNi₂S₄), which exhibits a near Pt electrocatalytic activity towards the HER. Clearly MoS₂-g-CuNi₂S₄ has the potential to act as a cost effective alternative to Pt, when utilized as the cathodic electrocatalyst implemented within the triple phase boundary of commercial PEM electrolyzers.

Acknowledgements

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Table 1. Comparison Table showing the HER activity of MoS₂ and MoS₂ containing compounds.

Catalyst	Supporting Electrode	Loading	Deposition Technique	Electrolyte	HER onset (V)	Tafel Slope (mV dec ⁻¹)	Reference
CD/MoS ₂	GC	–	Drop- cast	0.5 M H ₂ SO ₄	<i>ca.</i> – 0.5 (vs. RHE)	22	[5]
P-doped MoS ₂	GC	0.32 mg cm ⁻²	Drop- cast	0.5 M H ₂ SO ₄	– 0.015 (vs. RHE)	34	[25]
MoS ₂ -Ni ₃ S ₂ H	NF	–	Chemical synthesis	1.0 M KOH	– 0.037 (vs. RHE)	61	[46]
MoS ₂ /C*	SPE	252.80 μg cm ⁻²	Drop- cast	0.5 M H ₂ SO ₄	– 0.44 (vs. SCE)	43	[33]
MoS ₂ -PB/NG	GC	–	Drop-cast	0.5 M H ₂ SO ₄	– 0.08 (vs. RHE)	62	[49]
MoS ₂	GC	0.24 mg cm ⁻²	Drop-cast	0.1 M H ₂ SO ₄	-0.117 (vs. RHE)	78	[24]
Ni-MoS ₂	CC	–	Chemical synthesis	1.0 M KOH	-0.098 (vs. RHE)	75	[43]
Ni-MoS ₂	CC	–	Chemical synthesis	0.5 M H ₂ SO ₄	-0.110 (vs. RHE)	74	[43]
CuNi-P-MoS ₂	NFL	–	Chemical synthesis	0.5 M H ₂ SO ₄	-0.225 (vs. RHE)	61	[2]
NiCo ₂ S ₄ /MoS ₂	NF	3.00 mg cm ⁻²	Chemical synthesis	0.1 M KCl	-0.40 (vs. RHE)	–	[14]
MoS ₂ -ZnO-Ni	NF	–	Chemical synthesis	1.0 M KOH	-0.129 (vs. RHE)	78	[45]
MoS ₂ -NiS	GC	0.20 mg cm ⁻²	Drop-cast	1.0 M KOH	-0.083 (vs. RHE)	66	[41]
DAC/MoS ₂	GC	2-5 mg cm ⁻²	Drop-cast	0.5 M H ₂ SO ₄	-0.090 (vs. RHE)	84	[36]
A-MoS ₂	GC	–	Drop-cast	2 M HNO ₃	-0.080 (vs. RHE)	97	[48]
RGO-MoS ₂	GC	–	Drop-cast	0.5 M H ₂ SO ₄	-0.147 (vs. RHE)	36	[12]
RGO-MoS ₂	GC	20 μg	Drop-cast	0.5 M H ₂ SO ₄	-0.130 (vs. RHE)	75	[27]
MoS ₂ /MoSe ₂	CF	–	Chemical synthesis	0.5 M H ₂ SO ₄	-0.162 (vs. RHE)	61	[22]
MoS ₂	GC	–	Drop-cast	0.5 M H ₂ SO ₄	-0.185 (vs. RHE)	45	[42]
MoS ₂	GC	–	Drop-cast	0.5 M H ₂ SO ₄	-0.230 (vs. RHE)	–	[30]
MoS ₂ -g- CuNi ₂ S ₄	SPE	0.30 mg cm ⁻²	Drop-cast	0.5 M H ₂ SO ₄	– 0.05 (vs. RHE)	29	This work

Key: CD/MoS₂; carbon nanodot MoS₂ ensembles, GC; glassy carbon, –; no value given, RHE; reversible hydrogen electrode, P; phosphorus, NF; nickel foam, H; heteronanorods *: produced by magnetron sputtering MoS₂ onto a nanocarbon substrate, SPE; screen-printed electrode, SCE; saturated calomel electrode, NC; nanocubes, MoS₂-PB/NG; Fe₄[Fe(CN)₆]₃ NC with MoS₂ N-doped on graphene; CC; Carbon cloth, NFL; Nickel foil, DAC; Defective activated carbon A-MoS₂; Acid engineered, RGO; Reduced graphene oxide, CF: Carbon fibre

Table 2. XPS elemental quantification of the CuNi₂S₄, g-CuNi₂S₄, MoS₂-CuNi₂S₄ and MoS₂-g-CuNi₂S₄ nanocomposites.

Element Composition (%)	CuNi ₂ S ₄	g-CuNi ₂ S ₄	MoS ₂ -CuNi ₂ S ₄	MoS ₂ -g-CuNi ₂ S ₄
Cu 2p _{3/2}	3.14	2.33	2.06	2.72
Ni 2p _{3/2}	5.72	5.37	4.11	4.41
O 1s	29.95	18.11	15.54	13.30
N 1s	7.88	3.97	2.73	4.28
C 1s	33.97	58.74	57.33	57.06
S 2p	19.33	11.48	15.95	17.04
Mo 3d	-	-	2.28	1.19

Table 3. XPS quantification of sulfur containing components of the CuNi₂S₄, g-CuNi₂S₄, MoS₂-CuNi₂S₄ and MoS₂-g-CuNi₂S₄ nanocomposites.

Sample	Atom % S	binding energy of 2p ₃ (eV)	% of total S	atom %	Chemical state
CuNi ₂ S ₄	19.33	161.1	36.69	7.09	metal-S
		162.5	22.12	4.28	metal bonded organic S <i>e.g.</i> metal-S-C
		164.6	5.89	1.14	organic S <i>e.g.</i> C-S
		168.5	35.3	6.82	sulfate, SO ₄ ²⁻
graphene-CuNi ₂ S ₄	11.48	161.9	31.81	3.65	metal-S
		163.1	43.86	5.04	metal bonded organic S <i>e.g.</i> metal-S-C
		164.4	13.86	1.59	organic S <i>e.g.</i> C-S
		168.4	10.48	1.2	sulfate, SO ₄ ²⁻
MoS ₂ -CuNi ₂ S ₄	15.95	161.4	40.02	6.38	metal-S
		162.6	45.56	7.27	metal bonded organic S <i>e.g.</i> metal-S-C
		164.4	6.77	1.08	organic S <i>e.g.</i> C-S
		167.7	6.66	1.06	sulfate, SO ₄ ²⁻
MoS ₂ -g-CuNi ₂ S ₄	17.04	161.5	48.83	8.32	metal-S
		162.7	36.55	6.23	metal bonded organic S <i>e.g.</i> metal-S-C
		164.6	6.57	1.12	organic S <i>e.g.</i> C-S
		168.4	8.04	1.37	sulfate, SO ₄ ²⁻

Figure 1. Transmission electron microscopy (TEM) MoS₂-g-CuNi₂S₄ nanocomposite. Five sites of energy-dispersive X-ray (EDX) analysis are shown in (B) with the corresponding elemental compositions given in Table S1.

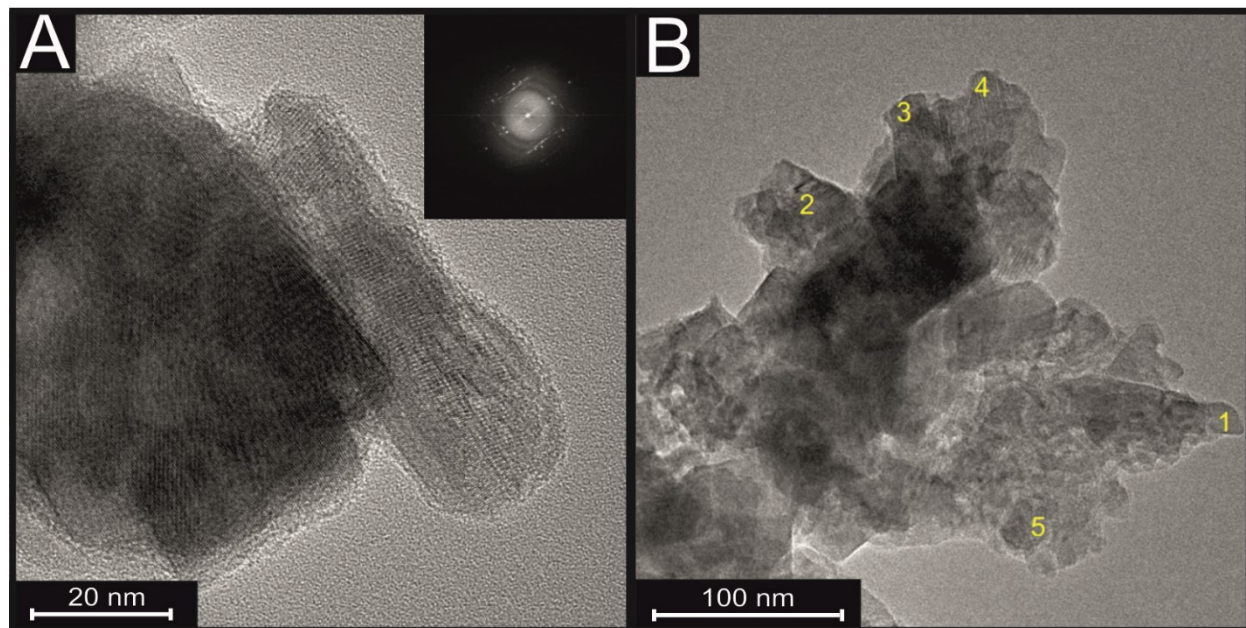


Figure 2. Physicochemical characterisation of the synthesized MoS₂-g-CuNi₂S₄ nanocomposites with FTIR (A), Raman (B), XPS (C) and XRD (D).

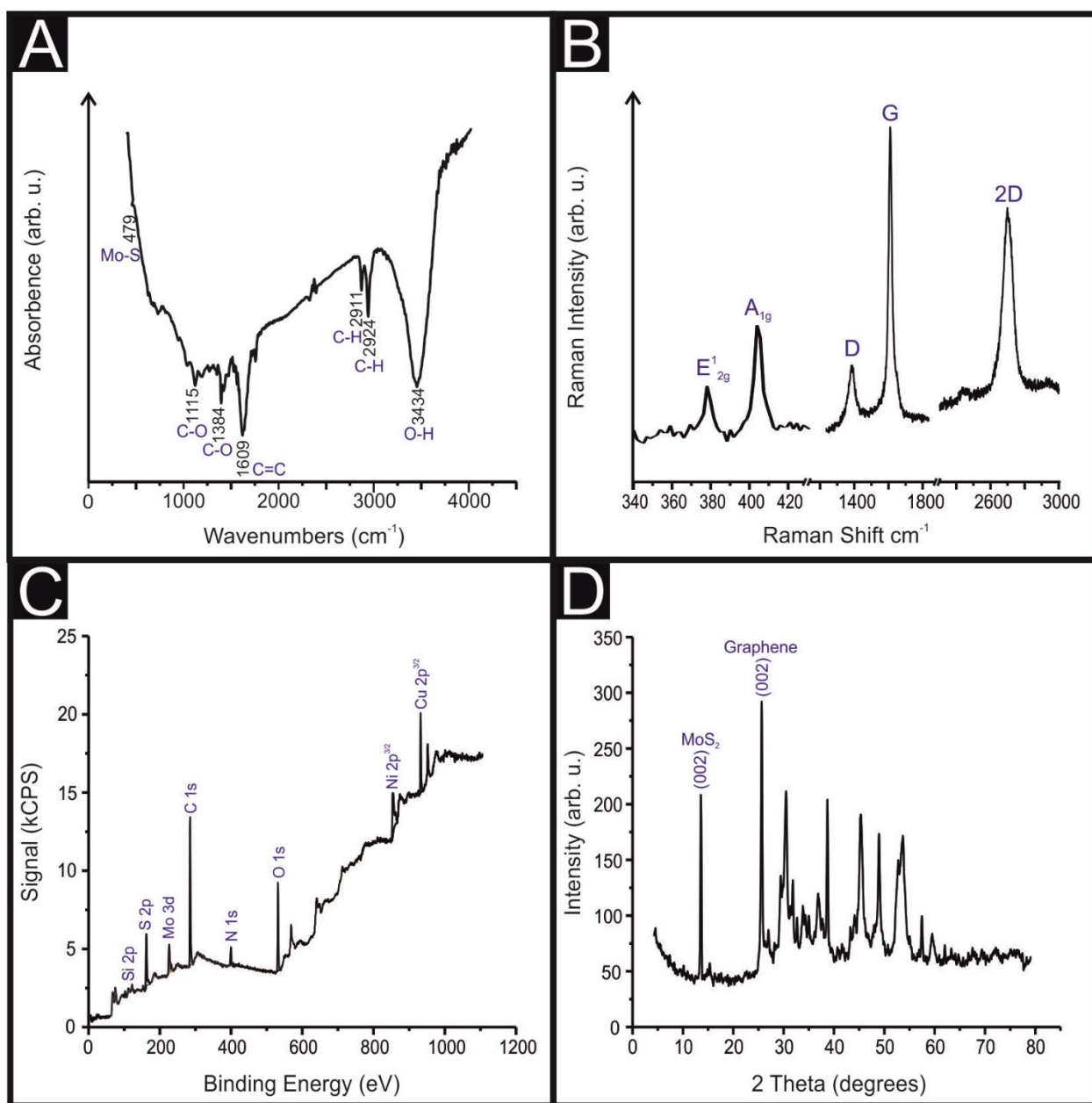
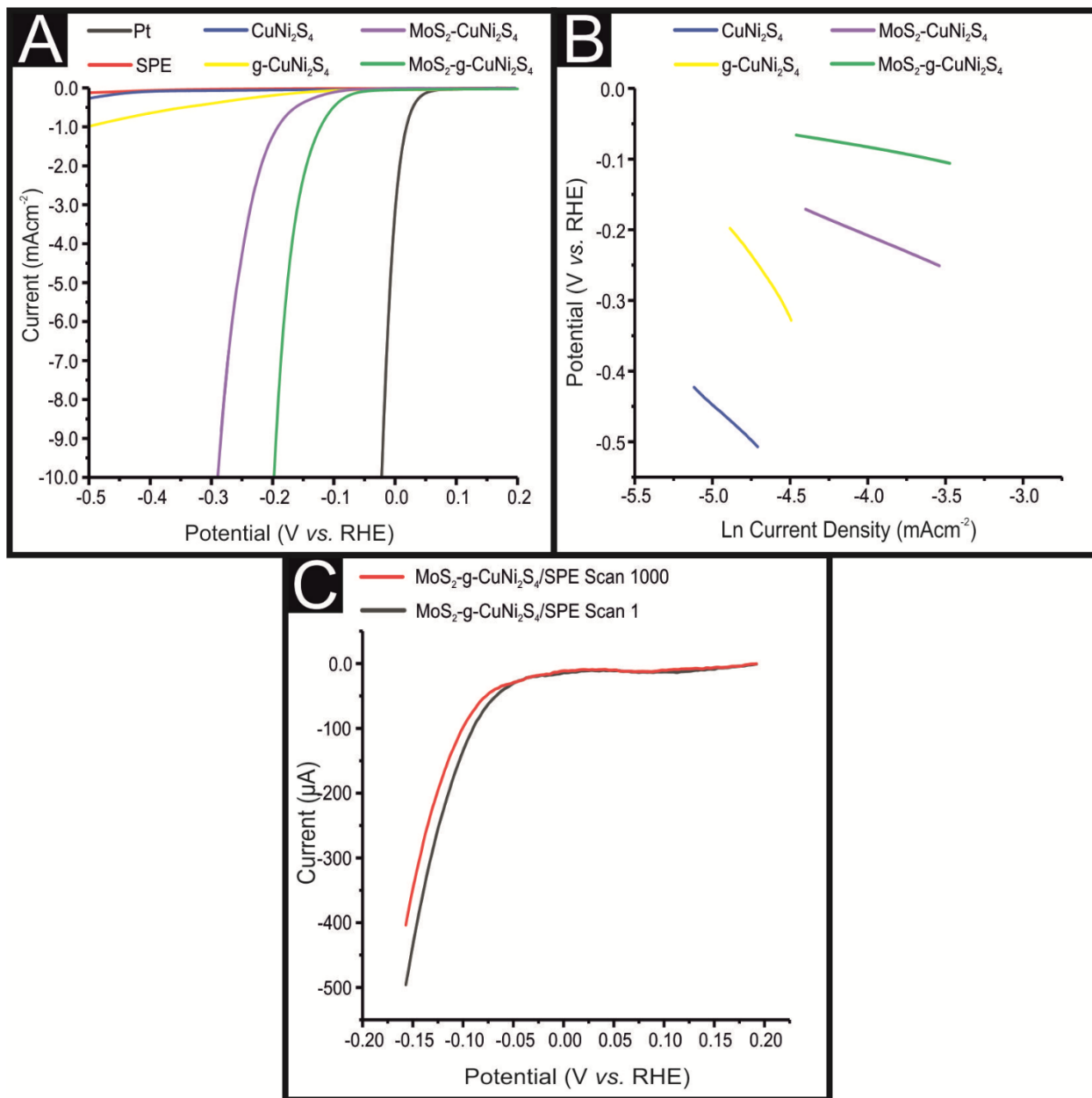


Figure 3. (A) Linear sweep voltammetry of unmodified and various modified electrodes showing HER activity of a bare/unmodified SPE, polycrystalline platinum electrode, CuNi₂S₄/SPE, g-CuNi₂S₄/SPE, MoS₂-CuNi₂S₄/SPE and MoS₂-g-CuNi₂S₄/SPE, Solution composition: 0.5 M H₂SO₄; Scan rate: 20 mVs⁻¹ (vs. RHE). (B) Tafel slopes corresponding to the Faradaic regions of the LSVs shown in (A). (C) Cyclic stability examination of a 10% MoS₂-g-CuNi₂S₄/SPE *via* LSV (scan rate: 100 mV s⁻¹ (vs. RHE)) was performed between the potential range of 0 to -0.35 V, repeated for 1000 cycles, this figure shows the first scan (black line), 1000th (red line).



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