

# **2D Nanosheet Molybdenum Disulphide (MoS<sub>2</sub>) Modified Electrodes Explored Towards the Hydrogen Evolution Reaction**

Samuel J. Rowley-Neale<sup>1</sup>, Dale A. C. Brownson<sup>1</sup>, Graham C. Smith<sup>2</sup>, David A. G. Sawtell<sup>1</sup>,  
Peter J. Kelly<sup>1</sup> and Craig E. Banks<sup>1\*</sup>

*<sup>1</sup>: Faculty of Science and Engineering, School of Science and the Environment,  
Division of Chemistry and Environmental Science, Manchester Metropolitan University,  
Chester Street, Manchester M1 5GD, UK.*

*<sup>2</sup>: Faculty of Science and Engineering, Department of Natural Sciences, University of  
Chester, Thornton Science Park, Pool Lane, Ince, Chester CH2 4NU, UK.*

\*To whom correspondence should be addressed.

Email: [c.banks@mmu.ac.uk](mailto:c.banks@mmu.ac.uk); Tel: ++(0)1612471196; Fax: ++(0)1612476831

Website: [www.craigbanksresearch.com](http://www.craigbanksresearch.com)

## Abstract

We explore the use of two-dimensional (2D) MoS<sub>2</sub> nanosheets as an electro-catalyst for the Hydrogen Evolution Reaction (HER). Using four commonly employed commercially available carbon based electrode support materials, namely edge plane pyrolytic graphite (EPPG), glassy carbon (GC), boron-doped diamond (BDD) and screen-printed graphite electrodes (SPE), we critically evaluate the reported electro-catalytic performance of unmodified and MoS<sub>2</sub> modified electrodes towards the HER. Surprisingly, current literature focuses almost exclusively on the use of GC as an underling support electrode upon which HER materials are immobilised. 2D MoS<sub>2</sub> nanosheet modified electrodes are found to exhibit a coverage dependant electrocatalytic effect towards the HER. Modification of the supporting electrode surface with an optimal mass of 2D MoS<sub>2</sub> nanosheets results in a lowering of the HER onset potential by *ca.* 0.33, 0.57, 0.29 and 0.31 V at EPPG, GC, SPE and BDD electrodes compared to their unmodified counterparts respectively. The lowering of the HER onset potential is associated with each supporting electrodes individual electron transfer kinetics/properties. The effect of MoS<sub>2</sub> coverage is also explored. We reveal that its ability to catalyse the HER is dependent on the mass deposited until a critical mass of 2D MoS<sub>2</sub> nanosheets is achieved, after which its electrocatalytic benefits and/or surface stability curtail. The active surface site density and turn over frequency for the 2D MoS<sub>2</sub> nanosheets is determined, characterised and found to be dependent on both the coverage of 2D MoS<sub>2</sub> nanosheets and the underlying/supporting substrate. This work is essential for those designing, fabricating and consequently electrochemically testing 2D nanosheet materials for the HER.

**Keywords:** Molybdenum disulphide (MoS<sub>2</sub>); Hydrogen evolution reaction; Hydrogen economy; Carbon; 2D Electrochemistry; Sustainability.

## 1. Introduction

The increasing scarcity of fossil fuels coupled with the consequences of anthropogenic climate change has produced a global need to find feasible alternatives to energy generation.<sup>1-3</sup> One scenario of change is creating a global hydrogen economy in which energy generation demands are met partially or entirely by hydrogen fuel cells.<sup>4-6</sup> Utilising hydrogen fuels in this manner would cause a dramatic decrease in the anthropogenic greenhouse emissions and ozone precursors released by fossil fuel combustion given that the major product of hydrogen oxidation is H<sub>2</sub>O.<sup>4,7</sup> The main barrier to the implementation of such a hydrogen economy is, of course, the production of hydrogen. This requires an energy input that could feasibly be drawn from renewable energy sources such as wind, solar, and wave.<sup>3,8-10</sup>

A common method of hydrogen production is the Hydrogen Evolution Reaction (HER) ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ), which involves the electrocatalytic splitting of water, known to occur *via* one of two routes; these being either the Volmer-Tafel or the Volmer-Heyrovsky reactions.<sup>11,12,13</sup> The efficiency of the HER is dependent on the choice of electrocatalyst, with an optimal catalyst having a binding energy for adsorbed H<sup>+</sup> close to that of the reactant or product.<sup>7</sup> Currently, the most proficient catalyst for the HER is platinum (Pt) which has a small binding energy for the reaction to occur, resulting in the reaction proceeding at a near zero over-potential.<sup>7,11,14,15</sup> Pt is a precious metal with a low natural abundance of 0.001–0.005 mg kg<sup>-1</sup> within the Earth's crust. This coupled with its high demand result in Pt having a very high cost.<sup>16</sup> Consequently, current research is focused on finding a cheaper, more sustainable catalyst for the HER whilst maintaining performance and offering a binding energy towards H<sup>+</sup> close to that of Pt,<sup>7</sup> thus making a hydrogen based energy economy substantially more feasible.

Carbon based materials have long been utilised as electrodes in a plethora of analytical and industrial electrochemical applications.<sup>17-23</sup> They have the distinct advantage of being comparatively cheap and easily obtainable compared to the traditional noble metal based electrodes, particularly out-performing said metals in numerous significant areas due to carbon's structural polymorphism, chemical stability, wide operable potential windows and relative inert electrochemistry.<sup>17,18</sup> Carbon based electrodes are often used as the supporting material for a plethora of electrocatalytic materials which lower HER onset potentials and thus greatly improve the HER kinetics in comparison to the bare/unmodified carbon based electrode.<sup>1,7,24-28</sup>

One example of where modified electrodes have been utilised to improve the HER has been reported by Liu, *et al.*<sup>29</sup> who utilised carbon nanotubes decorated with CoP nanocrystals deposited onto GC electrodes with a coverage of  $0.285 \text{ mg cm}^{-2}$  which resulted in the onset potential for the HER to reduce by to  $-40 \text{ mV}$ . Other prominent examples from the literature have used graphene as electrocatalyst supports.<sup>24, 27, 30, 31</sup> The current challenge within HER research is finding a low-cost, abundantly available, non-polluting catalyst which is capable of matching the HER onset potential observed when Pt is used as a catalyst. Towards this goal, Mo based catalysts have been explored towards the HER. Table 1 presents a through literature overview of Mo based electrocatalysts explored towards the HER which is a combination and adaptation of work presented in papers by Joesen, Li and Ji<sup>32-34</sup> in addition to recent literature reports. It is evident that  $\text{MoS}_2$  and  $\text{MoSe}_2$  have shown promising results as HER catalysts.  $\text{MoS}_2$  is a semiconductor with a direct band gap of *ca.*  $1.9 \text{ eV}$  and excellent charge carrier mobility (reported to be no less than  $200 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ ).<sup>35</sup> It has been beneficially implemented in numerous electrochemical applications, such as in transistors, sensors, solar cells, and lithium ion batteries.<sup>1, 36, 37</sup>

Researchers have directed attention towards 2D  $\text{MoS}_2$  where a single layer comprises of two monoatomic planes of hexagonally arranged sulphur atoms linked to molybdenum atoms<sup>7, 38</sup> and have been reported to be electrocatalytic towards the HER.<sup>26, 27, 34, 38</sup> For example,  $\text{MoS}_2$  has been reported to exhibit electrocatalytic behaviour, attributed to it having a Density Function Theory (DFT) calculated binding energy towards  $\text{H}^+$  of  $+0.08 \text{ eV}$  at its edge.<sup>7</sup> Such catalytic activity was however, shown to be anisotropic, with the basal plane of the  $\text{MoS}_2$  nanosheet being relatively inert and the exposed sulphur edges being the active sites of electron transfer.<sup>7, 13, 26, 33, 39, 40</sup> Resultantly, highly defected sheets of  $\text{MoS}_2$  have a greater catalytic activity due to the larger number of exposed edges.<sup>14</sup> The  $\text{MoS}_2$  edge-terminated sites have high energy kinetics,<sup>26</sup> thus making their production difficult as thermodynamic instability results in the active edges forming fullerene-like structures, which have few exposed edge sites.<sup>26</sup> In its ‘bulk’ form,  $\text{MoS}_2$  is an inefficient HER catalyst due to it possessing a low ratio of exposed electroactive edges to inert basal-like planes and a high resistance resulting in slow ion transfer.<sup>1, 34, 41</sup> Interestingly, 2D  $\text{MoS}_2$  nanosheets have been reported to possess  $13\times$  more active sites compared to the alternative bulk  $\text{MoS}_2$ .<sup>42, 50</sup>

Throughout the current literature (see Table 1) glassy carbon (GC) has been exclusively used as a supporting electrode material, with few attempts to use alternative carbon based supports;

this is clearly evident from inspection of Table 1.<sup>21, 34, 43-45</sup> For instance, Voiry, et al.<sup>43</sup> reported a low HER onset potential of *ca.* 100 mV for the HER using typical MoS<sub>2</sub> nanosheets deposited on a GC electrode. Yu, et al.<sup>46</sup> demonstrated a layer dependent electrocatalysis using MoS<sub>2</sub> (grown *via* chemical vapour disposition (CVD)) deposited on GC which is correlated with electron hopping in the vertical direction of the MoS<sub>2</sub> layers. Other work utilising modified GC electrodes has demonstrated that edge exposed MoS<sub>2</sub> nanosheets are efficient HER catalysts and that bulk MoS<sub>2</sub> has low activity.<sup>42, 47</sup> This work indicates that an MoS<sub>2</sub> structure with a greater proportion of MoS<sub>2</sub> edge sites to basal planes will likely give rise to improved HER kinetics, with an optimal material having a small geometric basal plane contribution (which is reportedly less active to the HER).<sup>42</sup> It has been shown that electrocatalytic activity towards the HER correlates linearly with the number of MoS<sub>2</sub> edge sites.<sup>14</sup>

The above studies are elegant in their approaches towards HER; however, they are lacking significantly from not altering the underlying electrode material and in doing so neglecting the ability to de-convolute the true electrochemical performance of 2D MoS<sub>2</sub> nanosheets. It is also important to realise that a cheap electrode support will be required in the application of electrocatalysts utilised in the HER. Graphite screen-printed electrodes (SPEs) meet this criteria due their advantages over other carbon based electrodes which include scales of economy resulting in ultra-low cost of production, competitive electron transfer performance/properties, versatility, and the ability to tailor and mass-produce such electrodes.<sup>48</sup> Note that the performance of MoS<sub>2</sub> can only be truly understood *via* immobilisation using a range of support materials with varying electrode kinetics (electrochemical activities). Such control experiments are explored herein which are usually overlooked in the current literature. Secondly, it is usual practise within the literature to modify electrodes with only one mass (coverage) of MoS<sub>2</sub>, which again makes it difficult to extrapolate a true understanding of 2D MoS<sub>2</sub> nanosheets electrochemical behaviour; again this critical parameter is explored in this paper.

Inspired by the above insights and attempts in the literature to utilise MoS<sub>2</sub> as an alternative catalyst to Pt for the HER, this paper explores the use of 2D MoS<sub>2</sub> nanosheet modified carbon based electrodes towards the possible electrocatalysis of the HER. The 2D MoS<sub>2</sub> nanosheets are thoroughly characterised with scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), UV-visual spectroscopy and X-ray photoelectron spectroscopy (XPS). Linear

sweep voltammetry is utilised to measure the onset of the HER with four carbon based electrodes as the underlying support materials, namely edge plane pyrolytic graphite (EPPG), glassy carbon (GC), boron-doped diamond (BDD) and screen-printed graphite electrodes (SPE). This work is distinct from the literature given that we explore a range of electrodes substrates, correlate our electrochemical responses with supplementary Raman mapping of the electrode surface (and other complementary physicochemical characterisation) and explore the effect of MoS<sub>2</sub> coverage; each noted component is routinely overlooked in the literature. We also benchmark the electrochemical performance of the 2D MoS<sub>2</sub> nanosheets towards the HER (utilising turn over frequency (ToF) calculations) and compare our results to Pt and literature reports.

## 2. Experimental section

All chemicals used were of analytical grade and were used as received from Sigma-Aldrich without any further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm and were vigorously degassed prior to electrochemical measurements with high purity, oxygen free nitrogen. The above ensures the removal of any trace of oxygen from test solutions, which if present would convolute the observed results for HER with the competing oxygen evolution reaction (OER); this is common practice in the literature.<sup>49,50</sup> All measurements were performed in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Electrochemical measurements were performed using an Ivium Compactstat<sup>TM</sup> (Netherlands) potentiostat. Measurements were carried out using a typical three electrode system with a Pt wire counter and a saturated calomel electrode (SCE) reference electrode. The working electrodes used were as follows: an edge plane pyrolytic graphite (EPPG) (Le Carbone, Ltd. Sussex, UK) electrode, which was machined into a 4.9 mm diameter, with the disc face parallel with the edge plane as required from a slab of highly ordered pyrolytic graphite (HOPG, highest grade available with a lateral grain size,  $L_a$  of 1–10 μm and  $0.4 \pm 0.1^\circ$  mosaic spread); a glassy carbon (GC) electrode (3 mm diameter, BAS, USA); a boron-doped diamond (BDD) electrode (3 mm diameter, BAS, USA); a Pt electrode (3 mm diameter, BAS, USA); and screen-printed graphite electrodes (SPE), which have a 3 mm diameter working electrode. The SPEs were fabricated in-house with appropriate stencil designs using a DEK 248 screen-printing machine

(DEK, Weymouth, U.K.). For their fabrication first, a carbon-graphite ink formulation (product code C2000802P2; Gwent Electronic Materials Ltd., U.K.) was screen-printed onto a polyester (Autostat, 250  $\mu\text{m}$  thickness) flexible film (denoted throughout as standard-SPE); these electrodes have been used extensively in other work.<sup>48, 51-53</sup> This layer was cured in a fan oven at 60  $^{\circ}\text{C}$  for 30 minutes. Next, a silver/silver chloride reference electrode was included by screen-printing Ag/AgCl paste (product code C2040308D2; Gwent Electronic Materials Ltd., U.K.) onto the polyester substrates. Finally, a dielectric paste (product code D2070423D5; Gwent Electronic Materials Ltd., U.K.) was then printed onto the polyester substrate to cover the connections. After curing at 60  $^{\circ}\text{C}$  for 30 minutes the SPEs are ready to be used. SPEs have been reported previously and shown to exhibit a heterogeneous electron transfer rate constant,  $k^o$ , of *ca.*  $10^{-3} \text{ cm s}^{-1}$ , as measured using the  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  redox probe.<sup>48, 54-57</sup> Note that for the purpose of this work, electrochemical experiments were performed using the working electrode of the SPEs only and that external reference and counter electrodes were utilised as detailed earlier to allow a direct comparison between all the utilised electrodes.

The 2D  $\text{MoS}_2$  nanosheets were commercially procured from ‘Graphene Supermarket’ (Reading, MA, USA).<sup>58</sup> The 2D  $\text{MoS}_2$  nanosheets have a reported purity of >99 % and are dispersed in ethanol at a concentration of 18  $\text{mg L}^{-1}$ .<sup>58</sup> The suspended flakes are reported to have an average lateral flake size of 100–400 nm and a thickness of between 1 and 8 monolayers.<sup>58</sup> The modification of each electrode was carried out using a drop casting approach, where an aliquot of the 2D  $\text{MoS}_2$  nanosheet suspension was deposited onto the desired supporting electrode surface using a micropipette.<sup>54</sup> This deposition was then allowed 5 minutes to dry (at 35  $^{\circ}\text{C}$ ) to ensure complete ethanol evaporation. Finally, the electrode was allowed to cool to ambient temperature, after which the process was repeated until the desired mass was deposited onto the surface. The electrode was then ready to use.

An Agilent 8453 UV-visible Spectroscopy System (equipped with a tungsten lamp assembly, G1315A, 8453 for absorption between 250 nm and 1500 nm and a deuterium lamp, 2140-0605 for absorption between 200 nm and 400 nm) was used to obtain the absorption spectroscopy. The absorption spectra was analysed using the UV-Visible ChemStation software. Scanning electron microscope (SEM) images and surface element analysis were obtained using a JEOL JSM-5600LV model SEM equipped with an energy-dispersive X-ray microanalysis (EDS) package. Raman Spectroscopy was next 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. XRD was performed using an “X’pert powder PANalytical model” with a copper source of  $K_{\alpha}$  radiation (of 1.54 Å) and  $K_{\beta}$  radiation (of 1.39 Å), using a thin sheet of nickel with an absorption edge of 1.49 Å to absorb  $K_{\beta}$  radiation. The Omega was set to 3.00 and the  $2\theta$  range was set between 10 and 100  $2\theta$  in correspondence with literature.<sup>32</sup> Additionally, to ensure well defined peaks an exposure of 100 seconds per  $2\theta$  step was implemented. 2D MoS<sub>2</sub> nanosheets were utilised after deposition onto a sterilised glass slide (coated with excess 2D MoS<sub>2</sub> nanosheets in ethanol then allowed to dry). The XPS data was acquired using a bespoke ultra-high vacuum system fitted with a Specs GmbH Focus 500 monochromated Al K $\alpha$  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.<sup>59</sup> Survey spectra were acquired over the binding energy range 1100 – 0 eV using a pass energy of 50 eV and high resolution scans were made over the C 1s and O 1s lines using a pass energy of 20 eV. Under these conditions the full width at half maximum of the Ag 3d<sub>5/2</sub> reference line is  $\sim 0.7$  eV. In each case, the analysis was an area-average over a region approximately 1.4 mm in diameter on the sample surface, using the 7 mm diameter aperture and lens magnification of  $\times 5$ . The energy scale of the instrument is calibrated according to ISO 15472, and the intensity scale is calibrated using an in-house method traceable to the UK National Physical Laboratory.<sup>60</sup> Data were quantified using Scofield cross sections corrected for the energy dependencies of the electron attenuation lengths and the instrument transmission.<sup>61</sup> Data interpretation was carried out using CasaXPS software v2.3.16.<sup>62</sup>

### **3. Results and Discussion**

#### *3.1 Characterisation of 2D MoS<sub>2</sub> nanosheets*

##### *3.1.1 UV-VIS and lateral grain size calculations*

The lateral length ( $L_a$ ) and number of the commercially procured 2D MoS<sub>2</sub> nanosheets can be readily deduced from absorption spectroscopy. It has been observed that actually the terminology is more correctly optical extinction spectroscopy since the optical beam interacts with the dispersed nanosheets by both absorption and scattering.<sup>63-65</sup> The extinction coefficient of



dispersed 2D MoS<sub>2</sub> nanosheets is 6,820 L g<sup>-1</sup> m<sup>-1</sup> at the local minimum of 345 nm, using this information along with a spectra it is possible to determine the concentration of dispersed 2D MoS<sub>2</sub> nanosheets. <sup>64</sup> Varrla *et al* <sup>63</sup> uses this information to calculate the concentration as a function of mixing parameters whilst also showing that the extinction spectra can be used to determine information regarding the 2D MoS<sub>2</sub> nanosheet length and thickness. ESI Figure 1 shows the optical extinction spectra of the commercially procured MoS<sub>2</sub> nanosheets which are dispersed in ethanol. It is readily evident that the spectra displays A- and B- excitonic transitions as well as other pertinent features consistent with the 2H polytype of MoS<sub>2</sub> and is consistent with MoS<sub>2</sub> nanosheets produced *via* shear exfoliation. <sup>63, 64, 66</sup> The extinction spectrum of the 2D MoS<sub>2</sub> nanosheets allows one to readily determine the mean nanosheet lateral length due to the effect 2D MoS<sub>2</sub> nanosheet edges upon the spectral profile. The extinction spectrum also allows the number of layers (thickness) to be determined as a result of quantum confinement effects causing a well-defined shift A-exciton position corresponding to nanosheet thickness. <sup>64</sup> The lateral length,  $L(\mu\text{m})$  of the MoS<sub>2</sub> can be deduced from the following equation:

$$L(\mu\text{m}) = \frac{3.5(Ext_B / Ext_{345}) - 0.14}{11.5 - (Ext_B / Ext_{345})} \quad [1]$$

where  $(Ext_B / Ext_{345})$  is the ratio of extinction at the B-excitation to that at 345 nm since the spectral profile is dependent upon the lateral length of the MoS<sub>2</sub>. Further information can be obtained in terms of the number of nanosheets,  $N_{MoS_2}$  expressed as the number of monolayers per nanosheet can be determined from the wavelength associated with the A-excitation, since the quantum confinement effects result in well-defined shifts in the A-excitation position with the thickness of the nanosheet; this is summarized by the following equation:

$$N_{MoS_2} = 2.3 \times 10^{36} e^{-54888 \lambda_A} \quad [2]$$

From the spectra presented in ESI Figure. 1 the lateral length and number of MoS<sub>2</sub> nanosheets are determined to correspond to 61.5 nm and 3 (2.89) respectively. We note that the lateral size is smaller than the value given by the commercial supplier. The average of 3 monosheets per

nanosheets agrees strongly with the commercial supplier who notes the number of monolayers per nanosheet to be between 1-8 in solution.<sup>58</sup> It is important to point out that the lateral size and the number of MoS<sub>2</sub> sheets are for when these are in solution; when immobilised upon a surface these will deviate from these measured values, as we will see later, but is a common issue in the whole of the literature.

### 3.1.2 SEM, TEM, Raman, EDS and XRD

Independent physicochemical characterisation of the 2D MoS<sub>2</sub> nanosheets was performed. SEM and TEM images of the commercially sourced 2D MoS<sub>2</sub> nanosheets are shown in ESI Figures. 2 and 3. Despite some aggregation, which is the case for all nanosheet materials, upon close inspection, their appearance is within the acceptable widths with a lateral size of *ca* 100-400 nm evident as quoted by the supplier and measurements undertaken above. The 2D MoS<sub>2</sub> nanosheets immobilised upon the silicon wafer generally exhibit a uniform coverage. Complimentarily EDS mapping analysis was performed to offer insight into the elemental composition of the area shown in ESI Figure 2. Analysis of the EDS map shows uniform distribution of Mo and S atoms with a ratio of 0.55% At. and 1.35% At. and this composition correlates with expected values for the structure of 2D MoS<sub>2</sub> nanosheets (*ca.* 1:2 ratio of Mo and S respectively) agreeing with independent literature.<sup>35</sup> Additionally, XRD analysis showed characteristic peaks for MoS<sub>2</sub> with  $2\theta$  corresponding to 14 indicating the presence of MoS<sub>2</sub> via the reflection of separated MoS<sub>2</sub> layers, see ESI Figure. 4 which is in agreement with literature reports.<sup>32, 41</sup> The peak at 28  $2\theta$  is attributed to the supporting glass slide. Last, the Raman spectra for the 2D MoS<sub>2</sub> nanosheets after deposition on a serialised silicon disk are presented in Figure 1. The characteristic peaks associated with MoS<sub>2</sub> at *ca.* 380 and 405 cm<sup>-1</sup> are clearly evident, corresponding to that reported in the literature.<sup>67</sup> Further analysis is described later where Raman mapping is utilised to explore MoS<sub>2</sub> mass modifications deposited onto electrode surface.

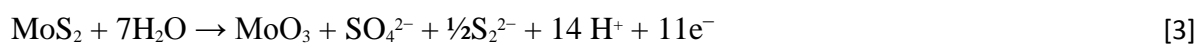
### 3.1.3 XPS

MoS<sub>2</sub> nanosheets suspended in ethanol were prepared for X-ray photoelectron spectroscopy (XPS) analysis by pipetting a few drops of the suspension onto a fragment of a clean Si (111) wafer and allowing the ethanol to evaporate. The XPS spectrum is shown in ESI Figure 5 and the results of the surface composition analysis (excluding hydrogen) are shown in ESI Table

1. The C and O present is likely a result of residuals from the ethanol used to disperse the MoS<sub>2</sub>. This is supported by the presence of a component peak at *ca.* 286.6 eV showing that alcohol groups were present on the sample surface. The Si present can be accounted for by the use of a Si (111) wafer as an underlying support material for the drop coating. Na is likely present from an organic Na contaminant or *via* contributions from the supporting wafer. The Mo to S % atomic concentrations are observed at a 1:2.2 ratio respectively, agreeing well with the Raman and EDS analysis performed above (further indicating the presence of the target material). Shin et al.<sup>68</sup> theorises the deviation from an expected stoichiometry ratio of 1:2 for Mo and S respectively in 2D MoS<sub>2</sub> nanosheets is due to the presence of MoS<sub>3</sub>.<sup>63</sup> It is of note that Mo is present in three valence states, with each of the valence states consisting of a Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> doublet. The curve-fitted high resolution Mo 3d spectral region is shown in ESI Figure 6. The area ratios of the doublets are constrained to the ratios of the Scofield cross sections (*i.e.* Mo 3d<sub>3/2</sub> = 0.6904 x Mo 3d<sub>5/2</sub>), the two components of each doublet are constrained to the same line shape and ‘full width at half maximum’, and their separations are fixed at the known reference value of 3.13 eV. The 3d<sub>5/2</sub> components were found at 229.4 eV (Mo<sup>4+</sup>), 231.6 eV (Mo<sup>5+</sup>) and 233.1 eV (Mo<sup>6+</sup>). The spectral region also includes the S 2s peak at 226.6 eV.

### 3.2 Electrochemical activity at assigned coverage

The electrochemical response of the 2D MoS<sub>2</sub> nanosheets (1266.7 ng cm<sup>-2</sup>) immobilised upon SPEs were studied using cyclic voltammetry (CV). Figure. 2 shows a typically observed CV where two oxidation peaks at + 0.65 and + 1.0 V are clearly visible in the first cycle followed by several minor reduction peaks in the – 0.5 to – 1.5 V range. The initiation of the HER is evident in the cathodic response, with an onset potential of *ca* 1.1 V. In terms of the anodic response, the two prominent oxidation peaks are due to irreversible reactions, likely the oxidation of Mo<sup>4+</sup> to Mo<sup>6+</sup> at edge and basal sites. Such oxidations are not observable in subsequent scans, which is likely due to the MoO<sub>3</sub> dissolving into solution or being reduced to Mo<sup>3+</sup>, at which point it dissolves, explaining the origin of the observed reduction peak. This is represented in the equation below.<sup>69</sup>



It may also be possible that the Mo within our 2D MoS<sub>2</sub> nanosheets has two dominant valence

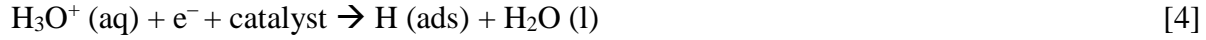
states, both of which are oxidised, resulting in the presence the double peak. This inference is supported by the independent XPS analysis (see earlier), which indicated the presence of Mo in three different valance states for the 2D MoS<sub>2</sub> nanosheet sample analysed. The double oxidation peak observed in Figure. 2 is of interest and further study is required to determine its exact cause. The observed voltammetry (see Figure 2) is in good agreement with Bonde et al. <sup>69</sup> who explored nano-MoS<sub>2</sub>, deposited onto toray carbon paper in 0.5 M H<sub>2</sub>SO<sub>4</sub>, towards the HER. If the potential window is kept below the range where reported oxidation peaks occur, the HER activity of nano-MoS<sub>2</sub> remains stable.<sup>70</sup> The reduction peaks can also be accounted for by the reduction of S<sub>2</sub><sup>2-</sup> to H<sub>2</sub>S.<sup>69</sup> The double oxidation peak has previously been mischaracterised as a single oxidation peak due to the peaks merging occurring as a result of performing cyclic voltammetry at too high a scan rate.<sup>71</sup> This is important to note as the double peak convolutes the understanding of the electrochemical process occurring.

Next, attention was turned to benchmarking our electrochemical system for the HER using commonly available electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub>, as is widespread practise within the literature.<sup>14, 69, 72</sup> As is evident in Figure. 3(A), the four unmodified carbon based electrodes are all significantly inferior to a Pt electrode with respect to the potential required for HER onset and the current density reached. Note that the onset of HER is analysed as the potential at which the observed current initially begins to deviate from background current. This is to be expected with Pt being a pure metal which has a very small binding energy for H<sup>+</sup>.<sup>7</sup> It is evident that the onset potential for the HER occurs at *ca.* -1.05, -0.78, -0.76-0.73, and -0.25 V at the GC, EPPG, BDD, SPE, and Pt electrodes respectively. The SPEs exhibit the lowest onset potential for the HER when compared to all of the carbon-based electrodes utilised herein. The bare GC electrode exhibited the largest HER onset potential, indicating that it is not a beneficial electrode for the HER.

It is of note that the current density obtained at each of the unmodified electrodes towards the HER and how this progressively alters during the course of the measurement. Although it is apparent that a higher potential is required to initiate the HER at the GC electrode (by *ca.* -0.3 V in contrast to the alternative carbon based electrodes), the current density recorded at this electrode appears to surpass that of the alternative materials.

### 3.2.1 Tafel analysis

A common approach in the literature is to employ Tafel analysis allowing the most likely electrochemical process to be theorised. Literature has suggested three possible steps in the reaction, each of which is capable of being the rate-determining step of the HER; this analysis is dependent on the corresponding Tafel slope. The initial H<sup>+</sup> discharge step being the Volmer reaction, leading to the following equation:<sup>11-13</sup>



$$\frac{2.303RT}{\alpha F} \approx 120\text{mV}$$

The Volmer step can then be followed by one of two possible steps; either the Heyrovsky step:



$$\frac{2.303RT}{(1+2)F} \approx 40\text{mV}$$

or the Tafel step:



$$\frac{2.303RT}{2F} \approx 30\text{mV}$$

where the transfer coefficient ( $\alpha$ ) 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 at. The values from the Tafel analysis (presented below each equation) are an indication of the reaction mechanism. Tafel analysis was performed on the Faradaic sections of the LSV plots which can be observed in Figure. 3(A). Tafel analysis was performed on the data presented in Figure. 3(A) where the corresponding analysis is presented in Figure. 3(B), which yielded Tafel values of *ca.* 89.2, 64.4, 94.4 and 81.2 mV dec<sup>-1</sup> for the unmodified EPPG, GC, SPE and BDD electrodes respectively. Using the above values for the unmodified electrodes, interpretation of the Tafel slopes reveals that the adsorption Volmer step is likely rate limiting for the SPE and EPPG electrodes. The discharge Heyrovsky step is most likely the rate limiting step at the GC

electrode.<sup>11-13</sup> In the case of BDD, Tafel analysis does not allow a definitive mechanism to be estimated.

We next explore the use of 2D MoS<sub>2</sub> nanosheet modified carbon based electrodes towards the HER. As detailed in the introduction, the aim of this paper is to tackle the current issue of finding a cheap, more abundant, electrocatalyst alternative to Pt for the HER.<sup>7, 11</sup> We investigate the potential current state of the art (2D MoS<sub>2</sub> nanosheets) and compare this to our benchmarking experiments with the aim of revealing valuable insights. First, the range of carbon based electrodes utilised above (namely GC, BDD, EPPG and SPEs) are modified with different masses of the 2D MoS<sub>2</sub> nanosheets. Note that using various underlying support materials is seldom seen in the current literature and thus it is important that such control experiments are explored and reported herein for the first time. Inspection of Figure. 4(A) reveals that using a 1267 ng cm<sup>-2</sup> modification of 2D MoS<sub>2</sub> nanosheets results in a lowering of the potential required for onset of the HER and is accompanied by an increase in the observed current density, signifying an improved electrochemical response at each of the underlying electrode substrates utilised. Specifically, the HER onset potential was lowered to *ca.* -0.45, -0.48, -0.44 and -0.45 V for EPPG, GC, SPE, and BDD electrodes respectively. Clearly, these newly obtained values are significantly closer to the reported value using a Pt electrode (*ca.* -0.25 V) than the initial values reported above at the unmodified carbon based electrodes. This implies that the 2D MoS<sub>2</sub> nanosheets are effective electrocatalysts for the HER.

Tafel analysis was performed on the modified LSV profiles. Tafel slope values of *ca.* 74.7, 41.4, 90.0, and 90.9 mV dec<sup>-1</sup> were estimated at the EPPG, GC, SPE and BDD electrodes respectively (shown in Figure. 4(B)). Comparison of the Tafel values suggests that modification of the support electrodes with 2D MoS<sub>2</sub> nanosheets does not cause a significant alteration in the mechanism or indeed the Faradic current density of the HER.<sup>42</sup> This however, is not the case when utilising the GC electrode, which exhibited a reasonable increase in current density resulting in the ‘discharge Heyrovsky’ step more likely becoming the rate limiting step. This implies that modification with the 2D MoS<sub>2</sub> nanosheets allows for increased and sufficient H<sup>+</sup> adsorption, thus in turn catalysing the HER process.

In terms of analysing the current densities obtained, deposition of the 2D MoS<sub>2</sub> nanosheets at a coverage of 1266.7 ng cm<sup>-2</sup> induces higher exchange current densities when compared to the unmodified alternative. It is likely that this results from the early onset of the HER (*i.e.* the

decreased over-potential) and is not directly due to an overall increased reaction rate at the modified SPE and BDD electrodes given that comparison is based on analysis at specific potentials. For the GC and EPPG electrodes there was an increase in the current density, which is due not only the earlier HER onset potential but also an increased current density slope. This is likely a result of the structure of MoS<sub>2</sub> on these electrodes having a high number of exposed active edge sites allowing for a greater amount of H<sup>+</sup> adsorption.

### *3.3 Electrochemical activity at differing 2D MoS<sub>2</sub> nanosheet coverages*

#### *3.3.1 Raman analysis*

The experimental data discussed above considers the use of 1267 ng cm<sup>-2</sup> (2D MoS<sub>2</sub> nanosheet) modified electrodes. Currently it is common practice in the literature to choose only one mass of MoS<sub>2</sub> coverage when exploring its electrochemical performance (in addition to exploring this on only one underlying electrode surface, typically GC). As highlighted in the introduction, this practice results in convoluted interpretations of the performance of 2D MoS<sub>2</sub> nanosheets and thus diligent controls are required in order to reveal the true electrochemical response. We next consider this parameter and explore the effects of different mass coverages of 2D MoS<sub>2</sub> nanosheets on a given electrode.

In order to ascertain the level of MoS<sub>2</sub> coverage and relate this to the observed voltammetry, we first investigate the respective Raman properties of our modified electrodes. Figure. 5 depicts the effect that larger deposition quantities of MoS<sub>2</sub> onto a SPE has upon the recorded Raman Spectroscopy, where the evolution of the two characteristic peaks is evident and is discussed in more detail below. We first analyse the effect of coverage on the electrode surface using Raman mapping and a SPE as the underlying support material (as a representative model). Through comparison of the underlying graphite peak area at *ca.* 1550 cm<sup>-1</sup> against the area of the MoS<sub>2</sub> Raman peaks at *ca.* 380 and 405 cm<sup>-1</sup>, the surface area coverage of the electrode was investigated. It is evident that increasing the mass deposition of MoS<sub>2</sub> on the SPE surface results in an increased intensity in the respective assigned Raman peaks (see Figure. 5(A)). Raman maps are presented in Figure. 6 which concur with the previous inference and show that with increased mass deposition a thicker (largely uniform) layered coverage is achieved across the entire electrode surface. Through analysis of the respective Raman maps depicted in Figures. 6 and 7, it is likely that the deposition of 504 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets results in the complete coverage of the

underlying SPE support material (which has a surface area of 0.0707 cm<sup>2</sup>). With each additional modification this layer of deposited MoS<sub>2</sub> will thicken (see Figure. 7). It is possible to determine the stacking number by comparison of E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> vibrational bands (VB) as the observed Raman spectrum evolves with the number of layers present. The E<sub>2g</sub><sup>1</sup> VB results (at *ca.* 382 cm<sup>-2</sup>) due to the opposite vibration of two S atoms in respect to a Mo atom, whereas the A<sub>1g</sub> peak (at *ca.* 407 cm<sup>-2</sup>) represents the S atoms vibrating in opposite directions and out of plane.<sup>67, 73</sup> Literature suggests that as MoS<sub>2</sub> moves from single layer to bulk the E<sub>2g</sub><sup>1</sup> VB downshifts from 384 to 382 cm<sup>-2</sup>, whilst A<sub>1g</sub> VB shifts upwards from 403 to 408 cm<sup>-1</sup>, where a separation of *ca.* 19 cm<sup>-1</sup> between the VBs is indicative of single layer MoS<sub>2</sub> and a value of *ca.* 25 cm<sup>-1</sup> represents the bulk material.<sup>73</sup><sup>26, 40</sup> In this work we observe an increase in the Raman shift of the E<sub>2g</sub><sup>1</sup> VB with greater mass additions from *ca.* 377 to 380 cm<sup>-1</sup>, see Figure. 5(A), however the response observed herein may result from the specific morphology and stacking structures of our MoS<sub>2</sub> on the underlying support material given that previous studies have reported a similar shift relating to the E<sub>2g</sub><sup>1</sup> band and attributed this to uniaxial strain or heterostructure stacking.<sup>74</sup> Interestingly, analysis of the A<sub>1g</sub> peak corresponds to the predicted theorem for a transition from single-layer to multi-layer 2D MoS<sub>2</sub> nanosheets with an increasing Raman shift from *ca.* 402 to 405 cm<sup>-1</sup>.<sup>40, 67</sup>

Furthermore, when considering the separation of the two VBs (given that this value is also indicative of the number of MoS<sub>2</sub> layers present) the shift in the difference of the VB positions between A<sub>1g</sub> and E<sub>2g</sub><sup>1</sup> gives a consistent value of 24.7 cm<sup>-1</sup> with increasing coverages, indicating that +4 layers (*i.e.* bulk) MoS<sub>2</sub> is present at all four mass coverages utilised herein (see Figure. 5(B)). Consideration of the above factors in conjunction with our independent lateral grain size calculations (UV-VIS) indicates that the structural model of the 2D MoS<sub>2</sub> nanosheets utilised herein is likely that of re-assembly, with the few-layer nanosheets forming bulk MoS<sub>2</sub> upon deposition onto the electrode surface. Further work on whether the morphology of a SPEs surface causes uniaxial strain and/or heterostructure stacking of the 2D MoS<sub>2</sub> nanosheets would be of great interest. Note that confirmatory tests were performed in which the aliquots deposited above were immobilised onto an alternative silicon wafer support in order to overcome potential issues with the underlying surface. Such control experiments (data not shown) exhibited the same separation values as identified above (*ca.* 25.1 cm<sup>-1</sup>) between the two VBs and thus confirms that our 2D MoS<sub>2</sub> nanosheets likely form bulk MoS<sub>2</sub> once deposited/immobilised onto a support surface. It is thus likely that further additions of our material result in the formation of thicker or rougher ‘bulk’



layers. We next explore the electrochemical implications of this, often overlooked in the literature.

### 3.3.2 *Electrochemical HER: critical mass of 2D MoS<sub>2</sub> nanosheets*

Returning to the analysis of the HER, the effects of different mass deposition on the different electrode surfaces was next explored. Using a fixed potential (−0.75 V) at which each electrode exhibits an observable current, the current densities relating to the HER were recorded. It is evident through inspection of Figure. 8 that a trend of increased current density (corresponding to increased 2D MoS<sub>2</sub> nanosheet coverage (ng cm<sup>−2</sup>)) is subsequently followed by a decrease in current density and/or plateauing effect. This is apparent upon modification of each of the four underlying electrode materials studied with our material of interest. Over the modification range tested, the maximum/optimal current density was found to correlate to a 2D MoS<sub>2</sub> nanosheet coverage of *ca.* 1014.4, 1266.7, 1266.7, 1266.7 ng cm<sup>−2</sup> for the GC, EPPG, SPE and BDD electrodes respectively. Tafel analysis on these optimal mass modifications reveals values of *ca.* 40, 74, 92 and 90.9 mV dec<sup>−1</sup>. GC and BDD when modified with the 2D MoS<sub>2</sub> nanosheets demonstrate a fast discharge mechanism, with H<sup>+</sup> adsorption no longer the rate-limiting step.<sup>1</sup> Through analysis of the values reported above and comparison to the values reported in section 3.2.1 it is clear that of the four electrodes modified, electrodes with slower kinetics (such as the GC and BDD) exhibit a favourable electrocatalytic effect when modified with 2D MoS<sub>2</sub> nanosheets towards the HER. Contrary to this, the EPPG, which possesses faster underlying rate kinetics, exhibited only a slight change towards an altered reaction mechanism and further in the case of the SPE there was no observable change.

### 3.4 *Assessment of 2D MoS<sub>2</sub> Nanosheets Catalytic Activity*

An array of approaches are employed to study the intrinsic catalytic activity of 2D MoS<sub>2</sub> nanosheets within the literature. In order to deduce how the observable catalytic activity alters with changes in the mass of 2D MoS<sub>2</sub> nanosheet modification we employ two commonly used techniques below: the assessment of catalytic turn over frequency (ToF) and the number of active sites present on the surface of the electrode.<sup>47, 68</sup>

#### 3.4.1 *Turn Over Frequency (ToF)*

In order to evaluate how the intrinsic catalytic activity of the 2D MoS<sub>2</sub> nanosheets alters

with varying modification on a ‘per active site’ basis, the ToF was deduced using a method reported previously by Benck et al.<sup>47</sup> their derivation is repeated here for clarity using values associated with the 257 ng cm<sup>-2</sup> modified SPE.<sup>47, 75</sup> In this calculation it is assumed that the surface of the 2D MoS<sub>2</sub> nanosheets is atomically flat (although the true modification will have a finite roughness).<sup>47</sup> Taking the sulphur to sulphur bond distance to be 3.15 Å which corresponds to an area of 4.296 Å<sup>2</sup>/S atom<sup>47, 76</sup> which can be used to calculate the surface area occupied by each MoS<sub>2</sub>:

$$4.296 \frac{\text{Å}^2}{\text{S atom}} * \frac{2 \text{ S atom}}{1 \text{ MoS}_2} = 8.593 \frac{\text{Å}^2}{\text{MoS}_2} \quad [7]$$

Using the derived area for a MoS<sub>2</sub> molecule (corresponding to the number of surface sites for a flat standard) it is possible to determine the number of MoS<sub>2</sub> molecules per cm<sup>2</sup> geometric area:

$$\frac{1 \text{ MoS}_2}{8.593 \text{ Å}^2} * \frac{10^{16} \text{ Å}^2}{\text{cm}^2} = 1.164 * 10^{15} \frac{\text{MoS}_2}{\text{cm}^2} \quad [8]$$

The number of electrochemically accessible surface sites can be determined from the following:

$$\frac{\# \text{ Surface Sites (Catalyst)}}{\text{cm}^2 \text{ geometric area}} = \frac{\# \text{ Surface Sites (Flat Standard)}}{\text{cm}^2 \text{ geometric area}} * R_F \quad [9]$$

It is also essential to accurately determine the roughness factor ( $R_F$ ) for each modified electrode surface, which was performed using white light profilometry (WLP) (See ESI Figure. 6). The described WLP technique yielded  $R_F$  values which represent the entire surface area of the electrode rather than electroactive area.  $R_F$  values can also be derived using the double layer capacitance of the electrode surface. Note that, the double layer capacitance technique is preferential to the WLP technique as it describes the true electroactive surface area of the electrode including accessible pores and the thickness of multiple layers deposited whereas WLP is flawed in that it bases its calculated value off only a scan of the topography of the uppermost surface in question. The double layer capacitance technique for determining  $R_F$  is reported in the ESI.

The 257 ng cm<sup>-2</sup> the modified SPE the number of surface sites cm<sup>-2</sup> corresponds to 2.687×10<sup>17</sup> surface sites / cm<sup>2</sup>. The following allows the ToF on a per-site basis to be determined:

$$\text{TOF per site} = \frac{\# \text{ Total Hydrogen Turn Overs} / \text{cm}^2 \text{ geometric area}}{\# \text{ Surface Sites (Catalyst)} / \text{cm}^2 \text{ geometric area}} \quad [10]$$

Selecting a value for current density (mA cm<sup>-2</sup>) and using the calculated  $R_F$ , per-site the ToF can be deduced:

$$\left(j \frac{mA}{cm^2}\right) \left(\frac{1 A}{1000mA}\right) \left(\frac{1 C/s}{1 A}\right) \left(\frac{1 mol e^-}{96,485.3 C}\right) \left(\frac{1 mol H_2}{2 mol e^-}\right) \left(\frac{6.02214*10^{23}}{1 mol H_2}\right) = 1.32 * 10^{16} \frac{H_2/s}{cm^2} per \frac{mA}{cm^2} \quad [11]$$

Using equation 12 and value derived from formula 11, it is possible to determine a ToF value:

$$\left(1.32 * 10^{16} \frac{H_2/s}{cm^2} \left/ \frac{mA}{cm^2}\right.\right) \left(10 \frac{mA}{cm^2}\right) \left(\frac{1 cm^2}{2.687*10^{17} surface sites}\right) = 0.5 \frac{H_2/s}{surface sites} \quad [12]$$

At 257 ng cm<sup>-2</sup> modification of 2D MoS<sub>2</sub> nanosheets upon an SPE (SPEs used as representative example of the carbon based electrodes utilised) the ToF value was 0.50  $\frac{H_2/S}{Surface Site}$ , which does not significantly increase with further additions of our target material (a value of 0.54  $\frac{H_2/S}{Surface Site}$  at 1009.5 ng cm<sup>-2</sup> and 0.55  $\frac{H_2/S}{Surface Site}$  with a modification of 2019 ng cm<sup>-2</sup>). Benck et al.<sup>47</sup> suggest that the upper and lower possible turnover frequencies could be one order of magnitude greater or less than the given value. The values estimated for the ToF are in agreement with Xie<sup>77</sup> who suggest that a ToF value close to 0.496  $\frac{H_2/S}{Surface Site}$  which is associated with a MoS<sub>2</sub> structure of “defect free ultra-thin nanosheets”.

### 3.4.2 Number of Active Sites

Determining the number of active sites present on the surface of an electrode offers valuable insight into its catalytic properties. Shin and co-workers<sup>68</sup> have shown that it is possible to derive the number of 2D MoS<sub>2</sub> nanosheet active sites ( $N$ ) present on the surface of the catalyst using the following equation:

$$N = R_F(N_A d / M_f)^{2/3} \quad [13]$$

where  $N_A$  is Avogadro's number,  $d$  is the film density (*ca.* 2.35 x10<sup>-4</sup> g cm<sup>-3</sup>, which was derived *via* the use of WLP to observe the step height, in this case 21.9 μm, between the bare electrode surface and a mass of 514 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets deposited),  $M_f$  is the formula weight of MoS<sub>2</sub>, and  $R_F$  is the roughness factor, which in this case is defined as the ratio of the real surface area to the geometric area. The geometric area (and the electrochemically active area) of the electrode surface can vary significantly due to the surface roughness and porosity of the sample. In this case the  $R_F$  was derived using double layer capacitance as it is linearly proportional to catalytic surface area (see roughness factor calculation method 2 in the ESI).<sup>78</sup> The double layer capacitance values determined (*via* cyclic voltammetry, see ESI Figure. 7) are 8.7, 68, 218, 322 μF cm<sup>-2</sup> for SPEs modified with 0, 257, 1009 and 2019 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets respectively.

As a benchmark the double layer capacitance value for amorphous MoS<sub>2</sub> is reported to be 66.7  $\mu\text{F cm}^{-2}$ .<sup>46</sup>  $R_F$  values for SPEs modified with 257, 1009 and 2019  $\text{ng cm}^{-2}$  of 2D MoS<sub>2</sub> nanosheets were estimated to be *ca* 1.02, 3.26 and 4.83 respectively. The  $R_F$  values derived using double layer capacitance show an increment with greater masses of 2D MoS<sub>2</sub> nanosheet modification.  $R_F$  values for BDD, EPPG, GC and SPE post modification are presented in Table 2. The number of active sites per  $\text{cm}^{-2}$  are summarised in Table 2 where there is a (positive) linear correlation between number of active sites and mass of MoS<sub>2</sub> deposited. It can therefore be asserted that there is a physicochemical change within the structure of the 2D MoS<sub>2</sub> present upon the surface of the electrode, which leads to the exposure of less active sites per additional  $\text{ng cm}^{-2}$  modification after a certain ‘critical mass’ (this is also evident through inspection of Figure 8), or no further increase in the number of the active sites accessible to the solution. It is clear that the number of active sites (and related HER performance) increase (improve) with the addition of larger quantities of MoS<sub>2</sub> onto the underlying electrode surface up until the specified critical mass is achieved.

It is evident that the increased mass deposition of 2D MoS<sub>2</sub> nanosheets on a given electrode surface results in an improvement in the current passed in addition to a lowered HER onset potential (improved electrochemical response). As is apparent from the above discussion (and inspection of Figure 8) this increase in the catalytic performance a given modified electrode material (which corresponds to the addition of 2D MoS<sub>2</sub> nanosheets) reaches a plateau after which further additions of our target material do not result in an improved electrochemical performance. This ‘critical mass’ of modification is likely due to the structure of the 2D MoS<sub>2</sub> nanosheet altering to that of a bulk formation (see earlier), thereby exposing less edge sites and thus inhibiting the beneficial electrochemical properties of single-, few-, quasi- MoS<sub>2</sub> nanosheets. Alternatively, this plateau could signify the mass (a critical mass of *ca.* 1009  $\text{ng cm}^{-2}$  of the 2D MoS<sub>2</sub> nanosheets) at which the structure of MoS<sub>2</sub> can no longer structurally support itself upon the electrode surface (becoming unstable) diminishing and detaching from the surface of the electrode, eliminating the catalytic advantages of further additions (such that in some cases the catalytic response begins to deteriorate). Similar observations have been reported for the case of graphene.<sup>79-82</sup> This could arise due to the disconnection of 2D MoS<sub>2</sub> nanosheet layers during the course of the experiment (*i.e.* instability of the modified layer on the electrode surface due to the large quantity/mass present) which is brought about once such a ‘critical mass’ is achieved.

The intra-repeatability of the modified and unmodified SPEs were tested ( $N = 3$ ). The % Relative Standard Deviation (% RSD) in the onset potential of the HER was found to be *ca.* 0.8, 1.4, 1.5, and 4.6 % at the 0 (unmodified), 257, 1009 and 2019  $\text{ng cm}^{-2}$  modified SPEs respectively. It is clear that the % RSD increases with greater modifications of the  $\text{MoS}_2$ , likely a result of the factors stated above and potentially resulting in the reduced catalytic effects. Furthermore, the % RSD in the current densities observed were found to be *ca.* 12.4, 13.5, 10.5, and 15.5 % at the 0 (unmodified), 257, 1009 and 1771  $\text{ng cm}^{-2}$  modified SPEs respectively. The high RSD values in this case are indicative of the structural instability of the deposited 2D  $\text{MoS}_2$  nanosheet film on the underlying electrode surface, which likely leads to delamination and thus high levels of variation within the effective surface area and currents passed.

From the above inferences, we suggest that the structural model of 2D  $\text{MoS}_2$  nanosheets is likely that of re-assembly, such that upon modification with increasing amounts of 2D  $\text{MoS}_2$  nanosheets, bulk layers of  $\text{MoS}_2$  materialise upon the surface of our support electrodes.<sup>79, 81</sup>

Electrochemical impedance spectroscopy (EIS) was used to determine the impedance of the electrode system as coverage of 2D  $\text{MoS}_2$  nanosheets was increased, see ESI Figure. 9.<sup>70</sup> It was observed that the charge transfer resistance ( $\Omega$ ) for all electrodes decreased after modification with 257.1  $\text{ng cm}^{-2}$  2D  $\text{MoS}_2$  nanosheets and further decreased after modification with 1009.5  $\text{ng cm}^{-2}$ . Again a plateauing was observed in the response with increased coverage (for example after modification with 2019  $\text{ng cm}^{-2}$ ). The  $\Omega$  values of the unmodified SPE ( $3.51 \times 10^5 \Omega$ ) reduced to  $1.69 \times 10^5 \Omega$  after 257  $\text{ng cm}^{-2}$  and then to  $3.27 \times 10^3 \Omega$  upon a 1009  $\text{ng cm}^{-2}$  2D  $\text{MoS}_2$  nanosheet modification, after which the response plateaued, having an impedance value of  $3.21 \times 10^3 \Omega$  by modification with 2019  $\text{ng cm}^{-2}$ . Error values for the aforementioned results were recorded as  $1.78 \times 10^{-4}$ ,  $1.73 \times 10^{-3}$ ,  $1.2 \times 10^{-2}$ , and  $1.21 \times 10^{-2} \Omega$  respectively. This EIS supports the above inferences and indicates that the 2D  $\text{MoS}_2$  is an effective electrocatalyst with respect to the HER when deposited on a carbon electrode surface.

Finally, it is essential to assess the electrochemical stability of 2D  $\text{MoS}_2$  nanosheets as a catalyst for the HER when drop coated onto an electrode surface (following on from the reported % RSD values noted above). This is a practical consideration for real applications where durability and longevity are necessary.<sup>2, 27, 68</sup> SPEs were used as a representative example for the four carbon based electrodes used within this study. A 1000 cycle voltammetry scan from 0 to  $-0.8 \text{ V}$  at  $25 \text{ mVs}^{-1}$  was performed on SPEs modified with 257, 1009, 2019  $\text{ng cm}^{-2}$  of 2D  $\text{MoS}_2$  nanosheets.

A decrease in the catalytic activity of each electrode was observed (see Figure. 9). At 0.6 V the decrease from the initial scan current was 6.8%, 32.3%, 26.9% for the SPEs modified with 257, 1009 and 2019  $\text{ng cm}^{-2}$  respectively. The observed activity loss is significant especially for the 1009 and 2019  $\text{ng cm}^{-2}$  modified electrodes. According to Shin et al.<sup>68</sup> high stability of amorphous  $\text{MoS}_2$  is rarely reported with the decrease in activity being associated with either: surface absorptives which may poison the active sites of the 2D  $\text{MoS}_2$  nanosheets;<sup>47</sup> or the delamination of the 2D  $\text{MoS}_2$  nanosheets from the substrate.<sup>47</sup> However, it is likely a combination of these two effects with the delamination of 2D  $\text{MoS}_2$  nanosheets becoming more prevalent at higher modifications. This inference is supported by the EIS observations detailed earlier. Another consideration in terms of industrial application is cost of the four carbon based electrodes studied, the GC offered the greatest current density and most noted HER onset potential decrease upon modification with 2D  $\text{MoS}_2$  nanosheets. GC's production cost makes its application as a catalyst on an industrial scale economically unfeasible. The SPE offers an attractive alternative to using GC in real-world industrial applications. After modification with 2D  $\text{MoS}_2$  nanosheets, the HER onset potential is lowered to a value equivalent of GC's. One issue could potentially be that the modified SPE exhibits a lower current density compared to that of GC, however, due to the nature of SPE's production they can be produced to a wide manner of tailorability, varying in shape, surface area and carbon composition. As such SPEs can be produced with a larger surface area than that of GC, thereby increasing the currents possible and ultimately the amount of hydrogen produced. This combined with the ultra-low cost of fabricating SPEs makes them an exceptionally cost effective and easily producible supporting electrode material for HER. There is potential to incorporate 2D  $\text{MoS}_2$  nanosheets into the carbon based inks used to produce SPEs, thereby eliminating the time consuming modification step. Further research aimed at identifying and resolving the reason for the poor catalytic stability is essential if 2D  $\text{MoS}_2$  nanosheet modified SPEs have a future industrial application.

#### **4. Conclusions**

We have explored the catalytic performance of 2D  $\text{MoS}_2$  nanosheets towards the HER. In order to overcome issues prevalent within the literature and to enable us to ascertain the true electrochemical performance of our commercially sourced  $\text{MoS}_2$  we modified a range of carbon

based underlying support electrodes, namely GC, BDD, EPPG and SPEs; this approach is usually neglected within the literature; Application of the MoS<sub>2</sub> modified electrodes revealed a catalytic performance towards the HER, with lower onset potentials and higher current densities observed when utilising our target material; the supporting electrode was found to be of key importance, influencing the improvements observed in the electrochemical performance. This indicates that 2D MoS<sub>2</sub> nanosheet modified electrodes can potentially serve as a viable, low cost and more abundant replacement to current Pt based electro-catalysts.

This work is distinct from the literature given that we have also correlated our electrochemical responses with supplementary Raman mapping of the electrode surface (and other complementary physicochemical characterisation) whilst exploring the effect of MoS<sub>2</sub> coverage. Coverage studies revealed that the catalytic effect of the 2D MoS<sub>2</sub> nanosheets increased (as indicated by ToF and ‘number of active sites’ calculations) until a ‘critical mass’ (coverage) was achieved, after which the response was observed to plateau. The likely cause of this effect is inferred herein and has clear implications (in this case and) when employing other 2D nanosheet modified electrodes within the literature.

We have provided insights into the observable electrochemistry and HER mechanism prevalent at 2D MoS<sub>2</sub> nanosheet modified electrodes, which has clear potential to be beneficially applied/utilised as an electrocatalyst if the diligent control measures reported herein are sufficiently applied.

**Table 1.** Comparison of current literature reporting the use of MoS<sub>2</sub> as a catalyst explored towards the HER.

Catalyst	Electrode / supporting material	Loading ( $\mu\text{g cm}^{-2}$ )	Electrolyte	HER onset (-mV)	Tafel (mV dec <sup>-1</sup> )	Reference
MoS <sub>2</sub>	Au(111)	–	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -150	55-60	83
Narrow sheet MoS <sub>2</sub>	GC	280	0.5 M H <sub>2</sub> SO <sub>4</sub>	-103	49	45
MoS <sub>2</sub> / CoSe <sub>2</sub>	GC	~280	0.5 M H <sub>2</sub> SO <sub>4</sub>	11	36	84
MoS <sub>2</sub> / MCN	GC	190	0.5 M H <sub>2</sub> SO <sub>4</sub>	-100	41	85
MoS <sub>2</sub> /RGO	GC	285	0.5 M H <sub>2</sub> SO <sub>4</sub>	-100	41	27
MoS <sub>x</sub>	GC	9	1 M H <sub>2</sub> SO <sub>4</sub>	–	40	13
MoS <sub>3</sub>	GC	32	1 M H <sub>2</sub> SO <sub>4</sub>	~ -100	54	86
Fe- MoS <sub>2</sub>	GC	30.4	1 M H <sub>2</sub> SO <sub>4</sub>	–	39	87
MoS <sub>2</sub> nanosheets	GC	48	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -150 to -200	70	32
2D MoS <sub>2</sub>	GC	0.280 <sup>^</sup>	0.5 M H <sub>2</sub> SO <sub>4</sub>	-93	42	88
MoS <sub>2</sub>	GC	~8.5	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	86	72
MoS <sub>2</sub> film	GC	–	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	ca 140	46
Defect rich MoS <sub>2</sub> nanosheets	GC	285	0.5 M H <sub>2</sub> SO <sub>4</sub>	-120	50	77
MoS <sub>2</sub> nanosheets	GC	–	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -100	ca 40	43
Amorphous MoS <sub>x</sub> films	GC	–	1 M H <sub>2</sub> SO <sub>4</sub>	–	40	28
MoS <sub>2</sub> NAS	GC	–	0.5 M H <sub>2</sub> SO <sub>4</sub>	-54	100	26
Annealed MoS <sub>2</sub> /Ag	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	154	33
MoS <sub>2</sub> /Ag Strain 0% *	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	145	33
MoS <sub>2</sub> /Ag Strain 0.005% *	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	141	33
MoS <sub>2</sub> /Ag strain 0.01% *	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	138	33
MoS <sub>2</sub> /Ag strain 0.02% *	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	135	33
MoS <sub>2</sub> /Ag	Ag/PET	2	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	152	33
MoS <sub>2</sub> /Ag strain 0.01% *	Ag/PET	2	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	142	33
MoS <sub>2</sub> /Ag	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	142	33
MoS <sub>2</sub> /Ag strain 0.01% *	Ag/PET	6	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	138	33
MoS <sub>2</sub> /Ag	Ag/PET	12	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	143	33
MoS <sub>2</sub> /Ag strain 0.01% *	Ag/PET	12	0.5 M H <sub>2</sub> SO <sub>4</sub>	–	140	33
MoS <sub>2</sub> nanoparticles	Graphite	–	–	-100 to -200	–	7
Ni-Mo nanopowder	Ti	1	2 M KOH	-70	–	89
Ni-Mo nanopowder	Ti	3	0.5 M H <sub>2</sub> SO <sub>4</sub>	-80	–	89
Ni-Mo nanopowder	Ti	13.4	2 M KOH	-100	–	89
Amorphous MoS <sub>x</sub>	GC	(10 <sup>17</sup> sites cm <sup>-2</sup> )	0.5 M H <sub>2</sub> SO <sub>4</sub>	-200	60	47



2D MoS <sub>2</sub> nanosheets	GC	1.019	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -480	40	This work
2D MoS <sub>2</sub> nanosheets	EPPG	1.267	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -450	74	This work
2D MoS <sub>2</sub> nanosheets	BDD	1.267	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -450	90.9	This work
2D MoS <sub>2</sub> nanosheets	SPE	1.267	0.5 M H <sub>2</sub> SO <sub>4</sub>	~ -440	92	This work

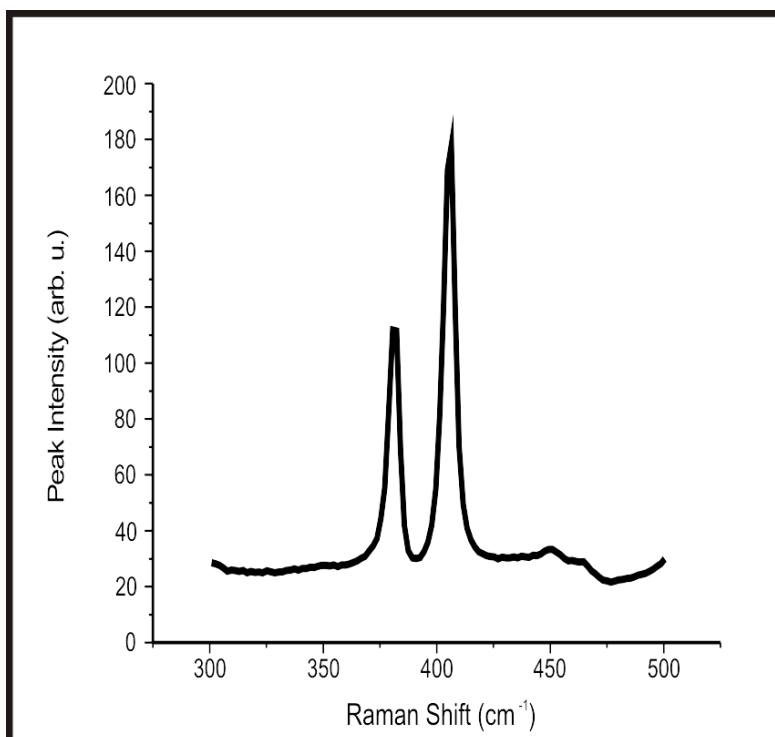
---

**Key:** -: Value unknown; **GC:** glassy carbon; **CP:** carbon paper; **MCN:** mesoporous carbon nanospheres; **RGO:** reduced graphene oxide; **•:** Optimised Loading; **NAS:** nano-assembled structures; **PET:** polyethylene terephthalate; **EPPG:** edge plane pyrolytic graphite; **BDD:** boron doped diamond; **SPE:** screen-printed graphite electrode; **\***: mechanical bent tensile-strain-induced two dimensional MoS<sub>2</sub> nanosheets

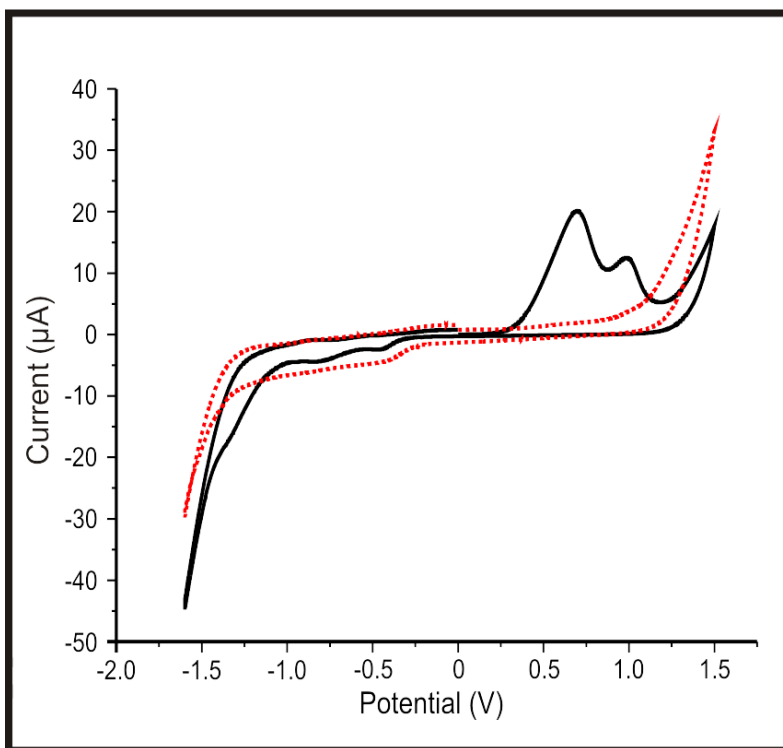
**Table 2.** The determined roughness factor ( $R_F$ ) values and the number of active sites (per  $\text{cm}^2$ ) for BDD, EPPG, GC and SPE all of which had been modified with 0, 257, 1009, 2019  $\text{ng cm}^{-2}$  2D  $\text{MoS}_2$  nanosheets. Values determined using double layer capacitance obtained *via* cyclic voltammetry between the potential range of 0.01V and 0.1V.

Electrode	$\text{MoS}_2$ Modification ( $\text{ng cm}^{-2}$ )	Roughness Factor	Number of active sites
<b>BDD</b>	2019	2.2	$2.01 \times 10^{12}$
	1009	1.5	$1.38 \times 10^{11}$
	257	0.3	$3.03 \times 10^{11}$
<b>EPPG</b>	2019	7.7	$7.05 \times 10^{12}$
	1009	5.5	$5.05 \times 10^{12}$
	257	4.2	$3.84 \times 10^{12}$
<b>GC</b>	2019	2.6	$2.35 \times 10^{12}$
	1009	2.1	$1.95 \times 10^{12}$
	257	1.0	$8.95 \times 10^{11}$
<b>SPE</b>	2019	4.8	$4.43 \times 10^{12}$
	1009	3.3	$3.00 \times 10^{12}$
	257	1.0	$9.36 \times 10^{11}$

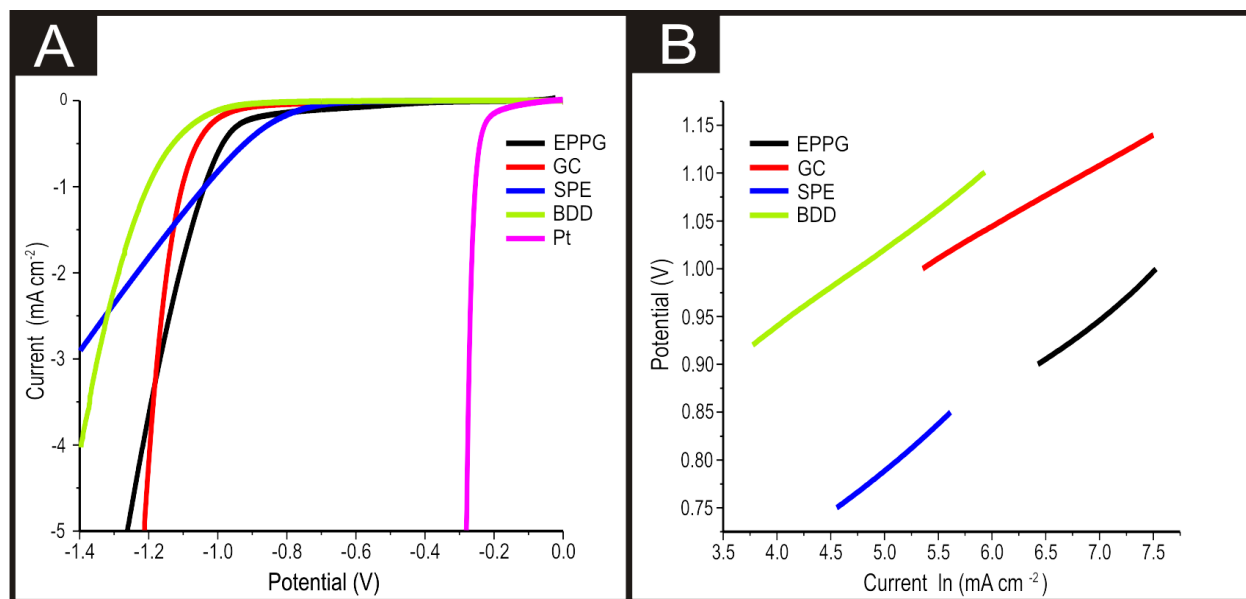
**Figure. 1** Raman spectra of the commercially sourced 2D MoS<sub>2</sub> nanosheets immobilised upon a silicon wafer.



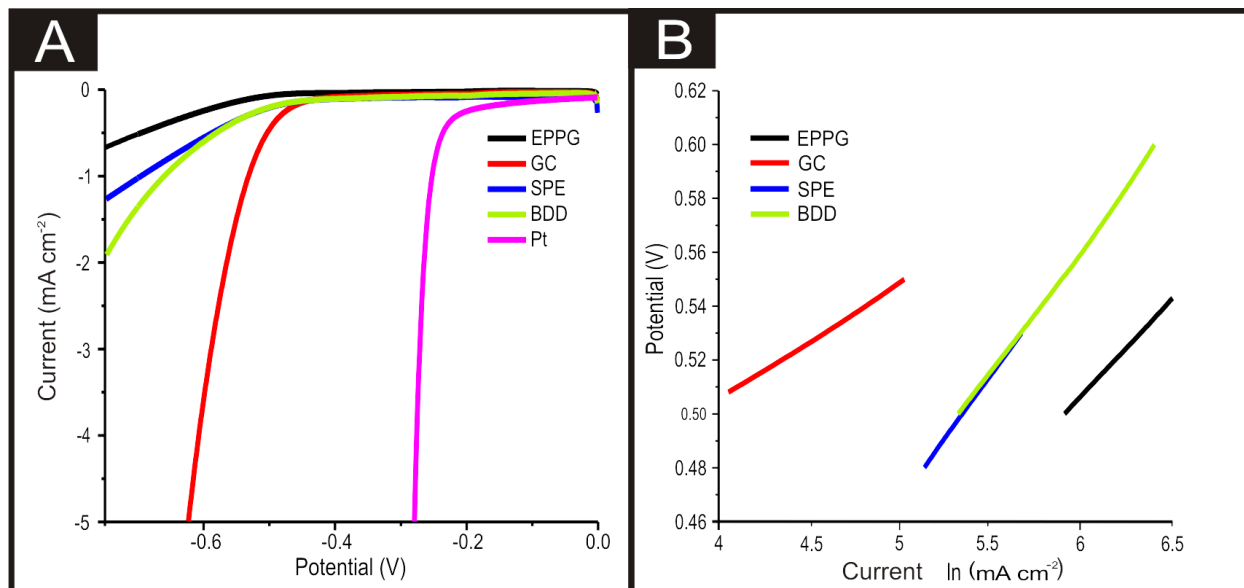
**Figure. 2** Typical cyclic voltammetric response of 2D MoS<sub>2</sub> nanosheets immobilised upon a SPE in pH 7 phosphate buffer solution (PBS). First scan: solid black line. Second scan (representative of subsequent scans): red dotted line. Scan rate: 5 mVs<sup>-1</sup> (vs. SCE).



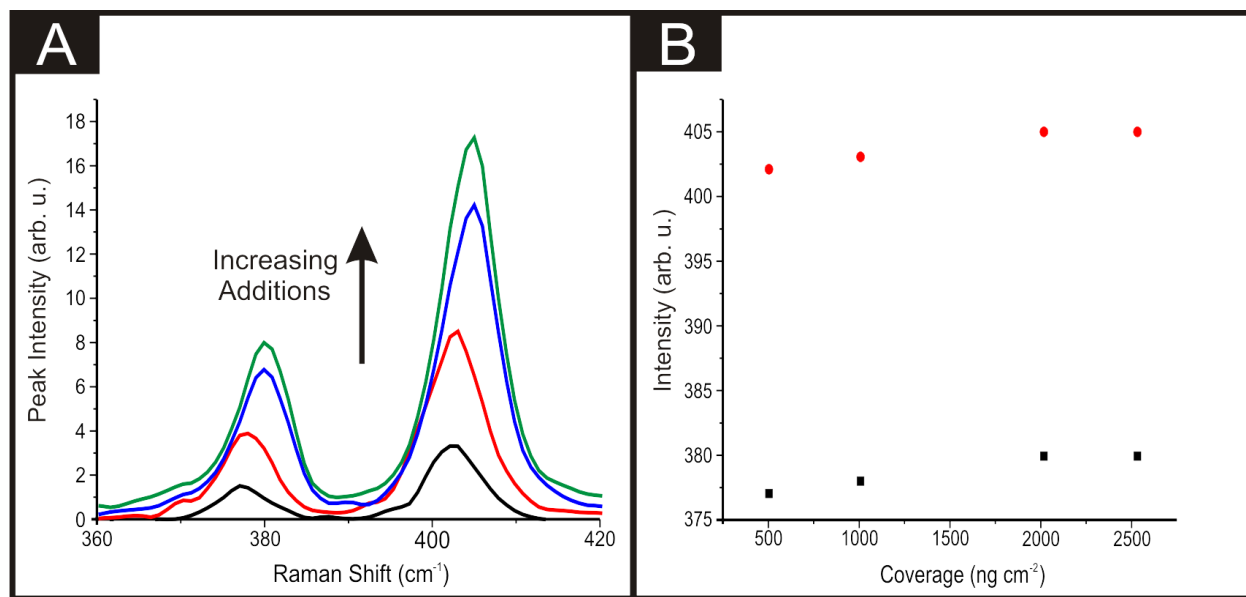
**Figure. 3** (A) Linear sweep voltammetry (LSV) of unmodified EPPG, GC, SPE, BDD and Pt electrodes showing the onset of the HER. In all cases, scan rate:  $25 \text{ mVs}^{-1}$  (vs. SCE). Solution composition:  $0.5 \text{ M H}_2\text{SO}_4$ . (B) Tafel analysis; potential vs. natural log ( $\ln$ ) of current density for faradaic section of the LSV presented in (A).



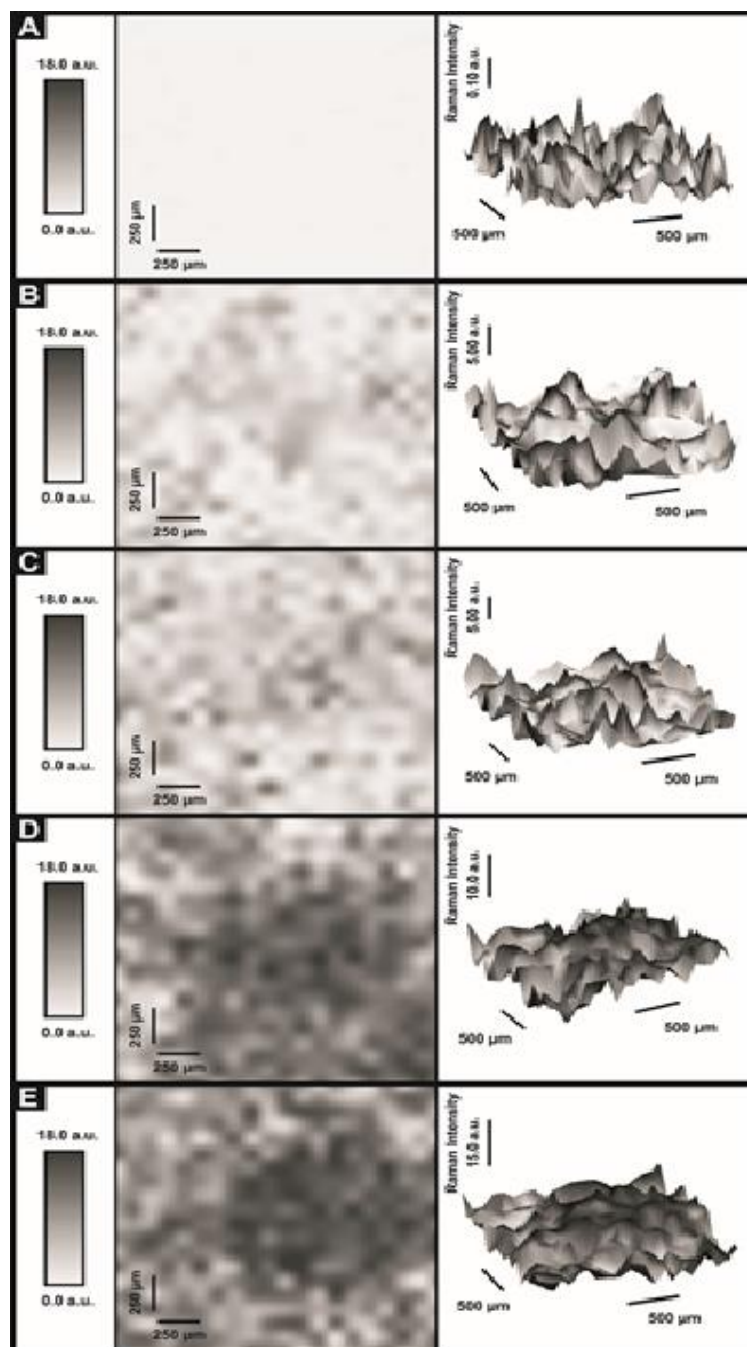
**Figure 4** (A) LSV of  $1267 \text{ ng cm}^{-2}$  modified EPPG, GC, SPE, BDD electrodes and an unmodified Pt electrode showing the onset of the HER. In all cases, scan rate:  $25 \text{ mVs}^{-1}$  (vs. SCE). Solution composition:  $0.5 \text{ M H}_2\text{SO}_4$ . (B) Tafel analysis; potential vs. natural log ( $\ln$ ) of current density for Faradaic section of the LSV presented in (A).



**Figure. 5** (A) Raman Spectra peak intensity and position for 504 (black), 1009 (red), 2019 (blue) and 2533 (green)  $\text{ng cm}^{-2}$  2D  $\text{MoS}_2$  nanosheet modifications on SPEs. (B) Depicts 2D  $\text{MoS}_2$  nanosheet coverage plotted against Raman peak intensity for  $E_{2g}^1$  (black) and  $A_{1g}$  (red) vibrational bands, showing a constant peak distance of  $24.7 \text{ cm}^{-1}$  at all coverages.

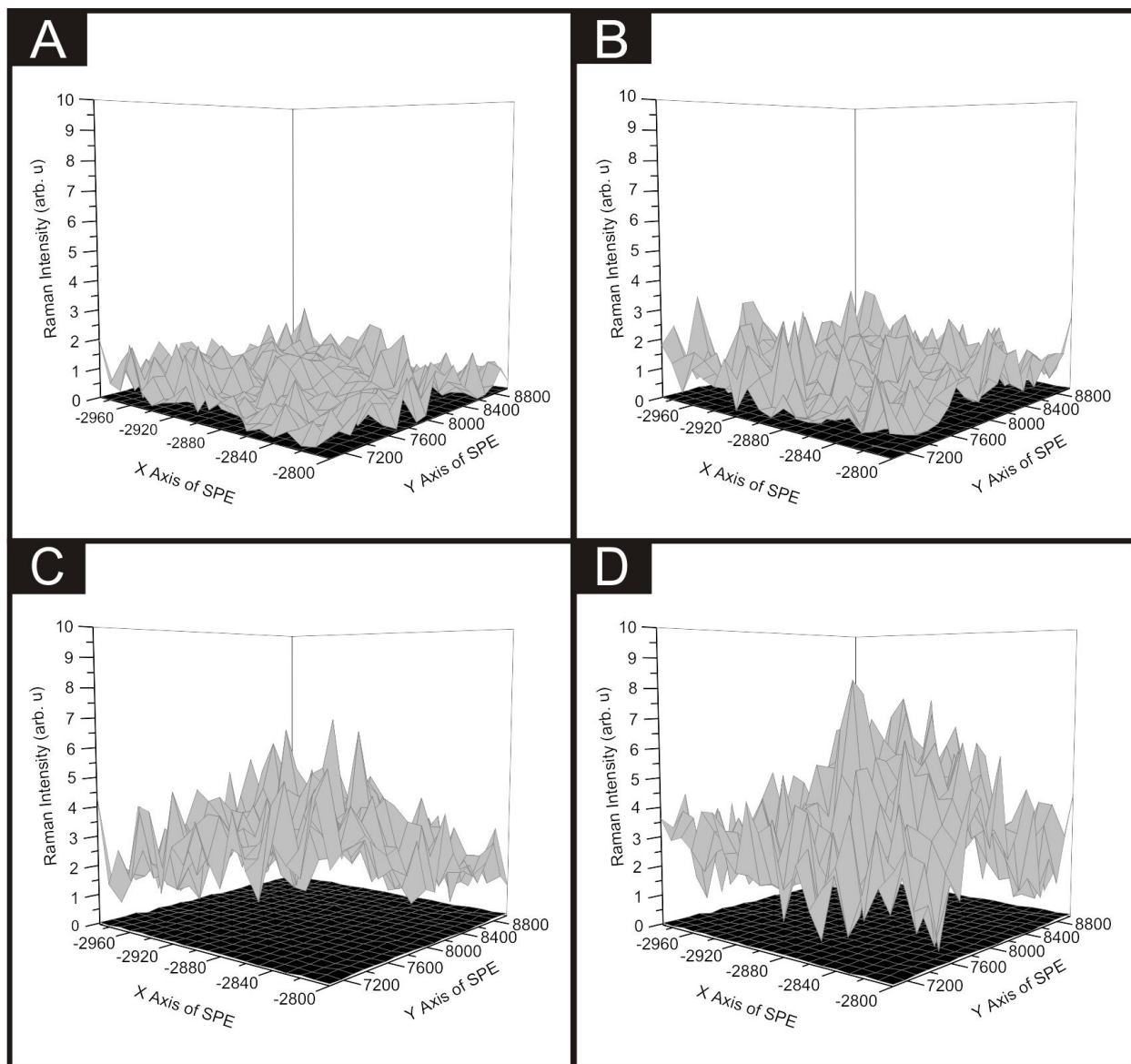


**Figure 6.** Raman maps representing various MoS<sub>2</sub> coverages onto an underlying SPE. Coverages of 2D MoS<sub>2</sub> nanosheets: 0 (A), 504 (B), 1009 (C), 2019 (D), and 2533 (E) ng cm<sup>-2</sup>. Raman intensities recorded at 405 cm<sup>-1</sup>.

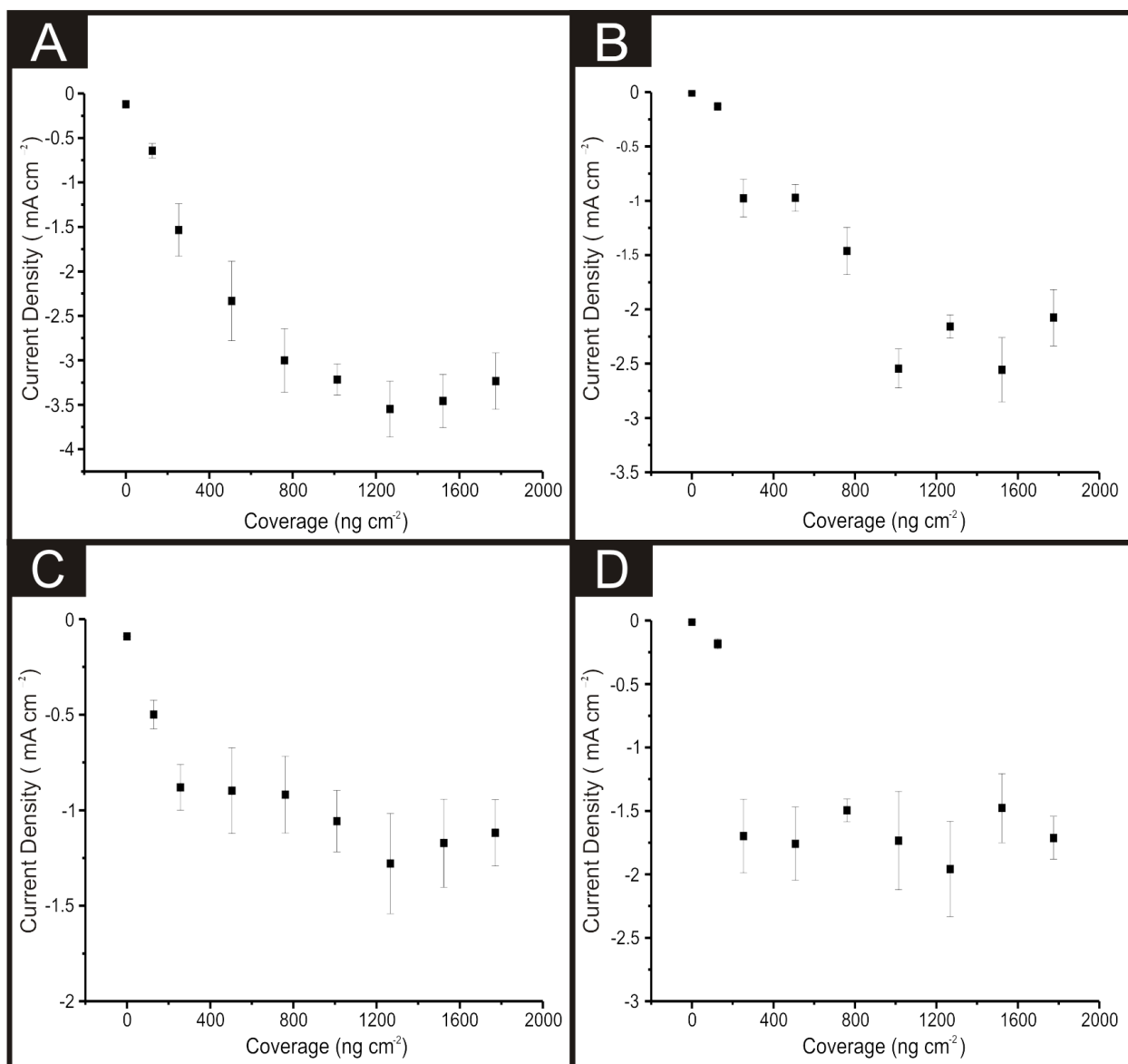




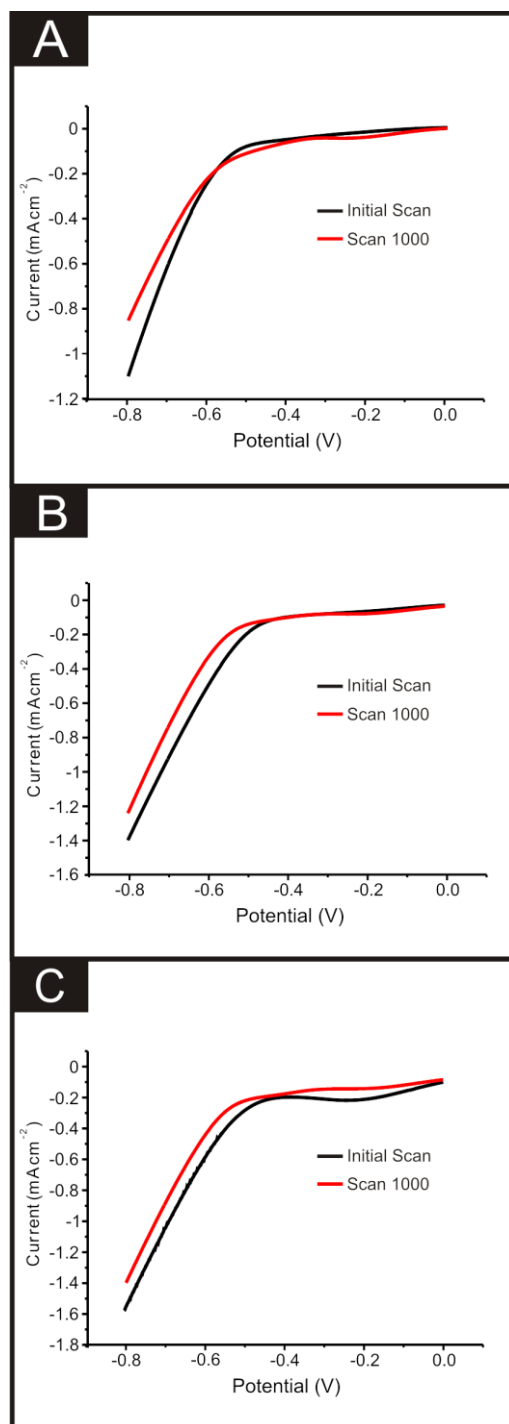
**Figure. 7** Raman maps of SPE surface, each point showing the intensity ratio between the sum of the characteristic MoS<sub>2</sub> peak areas (380 and 405 cm<sup>-1</sup>) against the area of the underlying graphite peak (1550 cm<sup>-1</sup>). Using varying surface coverages of our 2D MoS<sub>2</sub> nanosheets; 504 (A), 1009 (B), 2019 (C) and 2533 (D) ng cm<sup>-2</sup>. The grey maps are the modified electrodes and the black map in each represents an unmodified electrode surface.



**Figure. 8** Current density values taken at  $-0.75$  V from linear sweep voltammetry from 0, 128.6, 257.1, 504.8, 761.9, 1009.5, 1266.7, 1523.8 and 1771.4  $\text{ng cm}^{-2}$  2D MoS<sub>2</sub> nanosheets immobilised upon: (A) EPPG, (B) GC, (C) SPE (D) BDD. Each graph showing the plateauing effect of current density when a critical mass of the 2D MoS<sub>2</sub> nanosheets is deposited onto the electrodes surface. Error bars are the average and standard deviation of 3 replicates.

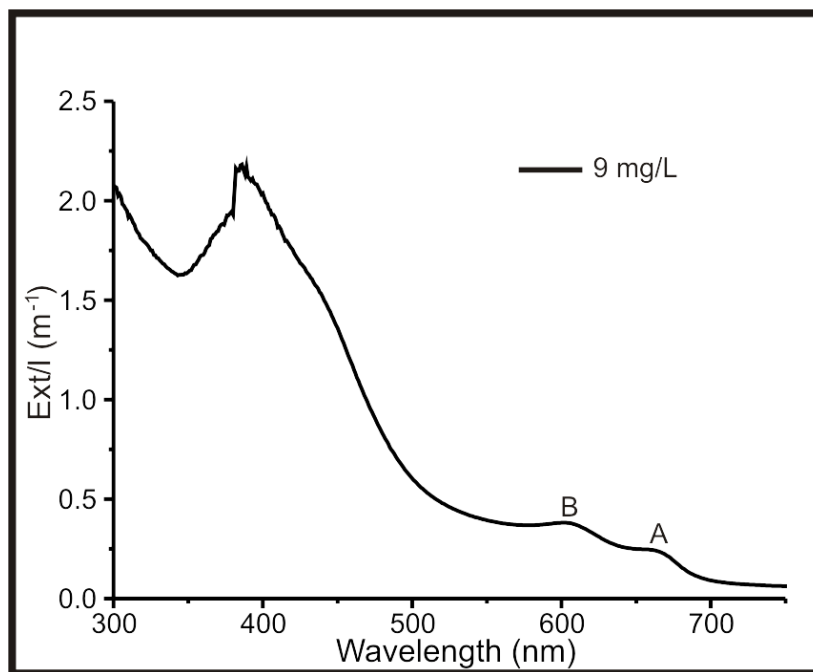


**Figure. 9** Stability studies using SPEs modified with (A) 257, (B) 1009 and (C) 2019  $\text{ng cm}^{-2}$  2D  $\text{MoS}_2$  nanosheets. Cyclic Voltammetry was performed between the potential range of 0 to  $-0.8$  V, repeated for 1000 cycles, these figures show the initial (black line) and 1000<sup>th</sup> (red line) scans.

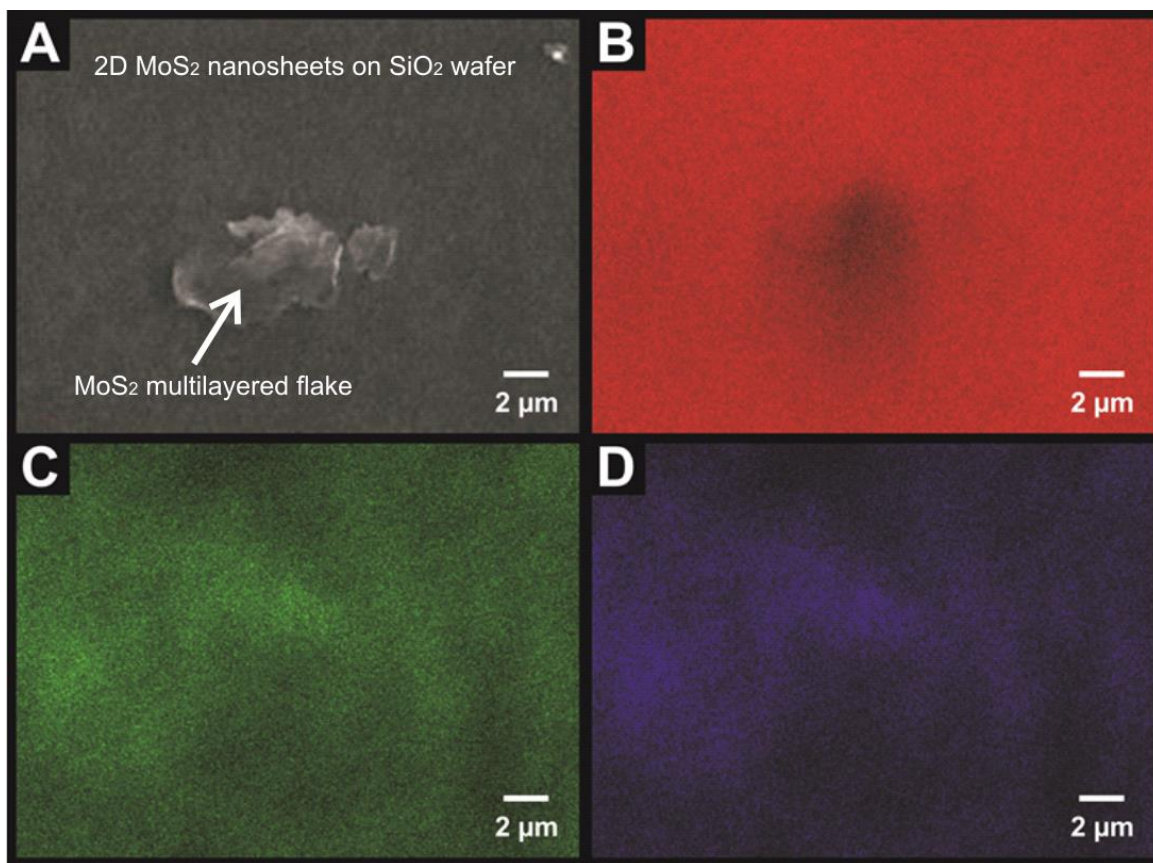


## Electronic Supporting Information

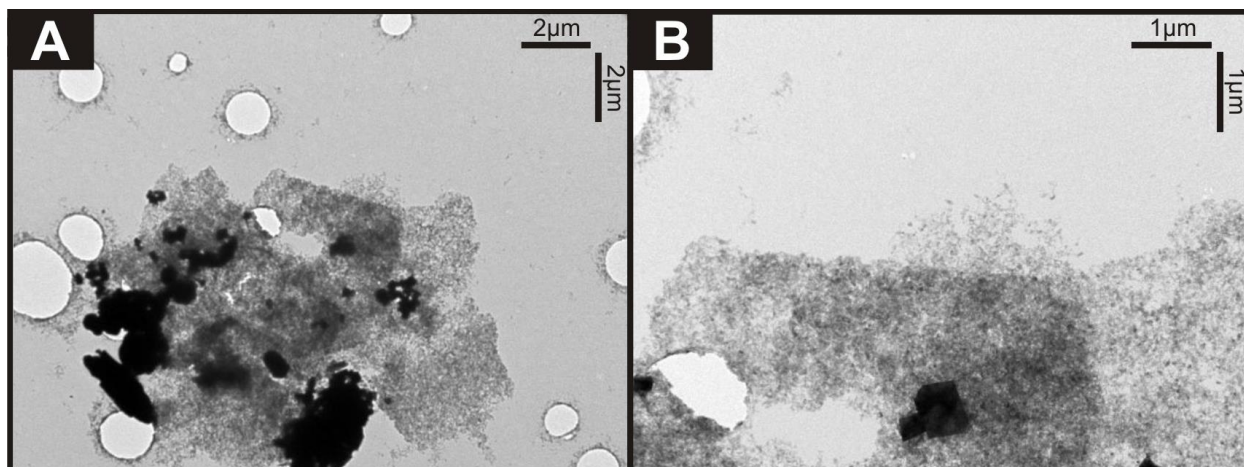
**ESI Figure. 1** Extinction spectra for the commercially sourced MoS<sub>2</sub> nanosheets dispersed in ethanol (9 mg L<sup>-1</sup>).



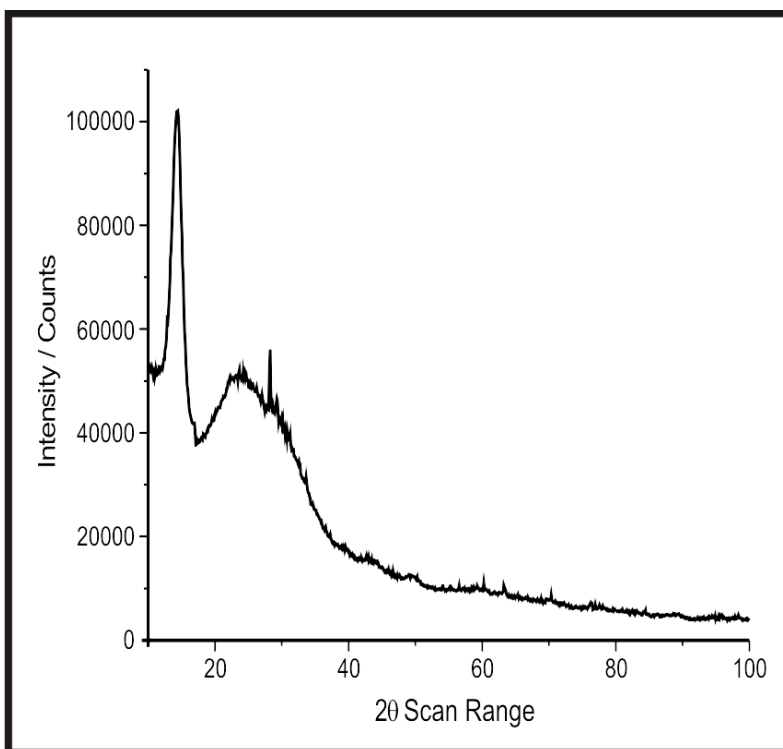
**ESI Figure. 2** (A) SEM image of a multi-layered 2D MoS<sub>2</sub> nanosheet flake on top of few layer 2D MoS<sub>2</sub> nanosheets immobilised on a silicon wafer along with EDS analysis highlighting the underlying silicon support (B, in red), molybdenum (C, in green) and sulphur (D, in blue) coverage of image A respectively.



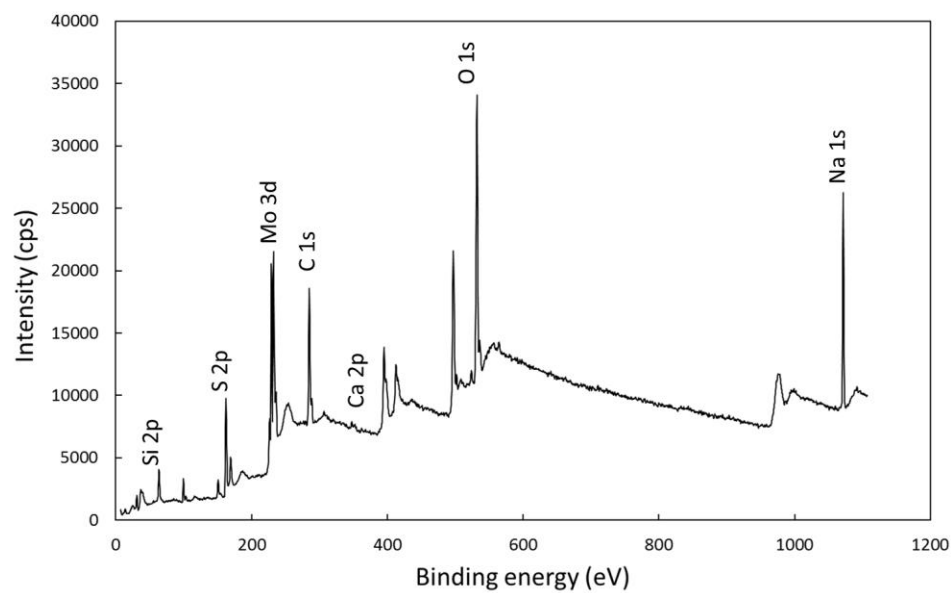
**ESI Figure. 3** TEM images of the commercially sourced 2D MoS<sub>2</sub> nanosheets deposited onto a carbon grid. (A) TEM image at 5,800 times magnification (scale bar: 2 μm), (B) TEM image at 13,500 times magnification (scale bar: 1 μm).



**ESI Figure. 4** XRD spectra of the 2D MoS<sub>2</sub> nanosheets deposited onto a glass slide between 10 and 100  $2\theta$ , showing a characteristic peak at 14°  $2\theta$ .

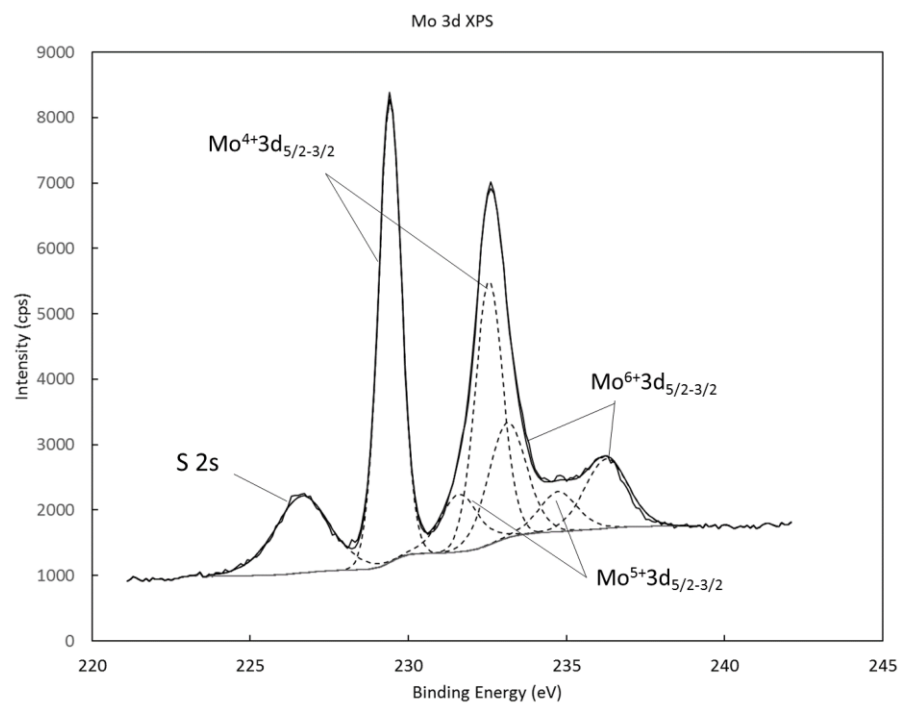


**ESI Figure. 5** XPS survey spectrum for a sample of the 2D MoS<sub>2</sub> nanosheets once deposited onto a Si (111) wafer showing a 1:2.2 concentration percentage for Mo and S respectively.





**ESI Figure. 6** Curve fitted XPS Mo 3d spectrum



**ESI Table 1.** Compositional analysis of XPS spectra presented in ESI figure 5, shown in atom percentage concentration, excluding H which is not detected by this technique.

<b>Element</b>	<b>Atom % Concentration</b>
Na 1s	8.36
Mo 3d	7.44
C 1s	34.41
Ca 2p	0.61
S 2p	16.3
Si 2p	5.47
O 1s	27.4

## Roughness Factor Calculations

### Method 1

In order to use the ToF formula described by Benck *et al.*<sup>47</sup> it was essential for roughness factors of the three modified SPE surfaces to be calculated. These were calculated using a ZeGage 3D Optical Surface Profiler, produced by Zygo. The surface topography of the 2D MoS<sub>2</sub> nanosheets was measured once deposited onto the SPEs, and these measurements were subsequently used to provide a value for the roughness factor ( $R_F$ ) used in this work. The surface profile maps are shown in ESI Figure 6 were analysed using a Matlab script based on the following equation:

$$R_F = \frac{\sum_{k=0}^{M-2} \sum_{i=0}^{N-2} A_{kl}}{(M-1)(N-1)\delta x \delta y} \quad [1]$$

where  $M$  and  $N$  are the total number of points in the  $x$  and  $y$  directions respectively,  $x$  and  $y$  are the distances between the points in the  $x$  and  $y$  directions, and where:

$$A_{kl} = \frac{1}{4} \left( \sqrt{\delta y^2 + (z(x_k, y_i) - z(x_k, y_{i+1}))^2} + \sqrt{\delta y^2 + (z(x_{k+1}, y_i) - z(x_{k+1}, y_{i+1}))^2} \right) + \left( \sqrt{\delta x^2 + (z(x_k, y_i) - z(x_{k+1}, y_i))^2} + \sqrt{\delta y^2 + (z(x_k, y_{i+1}) - z(x_{k+1}, y_{i+1}))^2} \right) \quad [2]$$

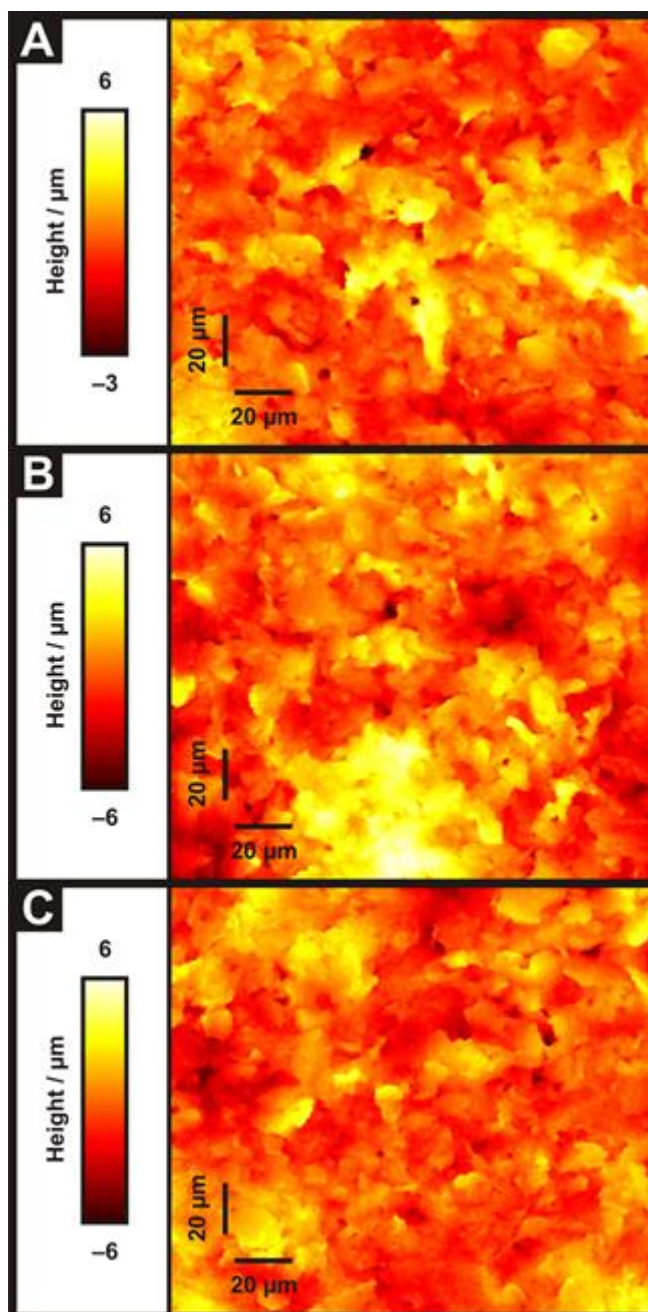
with  $z$  being the height above the surface at a coordinate  $(x, y)$ . Although similar to the surface area ratio ( $S_{dr}$ ) typically used for surface topology measurements,<sup>90</sup> the equation has been modified to provide the ratio of interfacial area to the area of the projected horizontal plane, rather than the increment of the interfacial surface area to the projected horizontal plane. This modification has been made as the roughness factor is described as the ratio of the catalyst active surface area to the substrate geometric surface area.<sup>47</sup> The roughness factors were consistently found to occur in the range 1.918 to 1.934 even for the three SPEs modified with 257, 1009 and 2019 ng cm<sup>-2</sup> of 2D MoS<sub>2</sub> nanosheets respectively. Clearly this shows that the WLP probes only the outside/upper layer of the exposed 2D nanosheets and is insensitive to the surface coverage/mass of material immobilised and does not provide us with the *electrochemically active area*. Clearly this approach will limited the interpretation of the ToF (see main text).

### Method 2

Following the method of Shin *et al.*<sup>68</sup> the double layer capacitance can be used to calculate the active surface area of the 2D MoS<sub>2</sub> nanosheet modified SPE electrode. Using an unmodified SPE

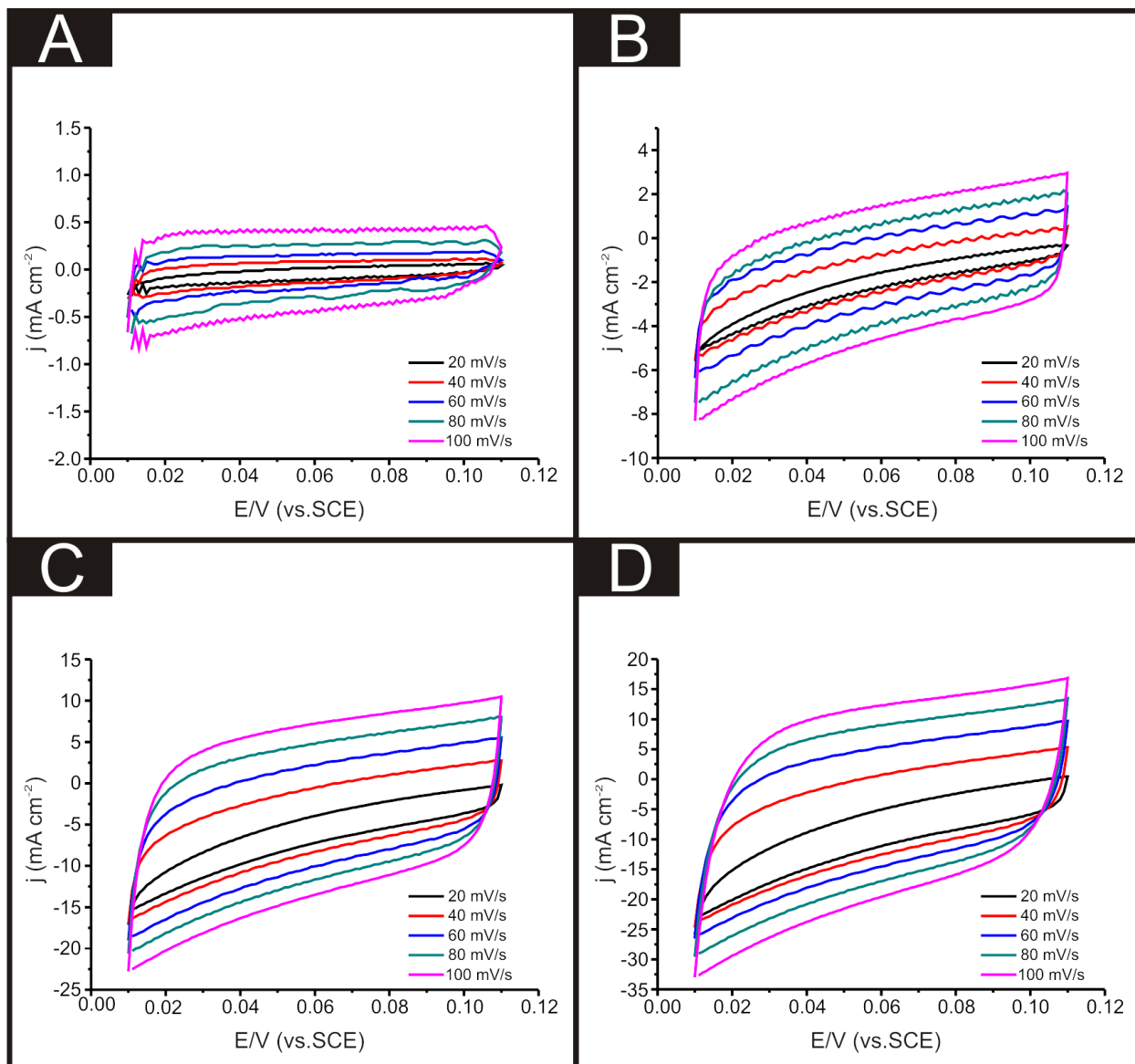
and SPEs modified with 0, 257, 1009 and 2019 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets, cyclic voltammetry was performed using a potential range of 0.01 to 0.011 V, which is in the non-Faradaic window, at each of the following scan rates (20, 40, 60, 80, 100 mV/s). The potential range used is presumed to have no Faradaic processes occurring, therefore cathodic and anodic current densities are associated with charging of the electrical double layer (see ESI Figure. 7). ESI Figure. 8 shows the difference between the anodic and cathodic current at 0.06 V *versus* the corresponding scan rate. The slope of each set of points in Figure. 8 being proportional to a doubling of the double layer capacitance. The double layer capacitance values determined are 8.7, 68, 218, 322 μF cm<sup>-2</sup> for SPEs modified with 0, 257, 1009 and 2019 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets respectively. The 7.8× increase in double layer capacitance from unmodified to 257 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheet modification reveals that post modification there is a significant adherence of 2D MoS<sub>2</sub> nanosheets upon the SPE electrode surface. There is a further 3.2× and 4.7× increase in the capacitance value from that of 257 to 1009 and 2019 ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets modifications respectively. It is inferred that this is associated with a thickening of the 2D MoS<sub>2</sub> nanosheets deposited. The disparity between the increase in capacitance and the increase in ng cm<sup>-2</sup> 2D MoS<sub>2</sub> nanosheets is of interest and further study on the matter is required.

**ESI Figure. 7** White light profilometry surface topography maps of SPE's modified with (A) 257.1, (B) 1009.5 and (C) 2019  $\text{ng cm}^{-2}$  of 2D  $\text{MoS}_2$  nanosheets. It is evident that the surface roughness remains relatively constant with the increasing 2D  $\text{MoS}_2$  nanosheet modification.

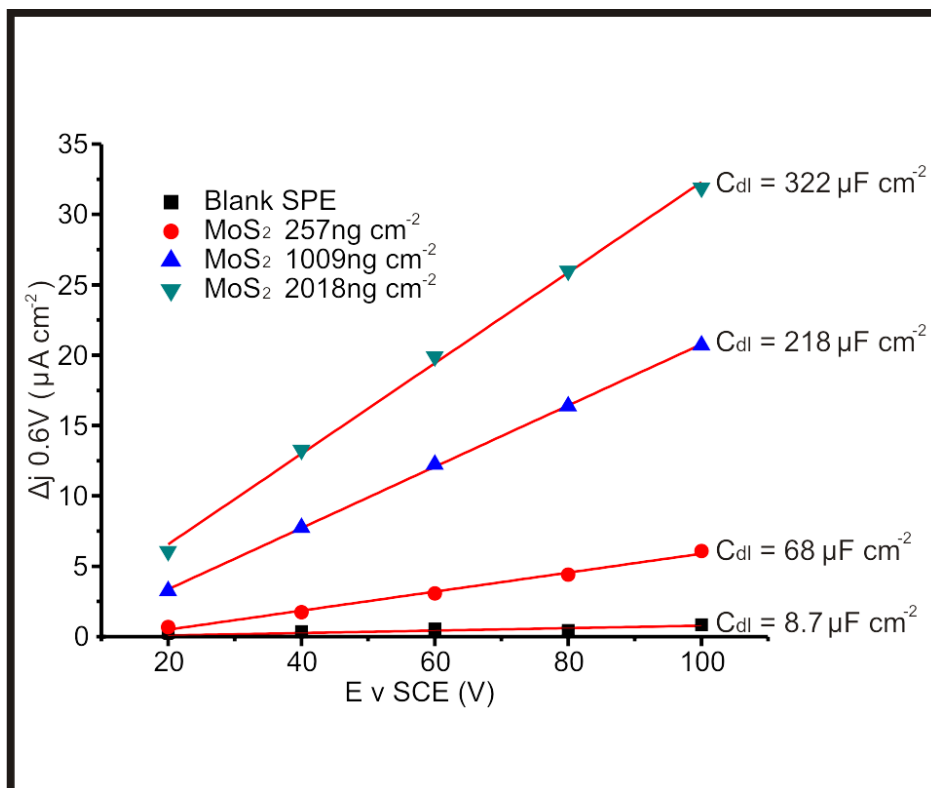


### ESI Figure. 8

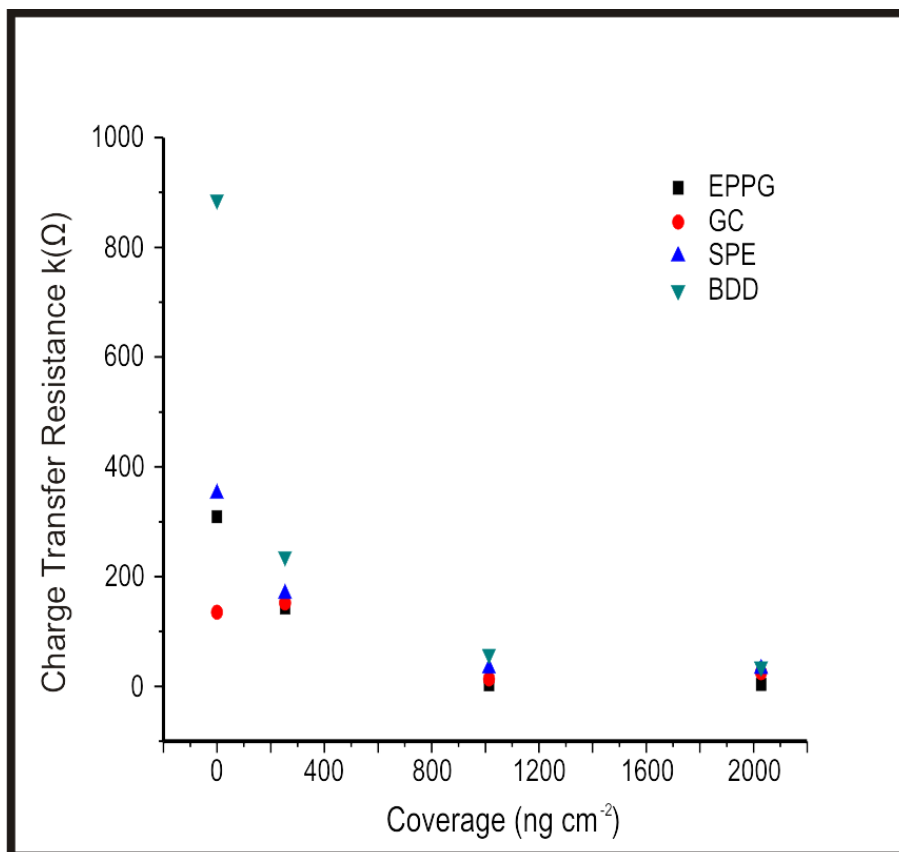
Cyclic voltammograms recorded in 0.5M H<sub>2</sub>SO<sub>4</sub> solution for SPE's with varying amounts of 2D MoS<sub>2</sub> nanosheet modification; (A) 0, (B) 257, (C) 1009, (D) 2019 ng cm<sup>-2</sup>.



**ESI Figure. 9** The difference in anodic and cathodic current density taken at +0.06 V *versus* scan rate ( $\text{mVs}^{-1}$ ). The slope of the linear regression indicates the value of double layer capacitance ( $C_{dl}$ ).



**ESI Figure. 10** An electrochemical impedance spectroscopy (EIS) study showing charge transfer resistance values (ohm) for EPPG, GC, SPE and BDD against 2D MoS<sub>2</sub> nanosheet coverages of 0, 257, 1009 and 2019 ng cm<sup>-2</sup>. Increasing coverage leading to a decrease in EIS followed by a plateau. The EIS study was carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub>, the frequency was from 0.1–100,000 Hz, and an amplitude of 10 mV (vs. SCE).





## References

1. Y. Z. Yufei Zhao, Zhiyu Yang, Yiming Yan and Kening Sun, *Sci. Technol. Adv. Mater* 2013, **14**.
2. T. Wang, L. Liu, Z. Zhu, P. Papakonstantinou, J. Hu, H. Liu and M. Li, *Energy Environ. Sci.*, 2013, **6**, 625-633.
3. A. J. López-Menéndez, R. Pérez and B. Moreno, *J. Environ. Manage.*, 2014, **145**, 368-373.
4. T. D. M. G. Schultz, G. P. Brasseur, W. Zittel, *Science* 2003, **302**, 624-627.
5. T. Hua, R. Ahluwalia, L. Eudy, G. Singer, B. Jermer, N. Asselin-Miller, S. Wessel, T. Patterson and J. Marcinkoski, *J. Power Sources*, 2014, **269**, 975-993.
6. J. Andrews and B. Shabani, *WIREs Energy Environ*, 2014, **3**, 474-489.
7. B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, I. Chorkendorff and J. K. Nørskov, *J. Am. Chem. Soc.*, 2005, **127**, 5308-5309.
8. M. Gratzel., *Inorg. Chem.*, 2005, **44**, 6841-6851.
9. J. P. Barton and D. G. Infield, *IEEE Trans. Energy Convers*, 2004, **19**, 441-448.
10. F. Blaabjerg, Z. Chen and S. B. Kjaer, *IEEE Trans. Power Electron.*, 2004, **19**, 1184-1194.
11. N. M. Marković and P. N. Ross Jr, *Surf. Sci. Rep.*, 2002, **45**, 117-229.
12. N. M. Marković, B. N. Grgur and P. N. Ross, *J. Phys. Chem. B*, 1997, **101**, 5405-5413.
13. A. B. Laursen, S. Kegnaes, S. Dahl and I. Chorkendorff, *Energy Environ. Sci.*, 2012, **5**, 5577-5591.
14. T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch and I. Chorkendorff, *Science*, 2007, **317**, 100-102.
15. B. X. Ya Yan , Zhichuan Xu , and Xin Wang *ACS Catal.*, 2014, 693-1705.
16. K. Ravindra, L. Bencs and R. Van Grieken, *Sci. Total Environ.*, 2004, **318**, 1-43.
17. R. L. McCreery, *Chem. Rev.*, 2008, **108**, 2646-2687.
18. D. A. C. Brownson and C. E. Banks, *Electrochem. Commun.*, 2011, **13**, 111-113.
19. M. Lu, K. E. Toghill and R. G. Compton, *Electroanalysis*, 2011, **23**, 1089-1094.
20. M. Musameh, J. Wang, A. Merkoci and Y. Lin, *Electrochem. Commun.*, 2002, **4**, 743-746.
21. A. Koca, *Int. J. Hydrogen Energy In*, 2009, **34**, 2107-2112.
22. Y. Shen, J. Liu, J. Jiang, B. Liu and S. Dong, *J. Phys. Chem. B*, 2003, **107**, 9744-9748.
23. J. Yin, J. B. Jia and L. D. Zhu, *In*, 2008, **33**, 7444-7447.
24. Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec and S. Z. Qiao, *Nat Commun*, 2014, **5**.
25. Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara and T. F. Jaramillo, *Nano Lett.*, 2011, **11**, 4168-4175.
26. D. Y. Chung, S.-K. Park, Y.-H. Chung, S.-H. Yu, D.-H. Lim, N. Jung, H. C. Ham, H.-Y. Park, Y. Piao, S. J. Yoo and Y.-E. Sung, *Nanoscale*, 2014, **6**, 2131-2136.
27. Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *J. Am. Chem. Soc.* , 2011, **133**, 7296-7299.
28. D. Merki, S. Fierro, H. Vrubel and X. Hu, *Chem. Sci*, 2011, **2**, 1262-1267.
29. Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, *Angew. Chem.*, 2014, **126**, 6828-6832.
30. L. F. Pan, Y. H. Li, S. Yang, P. F. Liu, M. Q. Yu and H. G. Yang, *Electrochem. Commun.*, 2014, **50**, 13135-13137.
31. Y. H. Chang, C. T. Lin, T. Y. Chen, C. L. Hsu, Y. H. Lee, W. J. Zhang, K. H. Wei and L.

- J. Li, *Adv. Mater.*, 2013, **25**, 756-760.
32. P. C. Joensen, E. D. Alberding, N. Frindt, R. F., *J. Phys. C: Solid State Phys.*, 1987, **20**, 4043-4053.
  33. J. H. Lee, W. S. Jang, S. W. Han and H. K. Baik, *Langmuir*, 2014, **30**, 9866-9873.
  34. S. Ji, Z. Yang, C. Zhang, Z. Liu, W. W. Tjiu, I. Y. Phang, Z. Zhang, J. Pan and T. Liu, *Electrochim. Acta*, 2013, **109**, 269-275.
  35. RadisavljevicB, RadenovicA, BrivioJ, GiacomettiV and KisA, *Nat Nano*, 2011, **6**, 147-150.
  36. S. Tongay, J. Zhou, C. Ataca, K. Lo, T. S. Matthews, J. Li, J. C. Grossman and J. Wu, *Nano Lett.*, 2012, **12**, 5576-5580.
  37. M.-L. Tsai, S.-H. Su, J.-K. Chang, D.-S. Tsai, C.-H. Chen, C.-I. Wu, L.-J. Li, L.-J. Chen and J.-H. He, *ACS Nano*, 2014, **8**, 8317-8322.
  38. C. Ataca, M. Topsakal, E. Aktürk and S. Ciraci, *J. Phys. Chem. C*, 2011, **115**, 16354-16361.
  39. N. A. Dhas and K. S. Suslick, *J. Am. Chem. Soc.*, 2005, **127**, 2368-2369.
  40. F. Cesano, S. Bertarione, A. Piovano, G. Agostini, M. M. Rahman, E. Groppo, F. Bonino, D. Scarano, C. Lamberti, S. Bordiga, L. Montanari, L. Bonoldi, R. Millini and A. Zecchina, *Catal. Sci. Technol.*, 2011, **1**, 123-136.
  41. S. S. Chou, M. De, J. Kim, S. Byun, C. Dykstra, J. Yu, J. Huang and V. P. Dravid, *J. Am. Chem. Soc.*, 2013, **135**, 4584-4587.
  42. D. Wang, Z. Pan, Z. Wu, Z. Wang and Z. Liu, *J. Power Sources*, 2014, **264**, 229-234.
  43. D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nano Lett.*, 2013, **13**, 6222-6227.
  44. N. Tateishi, K. Yahikozawa, K. Nishimura and Y. Takasu, *Electrochim. Acta*, 1992, **37**, 2427-2432.
  45. M.-R. Gao, M. K. Y. Chan and Y. Sun, *Nat Commun*, 2015, **6**.
  46. Y. Yu, S.-Y. Huang, Y. Li, S. N. Steinmann, W. Yang and L. Cao, *Nano Lett.*, 2014, **14**, 553-558.
  47. J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.*, 2012, **2**, 1916-1923.
  48. C. W. Foster, J. P. Metters and C. E. Banks, *Electroanalysis*, 2013, **25**, 2275-2282.
  49. A. B. Laursen, A. S. Varela, F. Dionigi, H. Fanchiu, C. Miller, O. L. Trinhammer, J. Rossmeisl and S. Dahl, *J. Chem. Educ.*, 2012, **89**, 1595-1599.
  50. D. Marin, F. Medicuti and C. Teijeiro, *J. Chem. Educ.*, 1994, **71**, A277.
  51. L. R. Cumba, J. P. Smith, D. A. C. Brownson, J. Iniesta, J. P. Metters, D. R. d. Carmo. and C. E. Banks, *Analyst*, 2015, **140**, 1543-1550.
  52. C. W. Foster, J. Pillay, J. P. Metters and C. E. Banks, *Sensors (Basel, Switzerland)*, 2014, **14**, 21905-21922.
  53. J. P. Metters, M. Gomez-Mingot, J. Iniesta, R. O. Kadara and C. E. Banks, *Sens. Actuators, B*, 2013, **177**, 1043-1052.
  54. E. P. Randviir, D. A. C. Brownson, J. P. Metters, R. O. Kadara and C. E. Banks, *PCCP*, 2014, **16**, 4598-4611.
  55. J. P. Smith, J. P. Metters, O. I. G. Khreit, O. B. Sutcliffe and C. E. Banks, *Anal. Chem.*, 2014, **86**, 9985-9992.
  56. O. Ramdani, J. P. Metters, L. C. S. Figueiredo-Filho, O. Fatibello-Filho and C. E. Banks, *Analyst*, 2013, **138**, 1053-1059.
  57. J. P. Smith, J. P. Metters, D. K. Kampouris, C. Lledo-Fernandez, O. B. Sutcliffe and C. E.

- Banks, *Analyst*, 2013, **138**, 6185-6191.
58. Graphene Supermarket, <https://graphene-supermarket.com/MoS2-Pristine-Flakes-in-Solution.html>, [24/11/2014].
  59. Innovation in Surface Spectroscopy and Microscopy Systems, [http://www.specs.de/cms/front\\_content.php?idcat=209](http://www.specs.de/cms/front_content.php?idcat=209), Accessed 22/05/2015.
  60. M. P. Seah and S. J. Spencer, *J. Electron. Spectrosc. Relat. Phenom.*, 2006, **151**, 178-181.
  61. J. H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.*, 1976, **8**, 129-137.
  62. CasaXPS, <http://www.casaxps.com/>, Accessed 22/05/2015.
  63. E. Varrla, C. Backes, K. R. Paton, A. Harvey, Z. Gholamvand, J. McCauley and J. N. Coleman, *Chem. Mater.*, 2015, **27**, 1129-1139.
  64. C. Backes, R. J. Smith, N. McEvoy, N. C. Berner, D. McCloskey, H. C. Nerl, A. O' Neill, P. J. King, T. Higgins, D. Hanlon, N. Scheuschner, J. Maultzsch, L. Houben, G. S. Duesberg, J. F. Donegan, V. Nicolosi and J. N. Coleman, *Nat Commun*, 2014, **5**.
  65. L. Yadgarov, C. L. Choi, A. Sedova, A. Cohen, R. Rosentsveig, O. Bar-Elli, D. Oron, H. Dai and R. Tenne, *ACS Nano*, 2014, **8**, 3575-3583.
  66. J. A. Wilson and A. D. Yoffe, *A. D. Adv. Phys.*, 1969, **19**, 193-335.
  67. H. Li, Q. Zhang, C. C. R. Yap, B. K. Tay, T. H. T. Edwin, A. Olivier and D. Baillargeat, *Adv. Funct. Mater.*, 2012, **22**, 1385-1390.
  68. S. Shin, Z. Jin, D. H. Kwon, R. Bose and Y.-S. Min, *Langmuir*, 2015, **31**, 1196-1202.
  69. J. Bonde, P. G. Moses, T. F. Jaramillo, J. K. Norskov and I. Chorkendorff, *Faraday Discuss.*, 2009, **140**, 219-231.
  70. S. Ding, D. Zhang, J. S. Chen and X. W. Lou, *Nanoscale*, 2012, **4**, 95-98.
  71. A. H. Loo, A. Bonanni, A. Ambrosi and M. Pumera, *Nanoscale*, 2014, **6**, 11971-11975.
  72. D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao and Y. Cui, *Nano Lett.*, 2013, **13**, 1341-1347.
  73. C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano*, 2010, **4**, 2695-2700.
  74. K. Zhang, S. Hu, Y. Zhang, T. Zhang, X. Zhou, Y. Sun, T.-X. Li, H. J. Fan, G. Shen, X. Chen and N. Dai, *ACS Nano*, 2015, **9**, 2704-2710.
  75. J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont and T. F. Jaramillo, *ACS Catal.*, 2014, **4**, 3957-3971.
  76. S. Helveg, J. V. Lauritsen, E. Lægsgaard, I. Stensgaard, J. K. Nørskov, B. S. Clausen, H. Topsøe and F. Besenbacher, *Physical Review Letters*, 2000, **84**, 951-954.
  77. J. Z. Xie, Hao. Li, Shuang. Wang, Ruoxing. Sun, Xu. Zhou, Min. Zhou, Jingfang. Lou, Xiong Wen. Xie, Yi, *Adv. Mater.*, 2013, **25**, 5807-5813.
  78. M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li and S. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10274-10277.
  79. D. A. Brownson, A. C. Lacombe, D. K. Kampouris and C. E. Banks, *Analyst*, 2012, **137**, 420-423.
  80. D. A. C. Brownson, L. C. S. Figueiredo-Filho, X. Ji, M. Gomez-Mingot, J. Iniesta, O. Fatibello-Filho, D. K. Kampouris and C. E. Banks, *J. Mater. Chem.A*, 2013, **1**, 5962-5972.
  81. D. A. Brownson, L. J. Munro, D. K. Kampouris and C. E. Banks, *RSC Adv.*, 2011, **1**, 978-988.
  82. D. A. C. Brownson, D. K. Kampouris and C. E. Banks., *Chem. Soc. Rev.*, 2012, **41**, 6944-6976.
  83. T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Hørch and I. Chorkendorff,

- Science*, 2007, **317**, 100-102.
84. M.-R. Gao, J.-Z. Liang, Y.-R. Zheng, Y.-F. Xu, J. Jiang, Q. Gao, J. Li and S.-H. Yu, *Nat Commun*, 2015, **6**.
  85. X. Bian, J. Zhu, L. Liao, M. D. Scanlon, P. Ge, C. Ji, H. H. Girault and B. Liu, *Electrochem. Commun.*, 2012, **22**, 128-132.
  86. H. Vrubel, D. Merki and X. Hu, *Energy Environ. Sci.*, 2012, **5**, 6136-6144.
  87. D. Merki, H. Vrubel, L. Rovelli, S. Fierro and X. Hu, *Chem. Sci.*, 2012, **3**, 2515-2525.
  88. H. Zhu, F. Lyu, M. Du, M. Zhang, Q. Wang, J. Yao and B. Guo, *ACS Appl. Mater. Interfaces*, 2014, **6**, 22126-22137.
  89. J. R. McKone, B. F. Sadler, C. A. Werlang, N. S. Lewis and H. B. Gray, *ACS Catal.*, 2012, **3**, 166-169.
  90. T. Patois, B. Lakard, S. Monney, X. Roizard and P. Fievet, *Synth. Met.*, 2011, **161**, 2498-2505.