2D Nanosheet Molybdenum Disulphide (MoS₂) Modified Electrodes Explored Towards the Hydrogen Evolution Reaction

(Electronic supporting information)

Samuel J. Rowley-Neale[1], Dale A. C. Brownson[1], Graham C. Smith[2], David A. G. Sawtell[1], Peter J. Kelly[1] and Craig E. Banks[1]*

[1]: 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.

[2]: Faculty of Science and Engineering, Department of Natural Sciences, University of Chester, Thornton Science Park, Pool Lane, Ince, Chester CH2 4NU, UK.
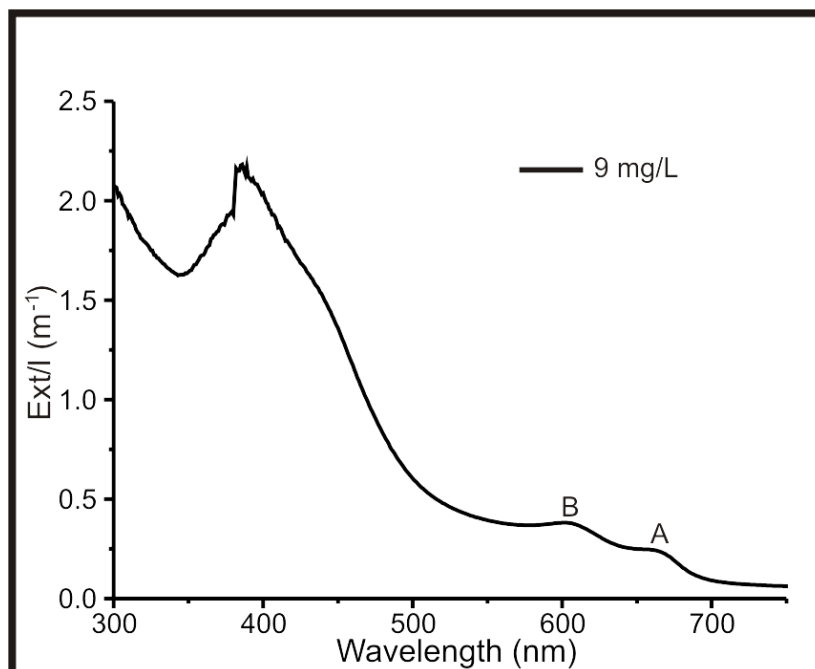
*To whom correspondence should be addressed.
Email: c.banks@mmu.ac.uk; Tel: ++(0)1612471196; Fax: ++(0)1612476831
Website: www.craigbanksresearch.com

ESI Figure. 1 Extinction spectra for the commercially sourced 2D MoS_2 nanosheets dispersed in ethanol (9 mg L^{-1}).

ESI Figure. 2 (A) SEM image of a multi-layered 2D MoS$_2$ nanosheet flake on top of few layer 2D MoS$_2$ 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.
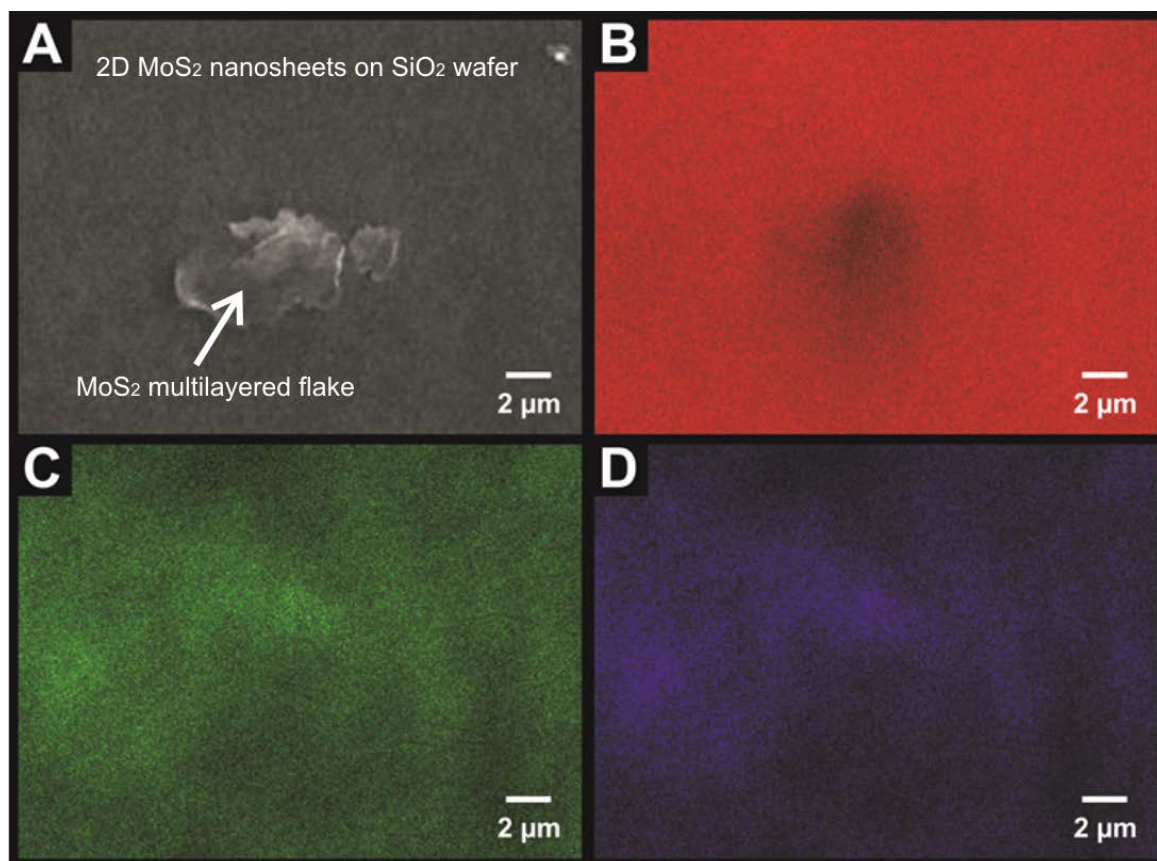
**ESI Figure. 3** TEM images of the commercially sourced 2D MoS_2 nanosheets deposited onto a carbon grid. (A) TEM image at 5,800 times magnification (scale bar: 2 µm), (B) TEM image at 13,500 times magnification (scale bar: 1 µm).
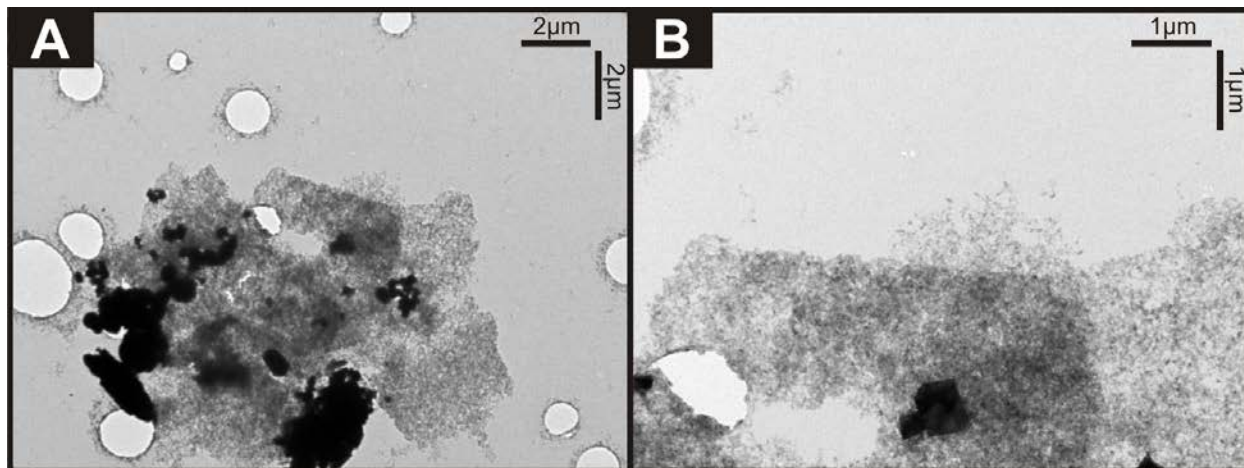
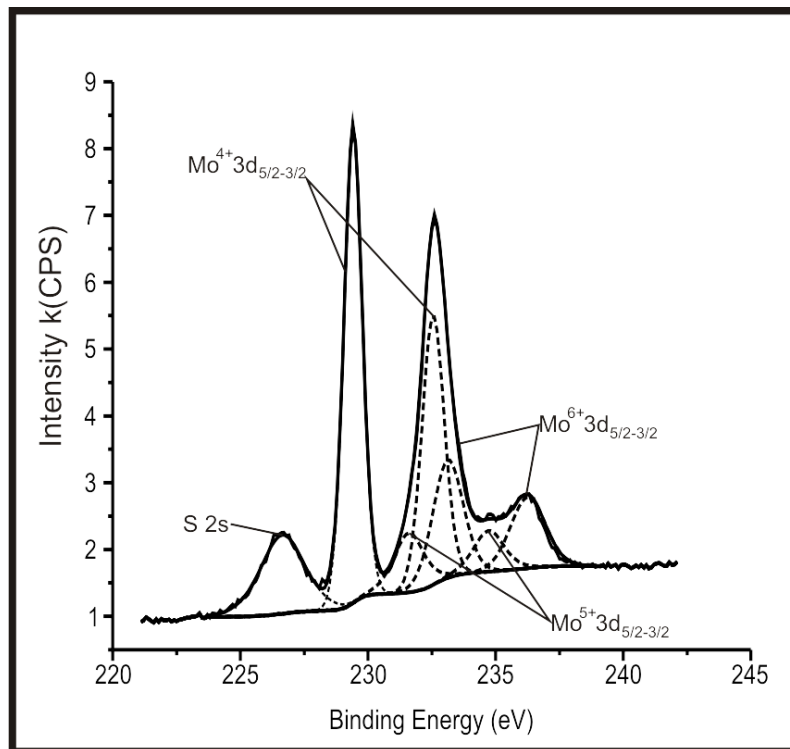**ESI Figure. 4** XRD spectra of the 2D MoS_2 nanosheets deposited onto a glass slide between 10 and 100 2θ, showing a characteristic peak at 14 2θ.
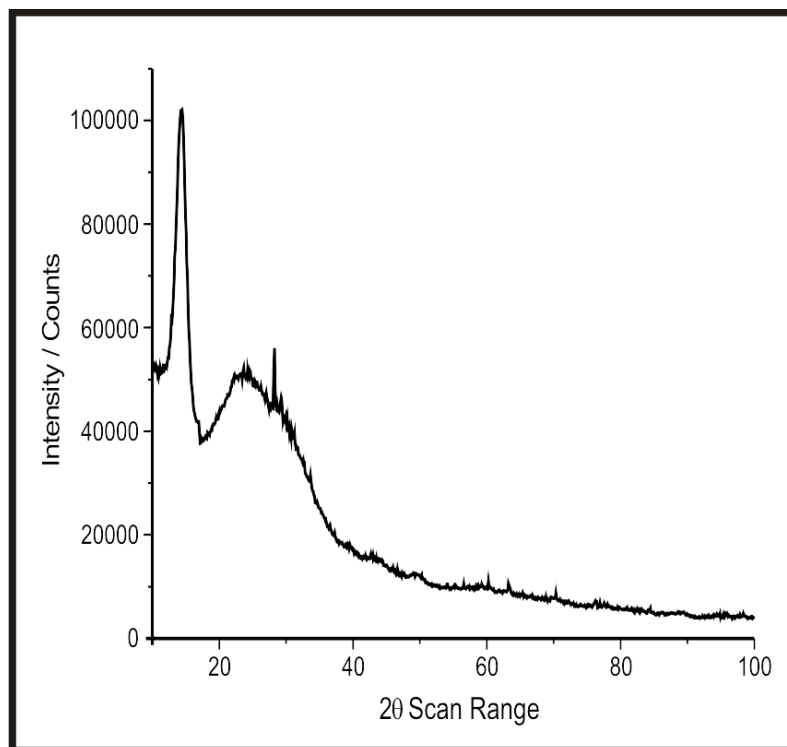
ESI Figure. 5 XPS survey spectrum for a sample of the 2D MoS_2 nanosheets once deposited onto a Si (111) wafer showing a 1:2.2 concentration percentage for Mo and S respectively.
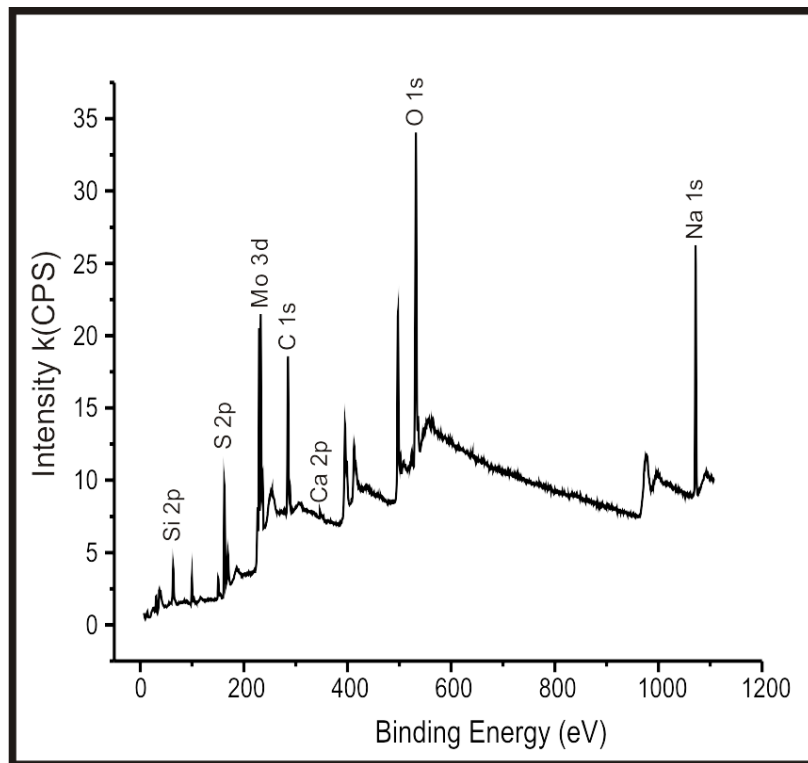
ESI Figure. 6 Curve fitted XPS Mo 3d spectrum

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.

Element	Atom % Concentration
Na 1s	8.36
Mo 3d	7.44
C 1s	34.41
Ca 2p	0.61
S 2p	16.30
Si 2p	5.47
O 1s	27.40

Roughness Factor Calculations

Method 1

In order to use the ToF formula described by Benck, *et al.* [1] it was essential for roughness factors (R_F) 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_2 nanosheets was measured once deposited onto the SPEs, and these measurements were subsequently used to provide a value for the roughness factor used in this work. The surface profile maps are shown in ESI Figure 7 were analysed using a Matlab script based on the following equation:

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

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:

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

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,[2] 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.[1] The roughness factors were consistently found to occur in the range 1.918 to 1.934 for the three SPEs modified with 252, 1009 and 2019 ng cm^{-2} of 2D MoS_2 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.* [3] the double layer capacitance can be used to calculate the active surface area of the 2D MoS_2 nanosheet modified SPE electrode. Using an unmodified SPE and SPEs modified with 0, 252, 1009 and 2019 ng cm^{-2} 2D MoS_2 nanosheets, cyclic voltammetry was performed using a potential range of 0.01 to 0.11 V, which is in the non-Faradaic window, at each of the following scan rates (20, 40, 60, 80, 100 mVs^{-1}).   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. 8). ESI Figure. 9 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 ESI Figure. 9 being proportional to a doubling of the double layer capacitance. The double layer capacitance values determined are 8.7, 68, 218, 322 μF cm^{-2} for SPEs modified with 0, 252, 1009 and 2019 ng cm^{-2} 2D MoS_2 nanosheets respectively. The 7.8× increase in double layer capacitance from unmodified to 252 ng cm^{-2} 2D MoS_2 nanosheet modification reveals that post modification there is a significant adherence of 2D MoS_2 nanosheets upon the SPE electrode surface. There is a further 3.2× and 4.7× increase in the capacitance value from that of 252 to 1009 and 2019 ng cm^{-2} 2D MoS_2 nanosheets modifications respectively. It is inferred that this is associated with a thickening of the 2D MoS_2 nanosheets deposited. The disparity between the increase in capacitance and the increase in ng cm^{-2} 2D MoS_2 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) 252, (B) 1009 and (C) 2019 ng cm^{-2} of 2D MoS$_2$ nanosheets. It is evident that the surface roughness remains relatively constant with the increasing 2D MoS$_2$ nanosheet modification.
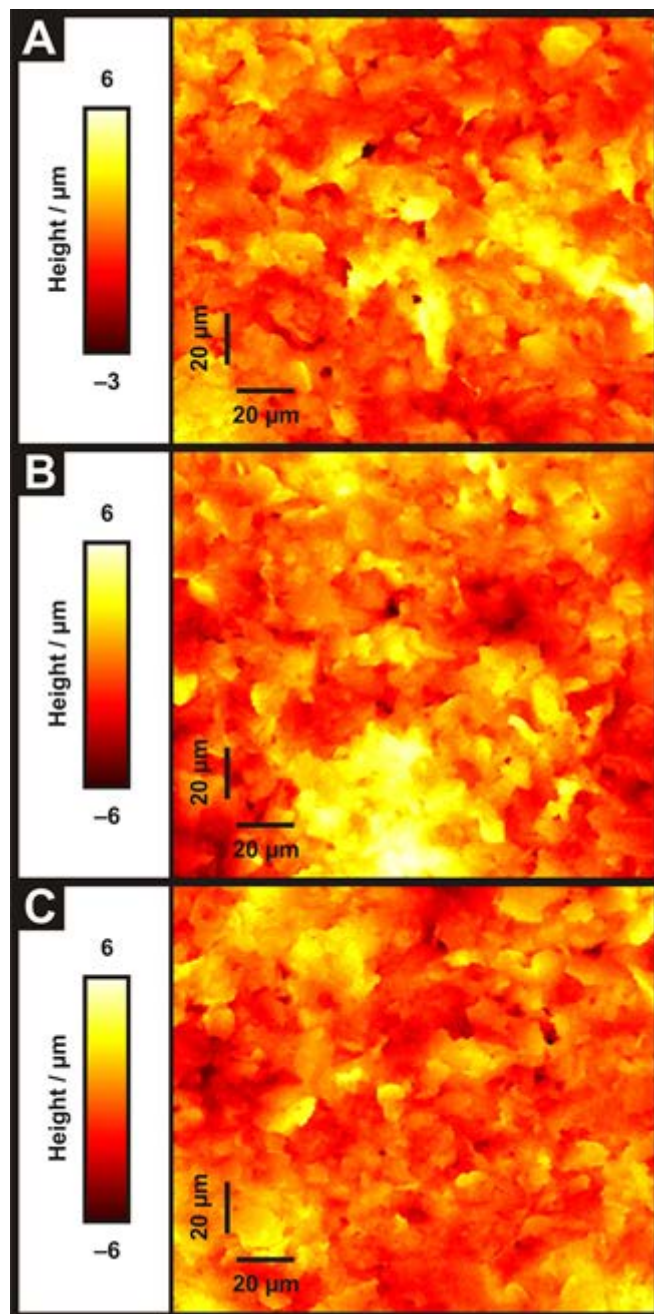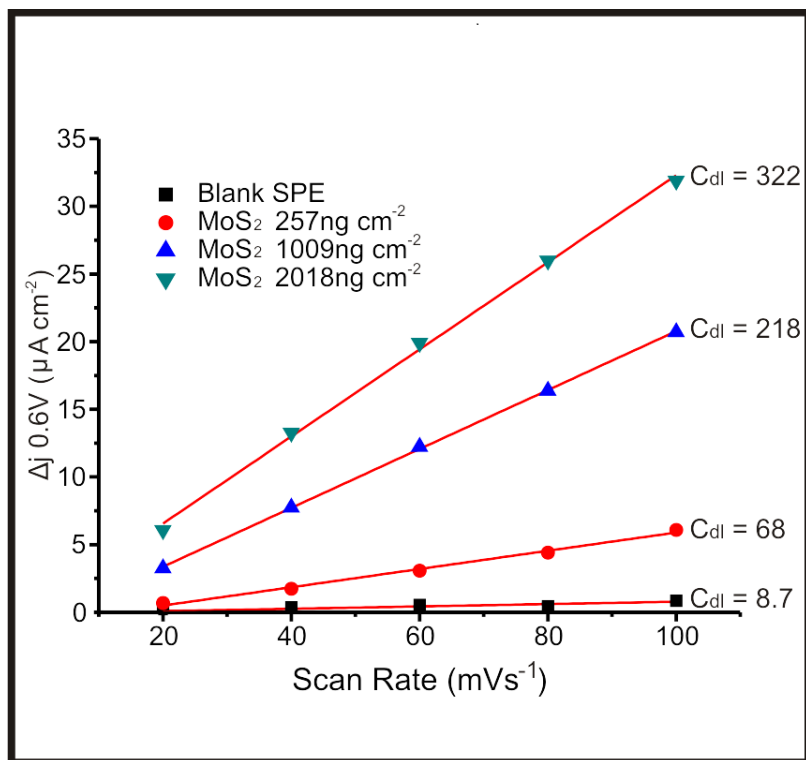
ESI Figure. 8

Cyclic voltammograms recorded in 0.5 M H_2SO_4 solution for SPE's with varying amounts of 2D MoS_2 nanosheet modification; (A) 0, (B) 252, (C) 1009, (D) 2019 ng cm^{-2}.
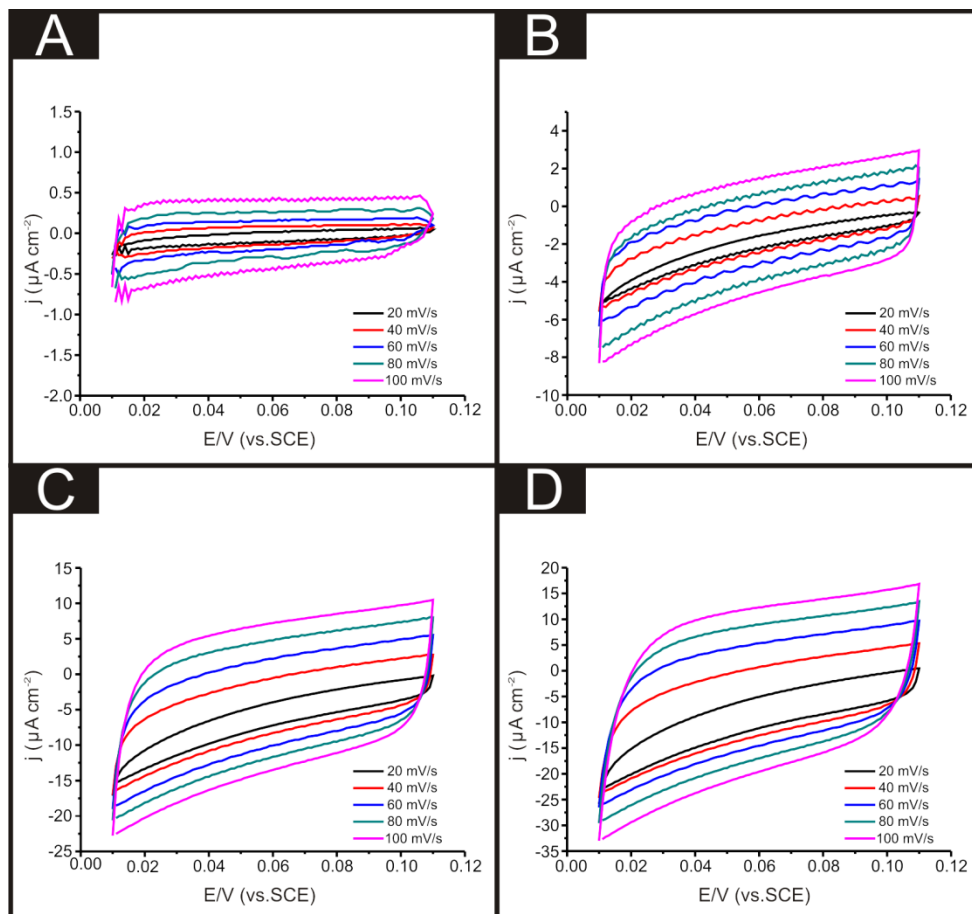
ESI Figure. 9 The difference in anodic and cathodic current density taken at +0.06 V *versus* scan rate (mVs^{-1} *vs.* SCE). The slope of the linear regression indicates the value of double layer capacitance (C_{dl}).

ESI Figure. 10 An electrochemical impedance spectroscopy (EIS) study showing charge transfer resistance (ohm) values for EPPG, GC, SPE and BDD against 2D MoS$_2$ nanosheet coverages' of 0, 252, 1009 and 2019 ng cm^{-2}. Increasing coverage leading to a decrease in EIS followed by a plateau. The EIS study was carried out in 0.5 M H$_2$SO$_4$, the frequency was from 0.1–100,000 Hz, and an amplitude of 10 mV (*vs*. SCE).
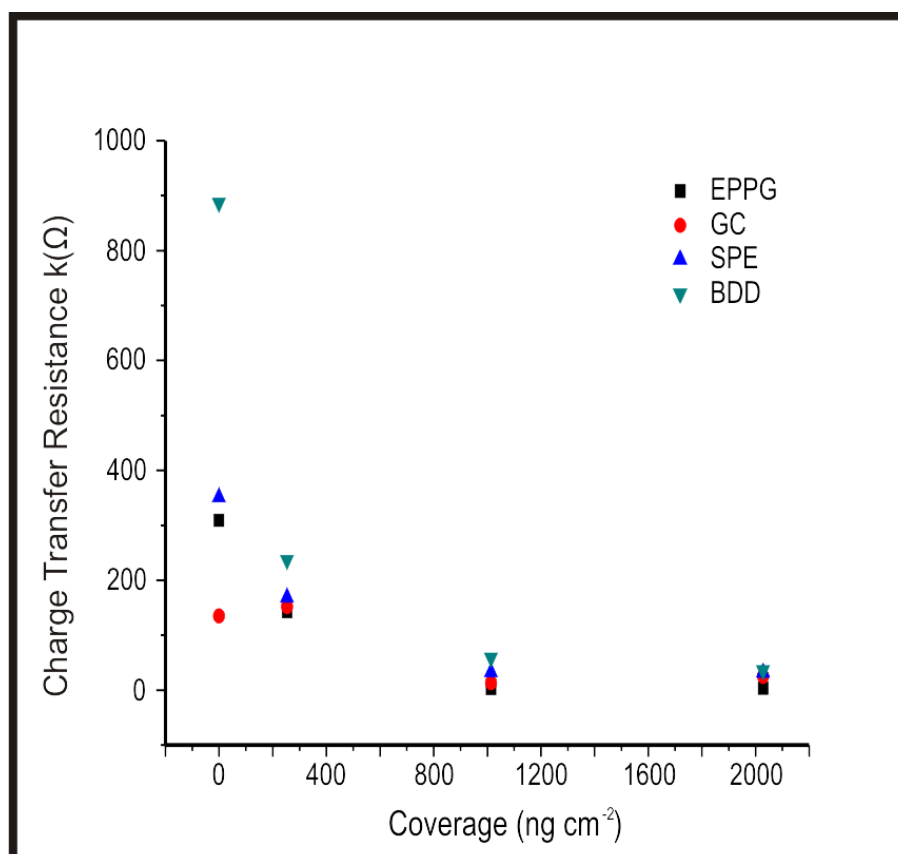
References

1. J. D. Benck, Z. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.*, 2012, 2, 1916-1923.
2. T. Patois, B. Lakard, S. Monney, X. Roizard and P. Fievet, *Synth. Met.*, 2011, 161, 2498-2505.
3. S. Shin, Z. Jin, D. H. Kwon, R. Bose and Y.-S. Min, *Langmuir*, 2015, 31, 1196-1202.