Electronic Supporting Information (ESI) for the following publication:

Mass-Producible 2D-$MoSe_2$ Bulk Modified Screen-Printed Electrodes Provide Significant Electrocatalytic Outputs towards the Hydrogen Evolution Reaction

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Turn Over Frequency (ToF) Calculation

In order to evaluate how the intrinsic catalytic activity of the 2D-$MoSe_2$ alters with varying percentage of ink modification on a ‘per active site’ basis, the ToF was deduced using a modified method reported previously.[1, 2] In this calculation is is assumed that the surface of the 2D-$MoSe_2$ nanosheets are atomically flat (altough the true modification will have a finite roughness).[1] Taking the selenium to selenium bond distance to be 2.735 Å which corresponds to an area of 4.12 $Å^2$/Se atom , which can be used to calculate the surface area occupied by each $MoSe_2$:

$$4.12\,\frac{Å^2}{S\ atom} * \frac{2\ Se\ atom}{1\ MoSe_2} = 8.24\,\frac{Å^2}{MoSe_2} \qquad [1]$$

Using the dervied area for a $MoSe_2$ molecule (corresponding to the number of surface sites for a flat standard) it is possible to determine the number of $MoSe_2$ molecules per cm^2 geometric area:

$$\frac{1\ MoSe_2}{8.24\ Å^2} * \frac{10^{16}Å^2}{0.0707\ cm^2} = 1.717 * 10^{16}\,\frac{MoSe_2}{cm^2} \qquad [2]$$

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

$$\frac{\#\ Surface\ Sites\ (Catalyst)}{cm^2\ geometric\ area} = \frac{\#\ Surface\ Sites\ (Flat\ Standard)}{cm^2\ geometric\ area} * R_F \qquad [3]$$

It is also essential to accurately determine the roughness factor (R_F) for each of the $MoSe_2$-SPE’s as is common within the literature (See Roughness Factor Calculation Section). The following allows the ToF on a per-site basis to be determined:

$$TOF\ per\ site = \frac{\#\ Total\ Hydrogen\ Turn\ Overs\ /\ cm^2\ geometric\ area}{\#\ Surface\ Sites\ (Catalyst)/\ cm^2\ geometric\ area} \qquad [4]$$

Taking the value of current density (mA cm^{-2}) at the potential of –0.75 V (at a 25 mVs^{-1} scan rate) and using the R_F calculated, per-site the ToF can be deduced from the following:

$$\left(j\,\frac{mA}{cm^2}\right)\left(\frac{1\ A}{1000mA}\right)\left(\frac{1\ C/s}{1\ A}\right)\left(\frac{1\ mol\ e^-}{96{,}485.3\ C}\right)\left(\frac{1\ mol\ H_2}{2\ mol\ e^-}\right)\left(\frac{6.02214*10^{23}}{1\ mol\ H_2}\right) = 5.358 * 10^{15}\,\frac{H_2/Se}{cm^2}\,per\,\frac{mA}{cm^2}$$

[5]

Using equation 6 and a value derived from formula 5, it is possible to determine a value for the ToF:

$$\left(5.358 * 10^{15}\,\frac{H_2/Se}{cm^2}\Big/\frac{mA}{cm^2}\right)\left(10\,\frac{mA}{cm^2}\right)\left(\frac{1\ cm^2}{3.604*10^{16}\ surface\ sites}\right) = 1.48\,\frac{H_2/Se}{surface\ sites} \qquad [6]$$

At the chosen potential (– 0.75 V) the current densities were found to correspond to -1.52, -1.72, -1.67 and -1.01 mA cm^{-2} for the 5, 10, 20 and 40% $MoSe_2$-SPE’s. Using these values the ToF values deduced from the above equations were found to correspond to 2.76, 1.48, 0.92

and 0.36 $\frac{H_2/Se}{\text{Surface Site}}$.

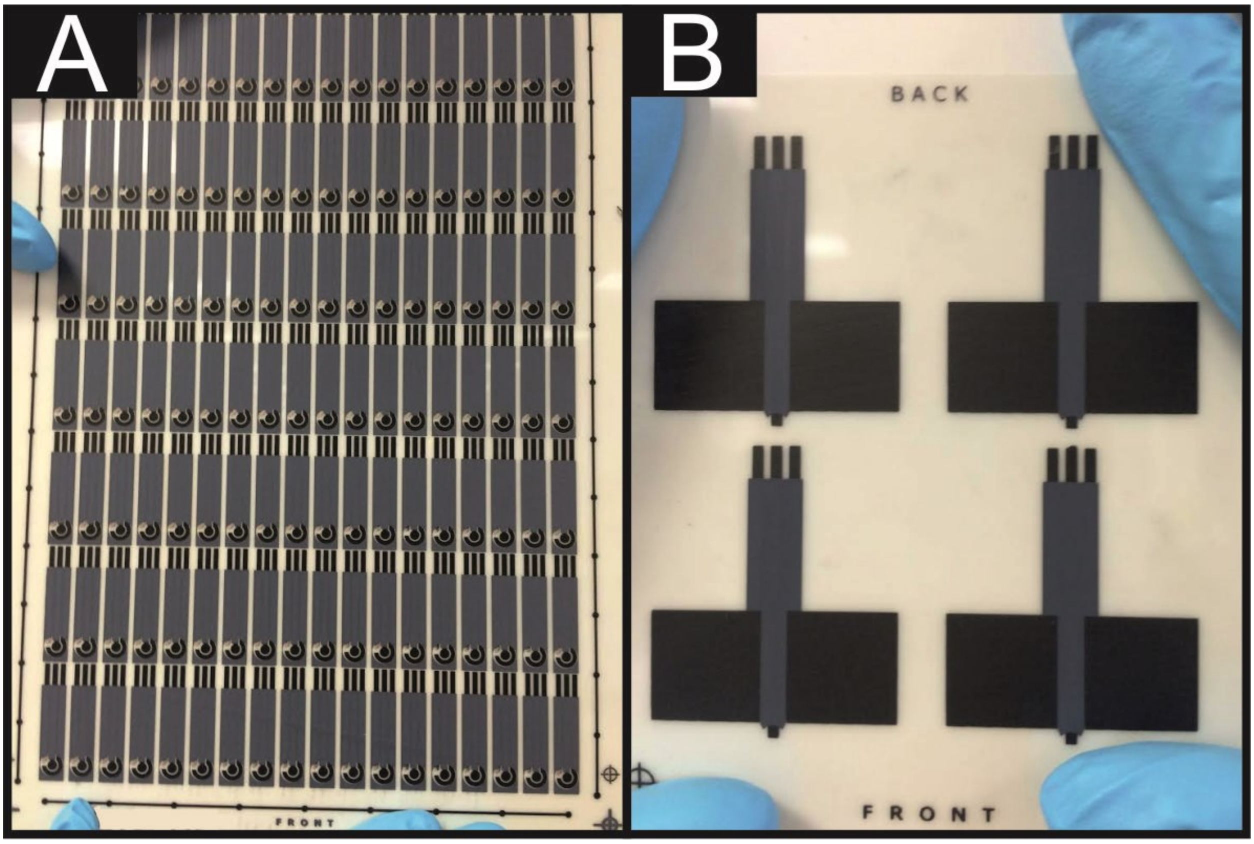
Roughness Factor Calculation

Modifying the method of Shin *et al.* [3] and Rowley *et al.*[2] the double layer capacitance can be used to calculate the active surface area of the $MoSe_2$-SPEs. 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. 3). ESI Figure 4 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 4 being proportional to a doubling of the double layer capacitance. The double layer capacitance values determined are 35.5, 75.8, 117.7, 191.6 $\mu F\ cm^{-2}$ for SPEs modified with the 5%, 10%, 20% and 40% $MoSe_2$-SPE's respectively.

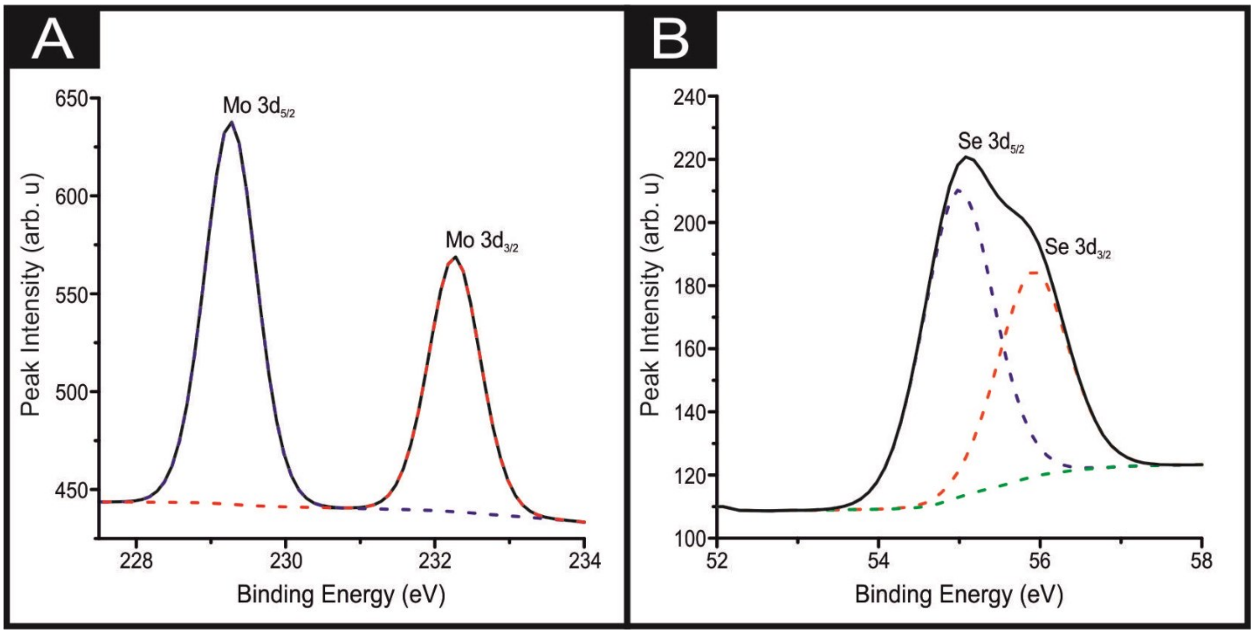
ESI Table 1. Compositional analysis of XPS spectra for a 10% $MoSe_2$-SPE pre and post 1000 repeat scan in 0.5 M H_2SO_4. Scan rate utilised 100 mVs^{-1} (*vs.* SCE). Results shown in atom percentage concentration, excluding H which is not detected by this technique.

Electrode	Element	Atom % Composition
10% $MoSe_2$-SPE *pre*-1000 repeat scans	C	84.51
	Cl	10.45
	O	4.35
	Se	0.43
	Mo	0.25
10% $MoSe_2$-SPE *post*-1000 repeat scans whilst utilising a platinum counter	Na	1.75
	O	16.65
	N	0.89
	C	72.48
	Cl	5.76
	Se	0.19
	Si	1.03
	P	0.51
	Al	0.64
	Mo	0.06
	Pt	0.04
10% $MoSe_2$-SPE *post*-1000 repeat scans whilst utilising a carbon counter	Na	0.09
	O	24.9
	N	1.45
	C	66.59
	Cl	4.51
	Se	1.01
	Si	0.55
	Mo	0.23
	Al	0.67

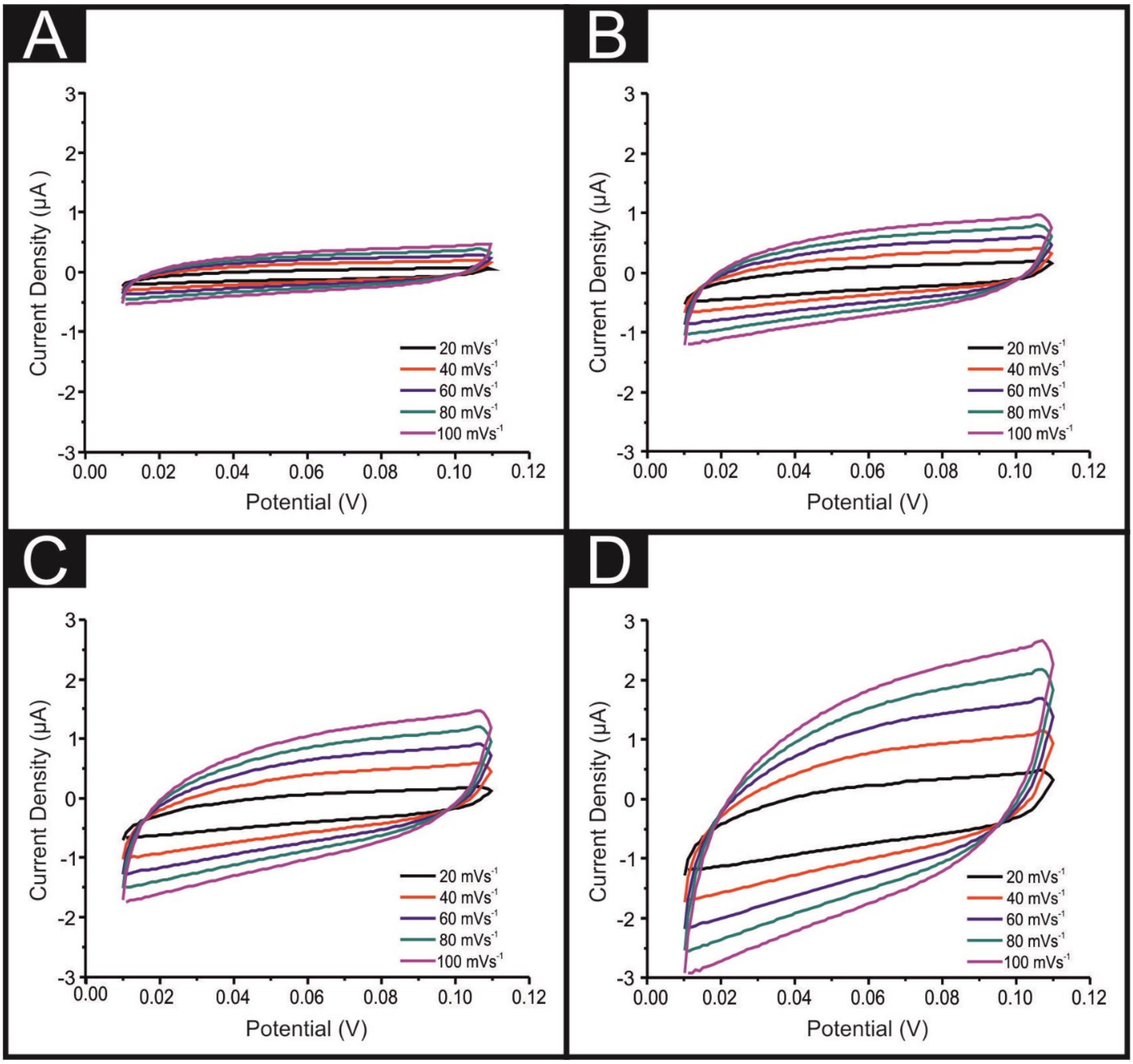
ESI Figure 1. Photographs of SPEs: (A) the SPE design utilised herein, with a working electrode surface area of 0.0707 cm^2; (B) a possible variant upon the subsequent design, with a working electrode surface that has an area of 4.5 cm^2.



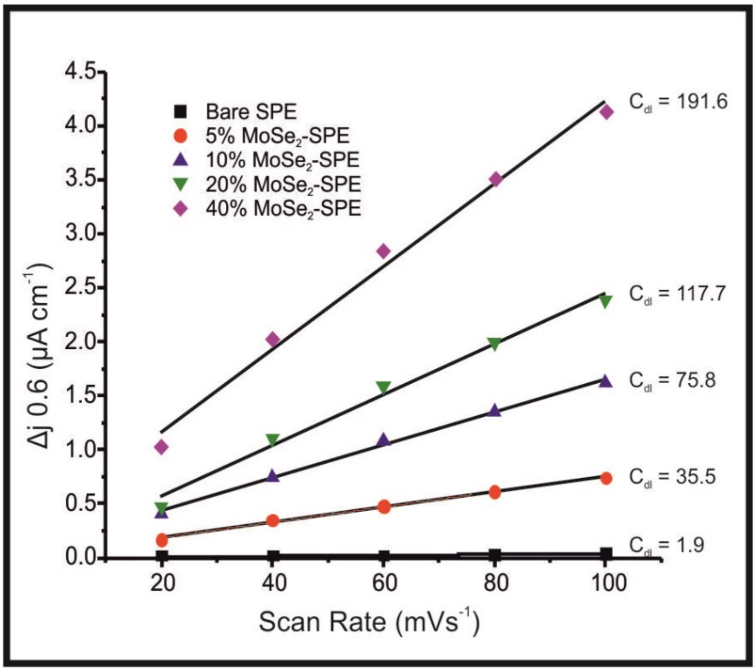
ESI Figure 2. High-resolution XPS spectra of Mo 3d and Se 3d regions of a 10% $MoSe_2$-SPE (A and B respectively).



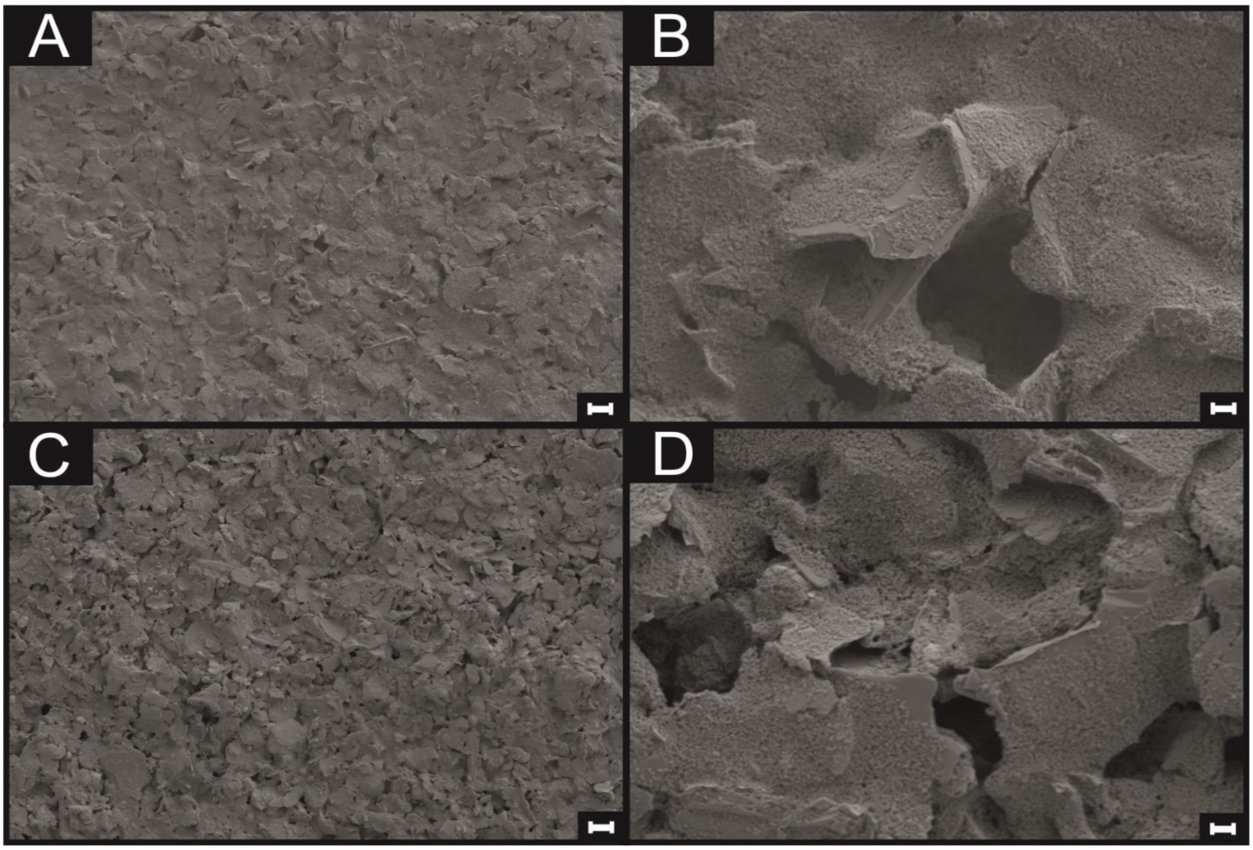
ESI Figure 3. Typical cyclic voltammograms recorded in a solution of 0.5 M H_2SO_4 using 5, 10, 20 and 40 $MoSe_2$-SPE. Scan rate: 100 mVs^{-1} (*vs.* SCE).



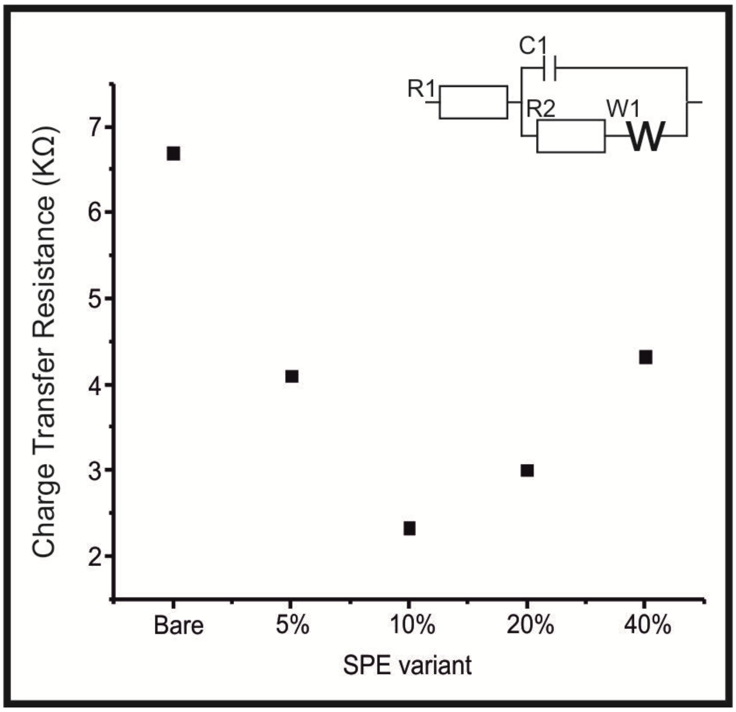
ESI Figure 4. The difference in anodic and cathodic current density taken at +0.06 V *versus* scan rate (mVs^{-1} *vs.* SCE). The slope of the linear regression indicates the value of double layer capacitance (C_{dl}: μF cm^{-2}).



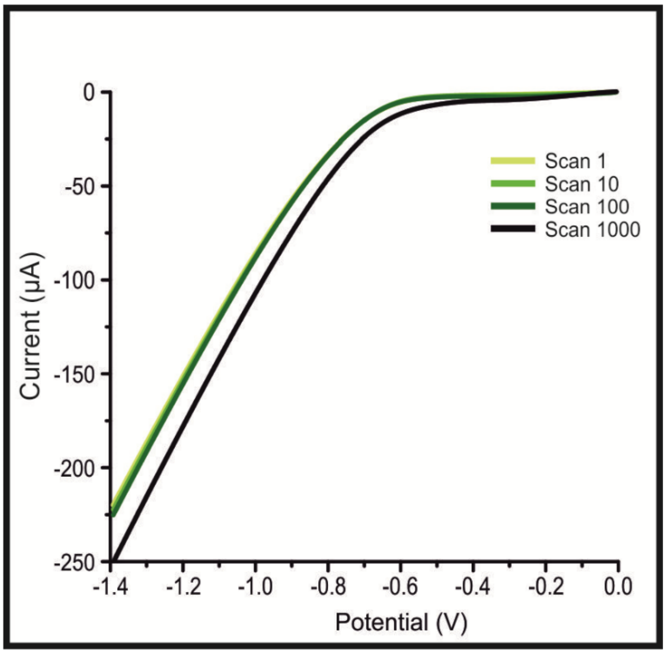
ESI Figure 5. SEM images of a bare/unmodified SPE surface (A and B) and a 10% $MoSe_2$-SPE (C and D). SEM magnifications were ×1k (scale bare, 10 μm) and ×10k (scale bare, 1 μm) respectively for the progressive images (A to B and C to D).



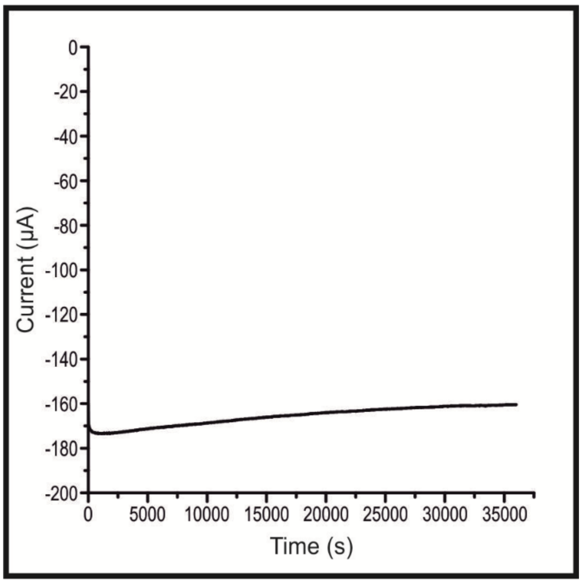
ESI Figure 6. An electrochemical impedance spectroscopy (EIS) study showing charge transfer resistance (ohm) values for the bare/unmodified, 5, 10, 20 and 40% $MoSe_2$-SPE's. The EIS study was carried out in 1 mM potassium ferrocyanide (II) in 1 M KCl, the frequency was from 0.1–100,000 Hz using an amplitude of 10 mV (*vs*. SCE). Inset: circuit utilised within experiments.



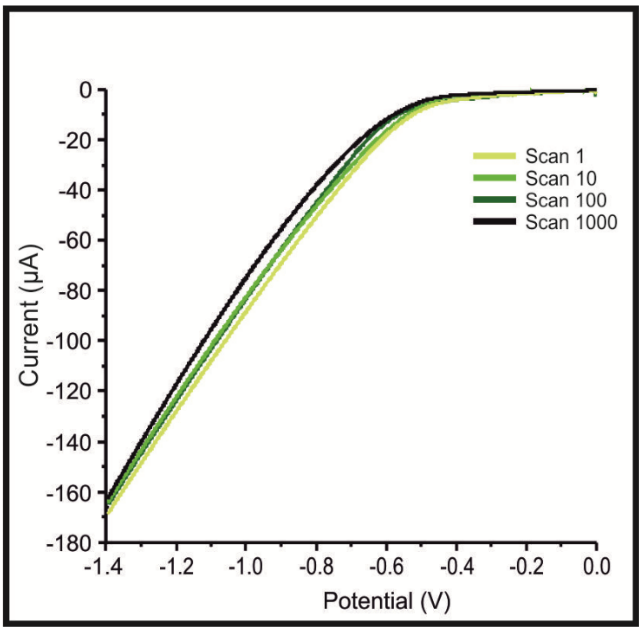
ESI Figure 7. Cyclic stability examination of a 10% $MoSe_2$-SPE linear sweep voltammetry performed between the potential range of 0 to –1.4 V using a carbon counter electrode, repeated for 1000 cycles. The figures shows the initial (yellow line), 10th (green line) scans, 100th (dark green) and 1000th scan (black line). Scan rate: 100 mVs^{-1} (*vs.* SCE).



ESI Figure 8. The current observed using chronoamperommetry with the potential held at –0.75 V (vs. SCE) for 36,000 seconds using a 10% $MoSe_2$-SPE recorded in 0.5 M H_2SO_4.



ESI Figure 9. Cyclic stability examination of a 400 mg cm^{-2} $MoSe_2$ SPE modified, *via* the drop-casting technique using linear sweep voltammetry. The potential range of 0 to –1.4 V was utilised and repeated for 1000 cycles. The figures show the initial (yellow line), 10th (green line) scans, 100th (dark green) and 1000th scan (black line). Scan rate: 100 mVs^{-1} (*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. S. J. Rowley-Neale, D. A. C. Brownson, G. C. Smith, D. A. G. Sawtell, P. J. Kelly and C. E. Banks, *Nanoscale*, 2015, 7, 18152-18168.
3. S. Shin, Z. Jin, D. H. Kwon, R. Bose and Y.-S. Min, *Langmuir*, 2015, 31, 1196-1202.