Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

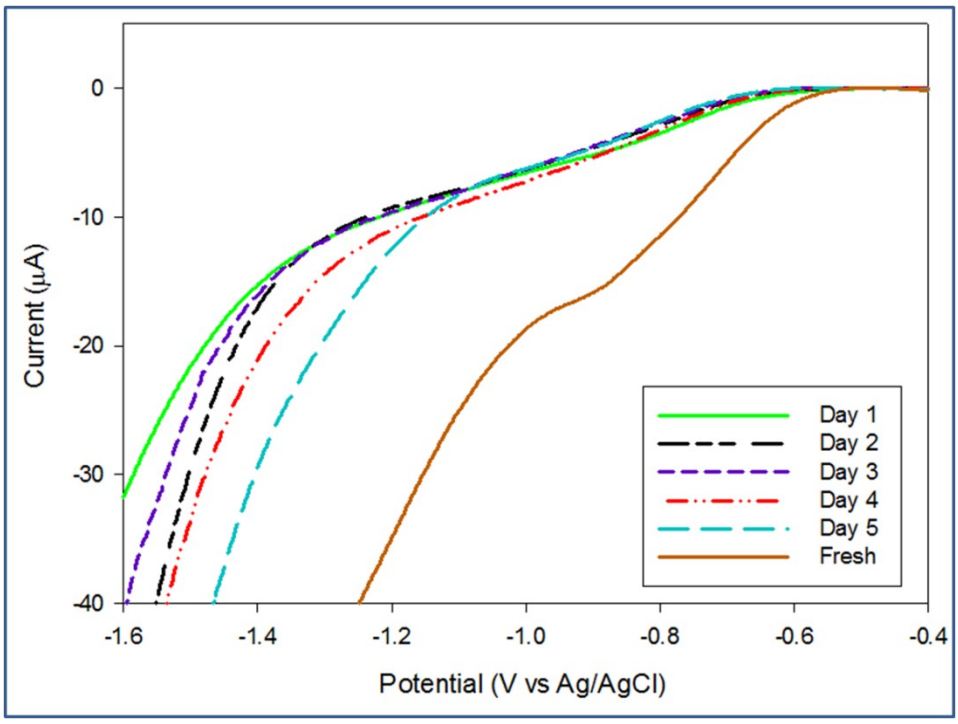

Fig S1. The structured MoS_2 was stored for 23 days. It was then HER tested on five consecutive days, and stored under ambient conditions between tests. The proton reduction peak was on all five measurements was significantly smaller than a fresh sample. As the peak current remained steady for five consecutive days it was concluded that the samples had fully degraded.

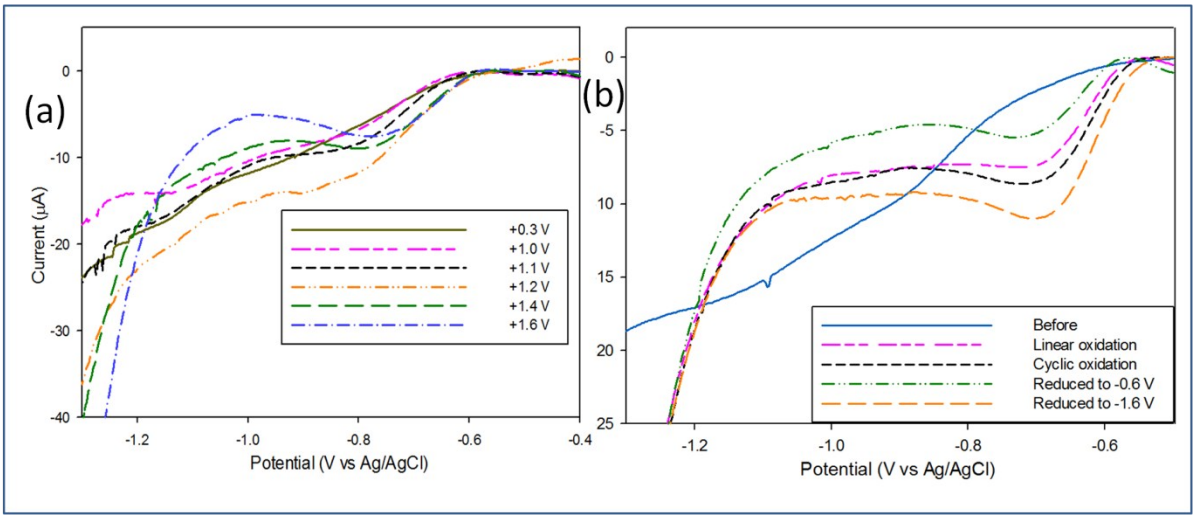

Fig S2. i-V curves showing the H^+ reduction following sulfidation of MoS_2 in sodium thiosulfate solution using progressively larger potential windows in order to determine the optimum sulfur deposition conditions. (a) The cyclic oxidation step was gradually increased from +0.3 V Ag/AgCl to +1.63 V. Each oxidation was followed by a linear reduction to -1.6 V, and a H^+ reduction test. (b) The sulfur deposition process was done in stages with H^+ reduction testing performed in between. First the sample was reduced to -1.6 V, then linearly oxidised, cyclically oxidised, reduced to -0.6 V and finally reduced to -1.6 V. Both linear and cyclic oxidation were performed to +1.2 V Ag/AgCl. The reduction of sulfur this has been observed at -0.6 V SHE on Ti[1], -0.4 V SHE on Pt[2], and -0.1 V SHE on FTO[3], but has no published value on Mo to the authors knowledge.

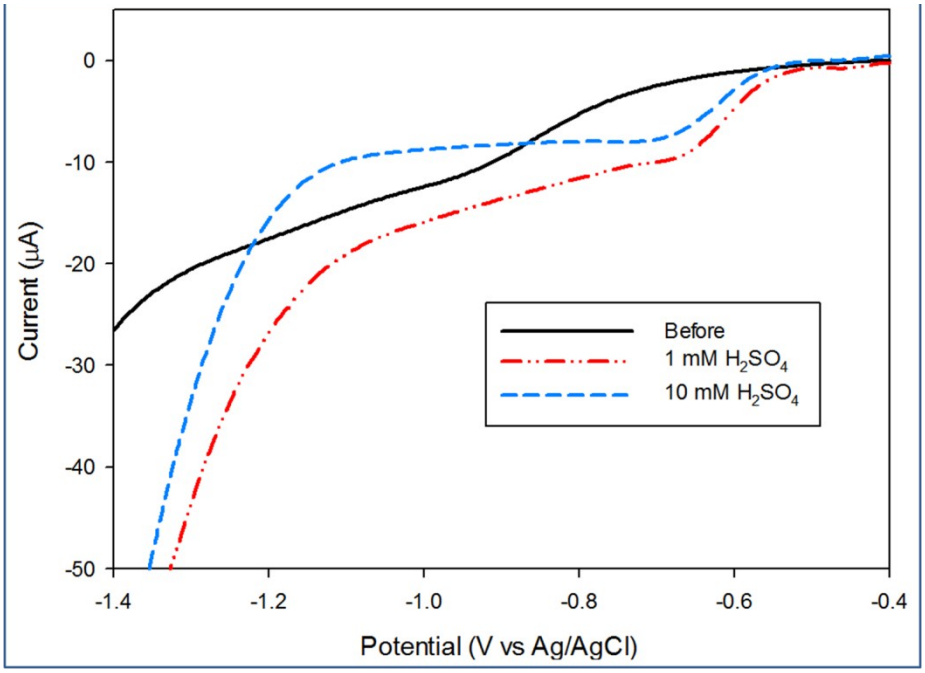

Fig S3. Optimum acid concentration determination for the sulfidation of MoS_2 from $Na_2S_2O_3$. The acid is necessary to reduce the sulfur to S^0 prior to deposition. The H^+ reduction performance was tested before sulfur deposition, and then following sulfur deposition with 1 mM and equimolar H_2SO_4. 1mM H_2SO_4 was determined as the optimum concentration.

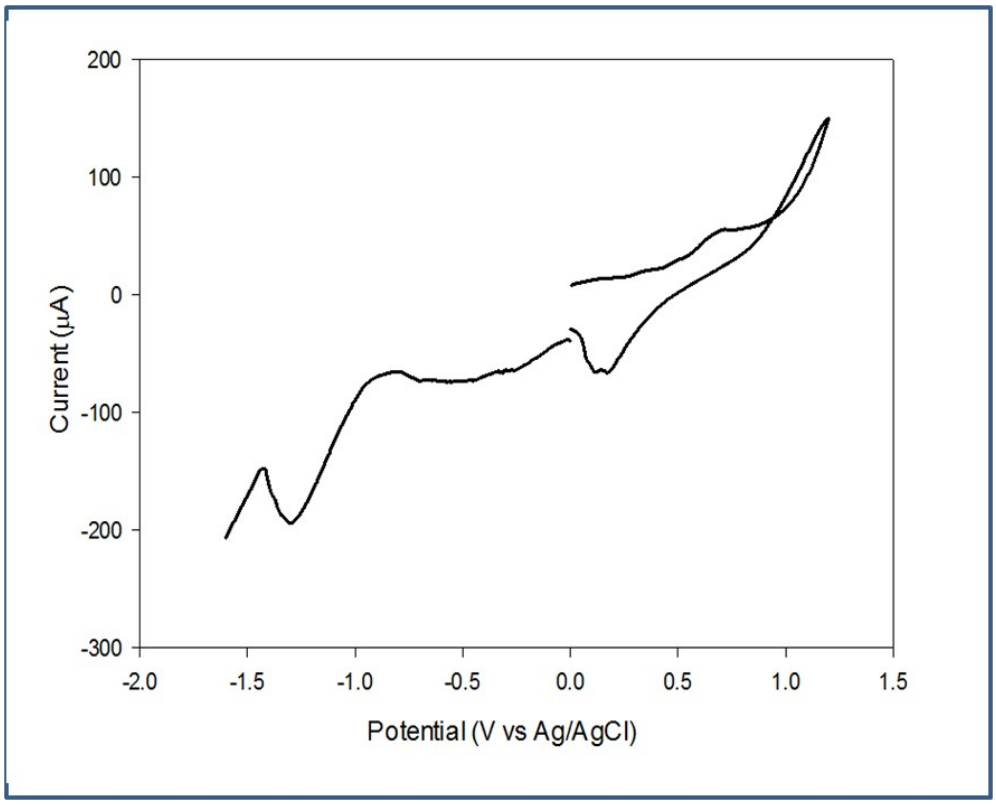

Fig S4. The i-V profile obtained from the sulfidation of MoS_2 in 10 mM sodium thiosulfate and 1mM H_2SO_4. The deposition was from 0V Ag/AgCl to +1.2V to -1.6V. The potential window used was determined from the information obtained from figure S2.

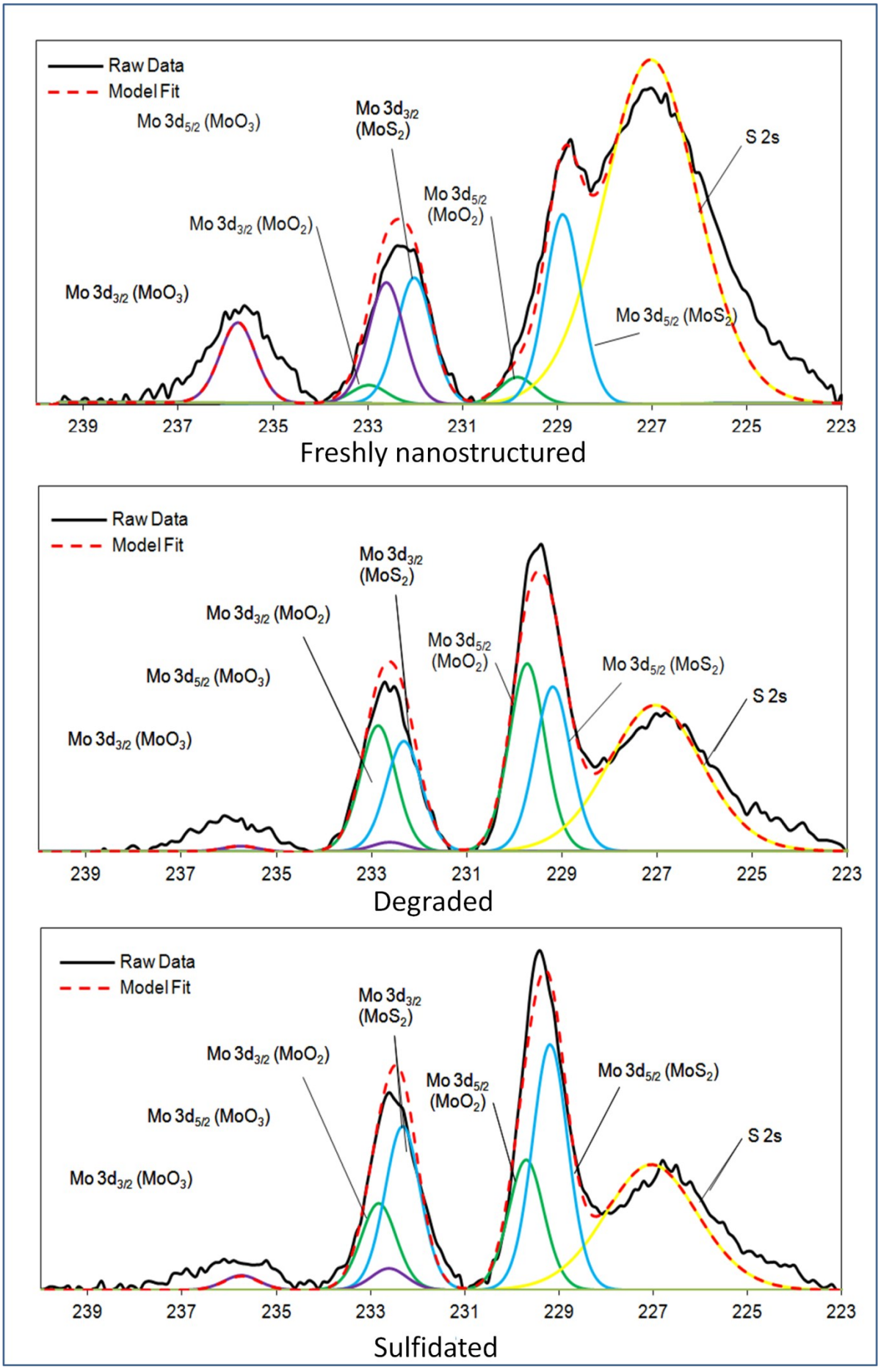
Raw Data
Model Fit
Mo 3d5/2 (MoO3)
Mo 3d3/2 (MoS2)
S 2s
Mo 3d5/2 (MoO2)
Mo 3d3/2 (MoO2)
Mo 3d3/2 (MoO3)
Mo 3d5/2 (MoS2)
239 237 235 233 231 229 227 225 223
Freshly nanostructured
Raw Data
Model Fit
Mo 3d3/2 (MoS2)
Mo 3d3/2 (MoO2)
Mo 3d5/2 (MoO2)
Mo 3d5/2 (MoO3)
Mo 3d5/2 (MoS2)
S 2s
Mo 3d3/2 (MoO3)
239 237 235 233 231 229 227 225 223
Degraded
Raw Data
Model Fit
Mo 3d3/2 (MoS2)
Mo 3d3/2 (MoO2)
Mo 3d5/2 (MoO2)
Mo 3d5/2 (MoS2)
Mo 3d5/2 (MoO3)
S 2s
Mo 3d3/2 (MoO3)
239 237 235 233 231 229 227 225 223
Sulfidated

Fig S5. The freshly nanostructured material produced molybdenum species corresponding to MoS2 (B.E. Mo 3d 5/2 = 229 eV), MoO2 (B.E. Mo 3d 5/2 = 229.7 eV) and MoO3 (B.E. Mo 3d 5/2 = 232.5 eV), alongside a strong signal at 227 eV corresponding to sulfur in the metal sulfide form. The degraded sample produced a broadened peak at ~229.5 eV, shifted to slightly higher binding energy, indicative of a shift towards a more oxidic Mo species, as well as a decrease in surface sulfur species. Decrease in MoO3 is clearly evident due to the diminished Mo 3d 3/2 species at 235.6 eV, indicating the sample consists of largely MoO2. After sulfidation, the major Mo photoelectron peak narrows and returns to a lower binding energy, consistent with the reformation of surface MoS2 species. The Mo(O3) 3d peak at 235.6 eV remains in a diminished form, suggesting the sample has returned to a majorly MoS2 composition.

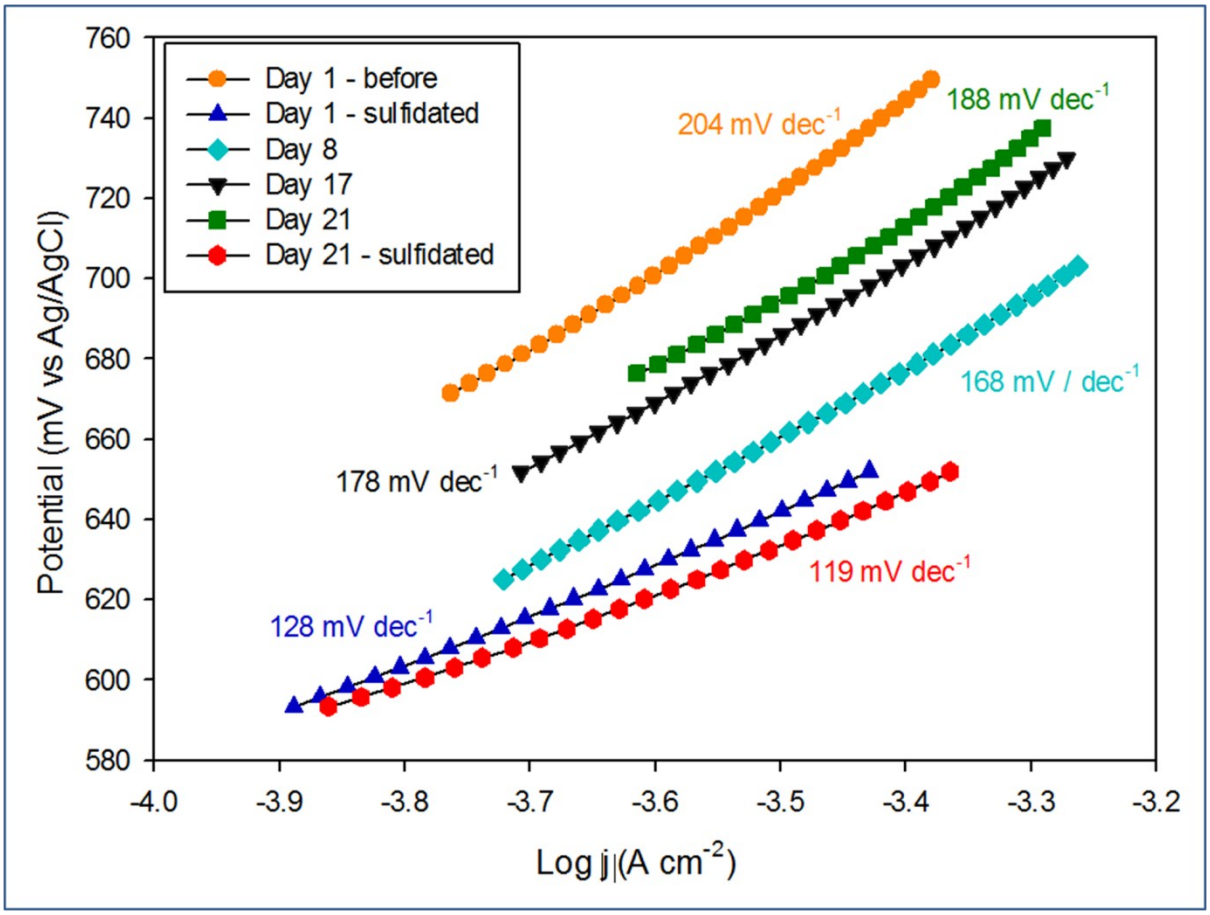

Fig S6. Tafel slopes derived from the H^+ reduction measurements shown in Fig. 3 (a). The MoS_2 sample had been exposed to air from ≈ 2 months prior to sulfidation. Following the initial test and sulfidation the sample was tested regularly during a 3 week period. After the final measurement it was re-sulfidated. As expected the HER kinetics were slow for the air-exposed state, and increased following the sulfidation. Air-exposure led to the kinetics slowing steadily, and the final sulfidation returned them to a similar rate as the initial sulfidation.

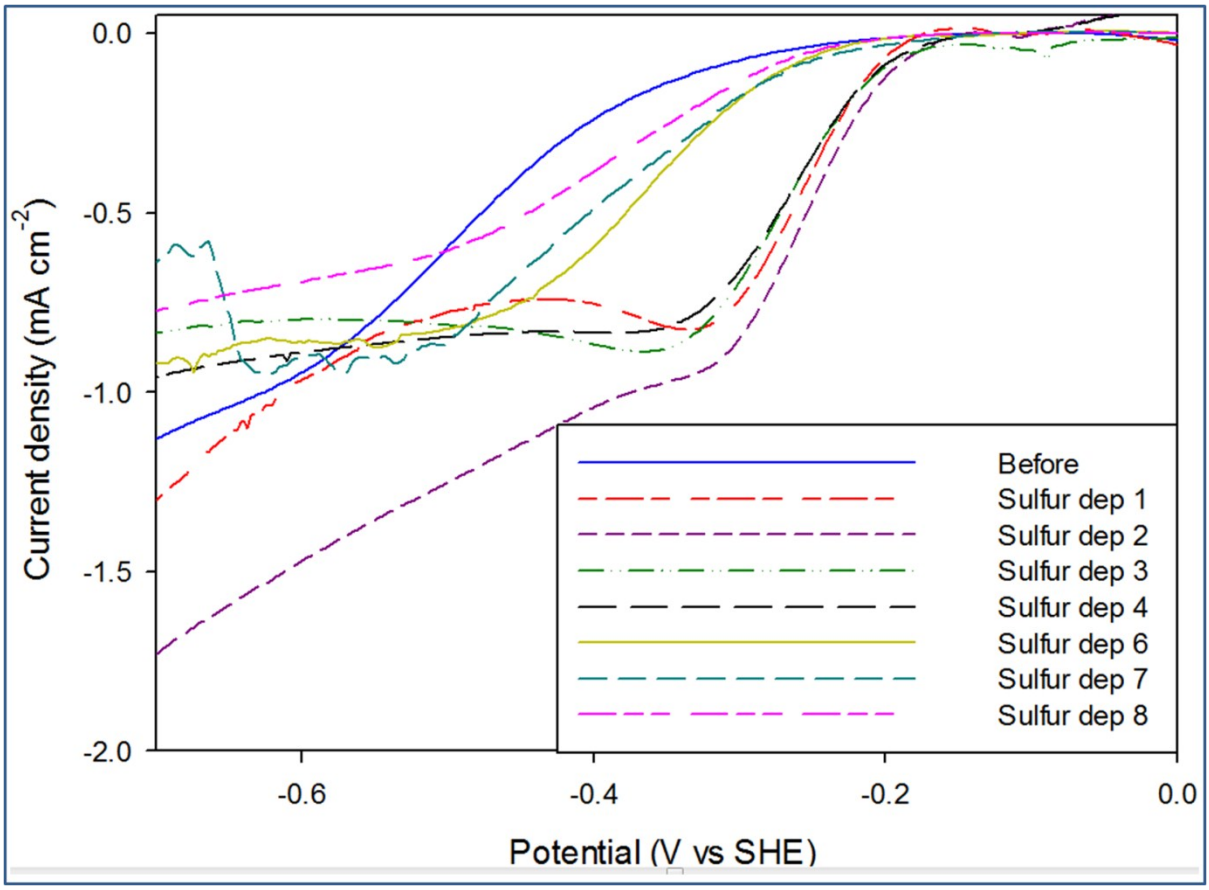

Fig S7. The proton reduction measurements following the 8 sulfidations on the sample presented in Fig. 1 (c) and (d). The proton reduction was not measured after the 5th sulfidation as this was an experiment to observe the deposition profile.

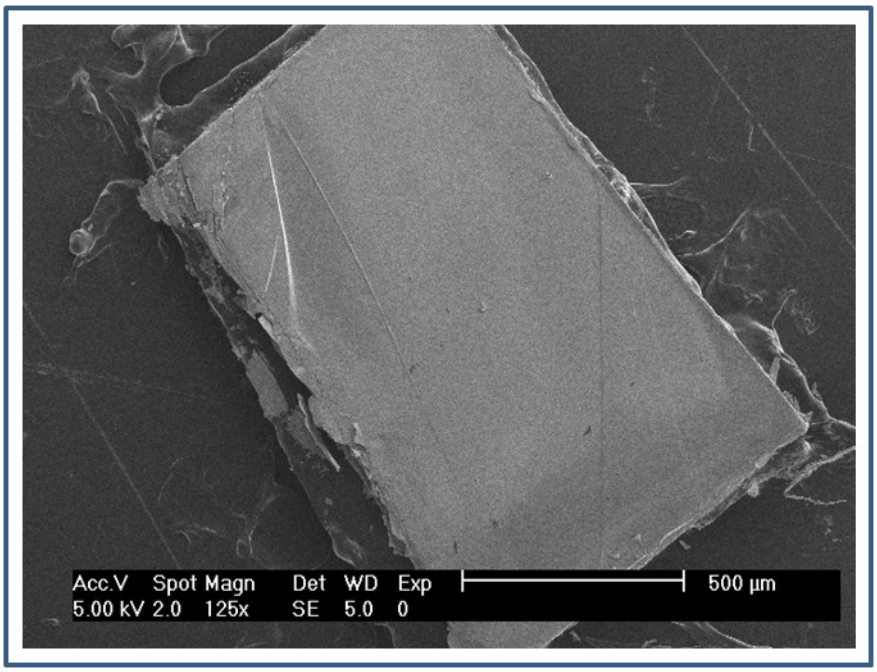

Fig S8. An SEM image of a piece of MoS_2 adhered to glassy carbon by conductive carbon tape. This was taken following cleaving, but prior to nanosphere deposition.

References

1 T. Yukawa, K. Kuwabara and K. Koumoto, *Thin Solid Films*, 1996, **286**, 151–153.

2 M. Elrouby, *Casp. J. App. Sci. R.*, 2013, **2**, 18–25.

3 M. Pac, X. Han and M. Tao, *ECS Trans.*, 2011, **41**, 157–166.