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# **ARTICLE TYPE**

# **Supplementary Information** Molybdenum disulfide/pyrolytic carbon hybrid electrodes for scalable hydrogen evolution

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## Ellipsometry

Spectroscopic Ellipsometry (SE) was performed to probe the 10 thickness of the various films analysed in this study. An Alpha SE tool (J. A. Woollam Co., Inc.) was used for SE measurements operating in the wavelength range of 380 - 900 nm at an angle of incidence of 70 °. While Mo was deposited directly on PyC in order to fabricate hybrid electrodes for HER catalysis, Mo was

15 simultaneously deposited on Si/SiO<sub>2</sub> wafers during the same electron beam evaporation runs. Following sulfurisation, the resultant Si/SiO<sub>2</sub>/MoS<sub>2</sub> stack allowed ellipsometry to be performed and fitting theoretical models to the measured data provided a measure of the MoS<sub>2</sub> film thickness.<sup>1</sup>

# 20 X-ray Photoelectron Spectroscopy

High resolution spectra of the S2p and Mo3d core levels for MoS<sub>2</sub> films 4.5, 10 and 53 nm thick were carried out. After the subtraction of a Shirley background and the satellite peaks arising due to non-monochromated incident Al Ka X-rays, spectral

- 25 contributions were fitted to these peak regions to ascertain chemical information about the films. Fig.S1 shows the S2p region for all three MoS<sub>2</sub> samples. The primary contribution to this is the doublet found at a binding energy of approximately 163 eV, which is associated with sulfur typically present in MoS<sub>2</sub>
- 30 (marked in blue). A second contribution to the spectral region is shifted by approximately 0.85 eV to higher binding energy than the sulfide and was found to increase in intensity for the thinner MoS<sub>2</sub> films. This doublet can be assigned to "edge-sulfur" or unsaturated sulfur along edge planes of the MoS<sub>2</sub> lattice. It has
- 35 been widely reported that such uncoordinated sites lead to increased HER activity. This finding is consistent with the measured HER activity in the main body of the text, where thinner MoS<sub>2</sub> samples displayed both reduced onset potentials and Tafel slopes. The thermal treatment involved in the vapour
- 40 phase sulfurisation during the  $MoS_2$  synthesis ensures that the entire sample will consist of the 2H polymorph. This is confirmed by the lack of evidence for 1T MoS2 in the S2p (and Mo3d) corelevel spectra, which would otherwise show as a sulphur (and
- 45 the 2H  $MoS_2$ <sup>2</sup> Thus, the enhanced HER catalysis can be

attributed to the presence of unsaturated sulfur atoms along edge planes of MoS2 crystallites.



Fig.S1: S2p spectral region for (a) 53 nm, (b) 10 nm and (c)  $4.5 \text{ nm MoS}_2$ molybdenum) component of slightly lower binding energy than 50 films showing contributions due to S in bulk (blue) and edge (green) MoS<sub>2</sub> configurations.

Analysis of the Mo3d spectral region allowed the nature and Mo3d peaks for each MoS<sub>2</sub> sample with contributions fitted. The S2s peak overlaps with the Mo3d region and must be considered

- 5 in the fitting as shown, but it does not itself reveal any information regarding the nature of any MoO<sub>x</sub> materials. Mo3d doublets were found to be shifted corresponding to the presence 30 an increased RMS roughness with that of the 53 nm sample being of MoO<sub>2</sub> and MoO<sub>3</sub>, in addition to the expected shift due to MoS<sub>2</sub>. These contributions were found at binding energies shifted
- 10 approximately 0.7 and 3.3 eV from the  $MoS_2$  contributions, respectively. The higher oxidation state of the Mo in the MoO<sub>3</sub> that of the MoO<sub>2</sub>. The oxide levels were found to remain invariant with MoS<sub>2</sub> film thickness, as determined from the XPS.
- 15 This leads to the conclusion that, although there are imperfections in the MoS<sub>2</sub> structure in the form of MoO<sub>x</sub>, this has no appreciable influence on the HER performance of the material and can be disregarded.





# **Atomic Force Microscopy**

Atomic Force Microscopy (AFM) was performed on the various quantities of any oxides present to be probed. Fig.S2 shows the 25 MoS<sub>2</sub>/PyC films in addition to the bare PyC substrate. The bare PyC displayed a very low RMS surface roughness of 0.55 nm, consistent with our previous measurements on PyC.<sup>3</sup> The RMS roughness of the MoS<sub>2</sub>/PyC electrodes was found to be 1.52 nm for the 4.5 nm sample. Increasing the MoS<sub>2</sub> thickness resulted in

- 3.69 nm. AFM also revealed the surfaces of the various MoS<sub>2</sub> films to be featureless and free of any obvious microstructures. This is shown in Fig.S3 where representative examples of AFM images are shown for the bare PyC, 4.5 nm MoS<sub>2</sub> and 53 nm
- caused a greater chemical shift in the binding energy relative to  $35 \text{ MoS}_2$  films. Clearly visible in these images is the increase in surface roughness as the MoS<sub>2</sub> thickness increases, as quantified above.



FigS3: AFM images of (a) bare PyC, (b) 4.5 nm MoS<sub>2</sub> and (c) 53 nm  $40 \text{ MoS}_2$  films. Scale bar is 1  $\mu$ m in each case.

#### Electron Microscopy

Further TEM analysis of the MoS<sub>2</sub>/PyC films was performed by imaging the cross-sectional lamellae using Scanning-TEM (STEM) mode. In this mode the contrast changes with heavier elements appearing brighter and lighter ones darker. A STEM

- 5 image of the 53 nm MoS<sub>2</sub> film is shown in Fig.S3 (a). The Energy Dispersive X-ray (EDX) spectrum was measured along line scans across the layers to determine the quantity of each element. This is shown in Fig.S4 (b), with the inset showing the line scan corresponding to the data. According to this
- 10 measurement, the MoS<sub>2</sub> film thickness at the position of the line scan is 54.7 nm. This is in good agreement with the ellipsometry data which gives a film thickness of approximately 53 nm. It should be noted that the ellipsometer measured over an area of several millimetres squared, while EDX line scans as shown here
- 15 only measure across a very specific region. The sputter deposition of the Au/Pd capping layer during the lamella preparation results in some apparent surface roughness of the  $MoS_2$  film when viewed in the cross section. This will account for the minor differences in measured film thickness according to the two 20 techniques.



Fig.S4: (a) STEM mode image of lamellar cross section of the thickest MoS<sub>2</sub>/PyC film. (b) EDX line scan intensity profile showing calculated the same thickness is shown in Fig.S6 (a) 50 electrodes exhibit near identical behaviour.

25 was performed. (c) Image of cross section  $MoS_2$ . (d) Intensity profile along line marked in panel (c).

The interlayer spacing was determined for individual crystallites of  $MoS_2$  by measuring the image intensity profile along a line as shown in Fig.S4 (c). This intensity profile as a function of 55

30 distance is represented in Fig.S4 (d). The average interlayer spacing was found to be approximately 6.6 Å, in accordance with the literature accepted values for this figure.

Scanning Electron Microscopy (SEM) was utilised to garner further information about the surface of the  $MoS_2$  film. The

- 35 surface morphology of the bare PyC and MoS<sub>2</sub>/PyC films according to SEM was consistent with that determined by AFM. While the bare PyC substrate was practically featureless, the MoS<sub>2</sub> layer displayed clear surface features. It was found that the level of surface detail increased with MoS<sub>2</sub> film thickness,
- 40 consistent with the RMS roughness measured by AFM. An illustrative selection of SEM images showing this trend in surface detail is displayed in Fig.S5.



Fig.S5: SEM images of (a) bare PyC, (b) 4.5 nm  $MoS_2$  and (c) 53 nm 45  $MoS_2$ . Scale bar is 100 nm.

## **Electrode Reproducibility and Stability**

The reproducibility of the  $MoS_2/PyC$  hybrid electrodes was investigated. Voltammetric data for several hybrid electrodes of the same thickness is shown in Fig.S6 (a). It is clear that these electrodes exhibit near identical behaviour.

Potentiostatic measurements were performed to assess the steady state performance of the hybrid electrodes as practical implementation of such electrodes involves continuous H<sub>2</sub> evolution at a constant electrode potential, rather than repeated 55 potential sweeps. Data for this measurement is shown in Fig.S6 (b), where a steady potential of -0.6 V was applied. The initial drop in current magnitude is explained by the formation of H<sub>2</sub> bubbles on the electrode passivating areas of the surface. After an initial settling period a steady current response is observed 60 which corresponds to the continuous formation and detachment

of  $H_2$  bubbles on the electrode surface. Behaviour like this has previously been observed in studies of the HER at  $MoS_2$  electrodes.<sup>4</sup>



**Fig.S6: (a)** Voltammetric response of several hybrid electrodes of the same thickness at 5 mV s<sup>-1</sup> (b) Potentiostatic current response of the electrode over a long period of time showing stable performance.

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- 15 Notes

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