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A rapid, room temperature, solution-phase method to sulfidise air-exposed MoS$_2$ has been investigated for hydrogen evolution reaction (HER) performance enhancement. Sulfidation of air-exposed MoS$_2$ nanoparticles resulted in an improved HER onset potential of -0.18 V (vs SHE) from -0.23 V, an improved Tafel slope of 282 mV dec$^{-1}$ from 309 mV dec$^{-1}$, and a decreased overpotential of 85 mV from 118 mV. SEM images of the sulfidation surface confirmed an increase in the number of catalytically active edge sites from 1.04% to 2.42%. The method demonstrated excellent stability and reproducibility with no loss of activity after 10 cycles of sulfidation and oxidation. This method provides an alternative to traditional methods for improving the HER performance of air-exposed MoS$_2$ catalysts, offering a promising approach for practical applications in energy conversion.
to -0.18 V, plus a decrease in the Tafel slope from 282 mV dec\(^{-1}\) to 87 mV dec\(^{-1}\). For comparison a freshly nanopatterned MoS\(_2\) was found to have an onset potential of -0.2 V SHE, and a Tafel slope of 120 mV dec\(^{-1}\). Ageing studies found that when left exposed to air for 21 days following sulfidation HER performance steadily decreases, but can be reinstated by further sulfidation.

Results and discussion

Nanostructuring and sulfidation

The structuring by nanosphere lithography and plasma etching is covered briefly here. \(^{19,20}\) First, naturally occurring MoS\(_2\) crystals were mounted onto a GC substrate, cleaved between basal planes, then placed at the bottom of a beaker of water. Polystyrene nanospheres were deposited from a suspension in ethanol onto the surface of the water, forming a self-assembled monolayer. The water level was lowered using a syringe until the nanospheres deposited onto the MoS\(_2\). The nanospheres were then exposed to oxygen plasma at 100 SCCM (standard cubic centimetres per minute) for 30 to 50 seconds in order to reduce their size before the MoS\(_2\) was etched with SF\(_6\) plasma at 25 SCCM for 25 to 40 seconds. After both etches the nanospheres were washed off the MoS\(_2\) with acetone, leaving a nanopatterned crystal, which was imaged by SEM. Following the nanopatterning the MoS\(_2\) samples were stored for a period of 5 to 28 days, it was found however, that the samples stored for longer than 23 days had already fully aged (Fig. S1). For this reason the bulk and freshly fabricated samples (Fig. 2) were electrochemically tested immediately following manufacture. Following exposure to air the crystals were sulfidated electrochemically and subsequently re-tested. The methodology was inspired by strategies to synthesise MoS\(_2\) and other metal sulphides from metal ions and sodium thiosulfate.\(^{21,22,27-29}\)

The air-exposed MoS\(_2\) modified GC working electrode was placed in a solution containing 10 mM Na\(_2\)S\(_2\)O\(_3\), and 0.1 M Na\(_2\)SO\(_4\) which has been acidified to pH3 in order to reduce the S\(_2\)O\(_3\)\(^2-\) via\(^{28,30}\)
\[
\text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightleftharpoons \text{S}_2\text{O}_3^{4-} + \text{H}_2\text{O} \quad \text{(eq. 3)}
\]
An oxidative voltage scan was then used to fully oxidise the Mo as this has previously been found to yield MoS\(_2\) on exposure to sulfur.\(^{22,26}\) A reductive voltage scan was then applied (at a scan rate of 25 mV s\(^{-1}\)) to electroreduce the colloidal sulfur onto the electrode (eq. 3).\(^{28}\)
\[
\text{S}_2\text{O}_3^{4-} + 2e^- \rightleftharpoons \text{S}^{2-} \quad \text{(eq. 4)}
\]
Experimental results confirmed that the sulfidation gave improved voltammetric results if the electrode was swept anodically prior to the reductive deposition (Fig. S2). The sulfidated MoS\(_2\) samples were then characterised by SEM and XPS, and the electrochemical performance as HER catalysts recorded and compared to the pre-sulfidated results.

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Fig 1. SEM images showing the effect of sulfidation on the surface of nanopatterned MoS\(_2\). (a) Sample 1 before sulfidation: the features are individual and distinct, and (b) after 2 sulfidations: the features remain distinct. (c) Sample 2 before sulfidation: the features are individual and distinct, and (d) after 8 sulfidations: the surface has homogenised though some features remain visible.
**Physical Characterisation**

The SEM images (Fig. 1) reveal that repeated deposition results in the filling of gaps between the pillars, which builds up over repeated sulfidations, and could explain the lowering of current as fewer catalytically active edge sites are available, provided that sufficient active sites are lost over a diffusionally-relevant area to effect a change in diffusional character of the nano-array from Case IV. The \( \text{H}^+ \) reduction measurements corresponding to each of these sulfidations are provided in Fig. S7. However the remaining edge sites appear to have improved catalytic properties, indicating this method would be well suited to robust morphologies, or electrodes that do not require multiple re-use.

Surface XPS data identified a decrease in the MoS\(_2\) content of the Mo 3d region and concurrent increase in MoO\(_2\) when the sample degraded in air, and that the sulfidation reverses this process (Table 1, Fig. S5). MoO\(_3\), readily identified by a significant Mo 3d\(_{3/2}\) peaks at 235.6 eV, appears to decrease largely to the Mo(IV) species, of which sulfidation is unable to reoxidise. MoS\(_2\) is identified at a binding energy of 229 eV for the 5/2 peak, with MoO\(_2\) existing at a slightly higher binding energy of 229.7 eV. The broadening and shift to a higher energy of the major Mo 3d\(_{3/2}\) species could therefore be deconvoluted to probe the chemical composition. The MoS\(_2\) composition of the freshly fabricated sample was very similar to that of the sulfidated sample indicating that sulfidation did indeed regenerate the samples surface. This conclusion is corroborated by the electrochemical measurements in Fig. 3 (a).

**Electrochemical characterisation**

The performance of the MoS\(_2\) as a \( \text{H}^+ \) reduction catalyst was tested as a means of comparison (see experimental). The electrode was immersed into a thoroughly degassed solution of 2 mM HClO\(_4\) and 0.1 M NaClO\(_4\) in ultrapure water along with a saturated Ag/AgCl reference electrode and Pt mesh counter electrode. Cyclic voltammograms were recorded from 0 V Ag/AgCl to -1.6 V at a scan rate of 25 mV s\(^{-1}\) (Fig. 2a).

It can be seen that following sulfidation the MoS\(_2\) displays improved catalysis for \( \text{H}^+ \) reduction (fig. 2(a) sulfidated) with the onset potentials, identified by where the trace departs from the baseline, changed from -0.23V SHE in the air-exposed state to -0.18V SHE. These values are favourable compared with bulk MoS\(_2\) (-0.65V SHE), and the sulfidated onset is comparable to the freshly prepared sample (-0.20V SHE). These results are in good agreement with other studies on nanostructured MoS\(_2\) HER, with an onset of \( \approx -0.20\)V SHE commonly reported.\(^{4,32-35}\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>%MoS(_2)</th>
<th>%MoO(_3)</th>
<th>%MoO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshly fabricated</td>
<td>56.07</td>
<td>35.83</td>
<td>8.10</td>
</tr>
<tr>
<td>Air-exposed</td>
<td>45.52</td>
<td>2.51</td>
<td>51.97</td>
</tr>
<tr>
<td>Sulfidated</td>
<td>57.99</td>
<td>5.03</td>
<td>36.98</td>
</tr>
</tbody>
</table>

Table 1. Molar percentage of molybdenum species in fresh, air-exposed, and sulfidated films obtained from XPS spectra (Fig. S5).
The magnitude of the post-sulfidation current is intermediate to the crystals’ aged state and freshly prepared state. Tafel plots were constructed from the voltammetric results in order to measure the effect of the sulfidation on the HER kinetics. The HER in acidic media is well known to proceed via two pathways, each composed of two reaction steps.

1. **Primary Discharge Step (Volmer Reaction)**
   
   \[
   
   \text{H}_2\text{O}^+ + \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O} \quad \text{b} = \frac{2.3RT}{F} \approx 120 \text{ mV} \quad (\text{eq. 5})
   
   \]

2. **Discharge and Desorption Step (Tafel Reaction)**
   
   \[
   
   \text{H}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H} \quad \text{b} = \frac{2.3RT}{2F} \approx 40 \text{ mV} \quad (\text{eq. 6})
   
   \]

   Where \( R \) is the gas constant, \( T \) is the absolute temperature, \( \alpha \) is the transfer coefficient, and \( F \) is the Faraday constant. \( 10,36,37 \)

The first step common to both pathways is the primary discharge step (Volmer reaction, eq. 5). What follows this is either an electrochemical desorption step (Heyrovský reaction, eq. 6) or a recombination/desorption step (Tafel reaction, eq. 7).

Due to the fast kinetics of the HER on Pt, it is widely considered a benchmark catalyst, and is known to proceed through the Volmer-Tafel reaction (eqs. 5 and 7). \( 36,37,38 \)

The precise pathway of hydrogen evolution on MoS\(_2\) is still unknown. \( 37 \) However, MoS\(_2\) has been combined with reduced-graphene oxide (RGO), as well as single-walled carbon nanotubes to achieve Tafel slopes of \( \approx 41 \text{ mV dec}^{-1} \) \( 32,37 \) indicating a Volmer-Heyrovský reaction.

Various structuring techniques have been applied to optimise the performance of MoS\(_2\) in the HER. The lowest measured Tafel slope for pure MoS\(_2\) is 49 mV dec\(^{-1}\) and was achieved through edge termination and layer expansion. \( 39 \)

Other structures include nanoparticulate MoS\(_2\), 2D MoS\(_2\) and vertically aligned layers; achieving 55 mV dec\(^{-1}\), \( 33 \) 67 mV dec\(^{-1}\), \( 32 \) and 86 mV dec\(^{-1}\). \( 4 \) Bulk MoS\(_2\) has a slope of \( \approx 120 \text{ mV dec}^{-1} \) which suggests the primary discharge step is rate limiting. \( 34,35,40 \)

The Tafel responses obtained from the above samples showed some variation, but all displayed a decrease in Tafel slope following sulfidation. The freshly nanopatterned MoS\(_2\) from this work had a slope of 120 mV dec\(^{-1}\) indicating the primary discharge step (eq. 4) was rate limiting (Fig. 2. (b)) as in the case of bulk MoS\(_2\). \( 34,35,40 \) When the samples were exposed to air for over 23 days the HER kinetics slowed considerably, evidenced by the increase in the Tafel slope to 282 mV dec\(^{-1}\). Sulfidation of the surface improved catalysis to a Tafel slope of 87 mV dec\(^{-1}\), comparable with other structured MoS\(_2\) reports. \( 4,32,33 \) This is consistent with the restoration of catalytically active sulfur atoms on the MoS\(_2\) (10\(\overline{1}\)0) edge enabling faster primary discharge kinetics as compared with the air-exposed state. \( 4 \)

Proton reduction measurements were used to record how the HER performance of the sulfidated crystals changed (Fig 3). A sulfidated sample was left exposed to air for 2 months and voltammetrically cycled from 0 V Ag/AgCl to -1.6 V in 2 mM HClO\(_4\) solution three times over a three week period. After the three weeks the H\(^+\) reduction kinetics were still faster than in the crystals’ (pre-sulfidated) air-exposed state.
Fig 4. H⁺ reduction on air-exposed and sulfidated MoS₂ under dark and light conditions. (a) i-V curves of air-exposed MoS₂ under light, dark and interrupted light conditions. The light had a slight increase in current, however the interrupted showed peaks and troughs of only ≈ 0.3 μA. (b) i-V curves of sulfidated MoS₂ under light, dark and interrupted conditions. Exposure to light led to an increase in current, and the difference between the peaks and troughs during the interrupted condition were ≈ 10 times that of the air-exposed state. However both the onset potential and current were inferior to the first H⁺ reduction test. The Tafel slope before sulfidation was 204 mV dec⁻¹, and decreased to 128 mV dec⁻¹ after the deposition (Fig S6). The slope steadily increased with each subsequent measurement to 188 mV dec⁻¹ after the three week period. After the final air-exposed measurement the sulfidation process was repeated and the catalytic ability remeasured. It was found that the performance was in very close agreement with the day one sulfidation, with a Tafel slope of 119 mV dec⁻¹. This result indicates the sulfidation process can be used to repeatedly cycle air-exposed MoS₂ without a permanent decrease in HER catalytic performance.

Photoelectrochemistry
A brief investigation into the photoelectrochemical H⁺ reduction of both air-exposed and sulfidated MoS₂ was performed under AM 1.5 (1 kW m⁻²) intensity from a Hg-Xe discharge lamp. The PEC measurements (Fig 4) were performed in the same 2mM HClO₄ electrolyte, and using the same experimental procedure as above, except the electrochemical cell was fitted with a quartz window. The H⁺ reduction performance of three samples that had been air-exposed for longer than one month was first tested under dark, light, and interrupted conditions, before undergoing sulfidation. The same sample was then retested in dark, light and interrupted conditions, and the results shown in Fig 4. It can be seen that the pre-sulfidation measurements showed little activity as a photocatalyst. The sulfidated sample displays a significant increase in light current as compared with dark current, the current increased tenfold compared to the pre-sulfidated sample, indicating that the sulfidation restores the photoelectrocatalytic activity of air-exposed MoS₂. The onset potential moves to lower overpotentials due to illumination providing additional applied potential as a result of separating charge carriers in the sulfidated MoS₂. This was not observed in the pre-sulfidated state implying that the sulfidation process has altered the material bandgap to a value more applicable for PEC HER.¹,²

Conclusion
The ageing of nanopatterned MoS₂ in air is detrimental to its use as a photocatalyst for the HER. We have demonstrated a simple room temperature technique by which oxygen aged MoS₂ can be restored to functionality. XPS data was used to verify the change in composition when MoS₂ is left exposed to air, and that the sulfidation technique proposed here causes a reversal. H⁺ reduction was used to measure the success of the method, it was found that both onset potential and current were improved post-sulfidation as compared with an air-exposed sample. Tafel slopes varied from sample to sample, but sulfidation always resulted in a decrease. The lowest Tafel slope for sulfidated MoS₂ was 87 mV dec⁻¹, indicating a substantially faster HER kinetics than the oxygen-aged state (282 mV dec⁻¹).
Once sulfidated the MoS₂ was found to age in air once more, however by repeating the sulfidation process catalytic performance was restored without loss in performance, enabling the same electrode to be recycled. The sulfidated electrodes also aged between the first and second H⁺ reduction i-V scans, but were then stable for at least 20 scans. Photoelectrochemical H⁺ reduction under AM 1.5 (1 kW m⁻²) demonstrated that the air-exposed electrodes have very little photocatalytic performance, while once sulfidated there is a significant increase in both current and onset potential in light over dark conditions.

**Experimental**

Naturally occurring MoS₂ (99% purity, SPI Supplies Ltd) was adhered to a glassy carbon (GC) substrate (Alfa Aesar Ltd, 5mm dia., type 2) using conductive double sided carbon adhesive tape (SPI Supplies Ltd) and cleaved between basal planes to present a flat surface (Fig. S8). The GC was then coated with epoxy resin (Permatex quick set epoxy glue) leaving only the MoS₂ exposed for use as the working electrode. Nanosphere solution (0.22µm, Thermo Scientific Microparticle Technology) was deposited on the surface, and the nanospheres shrunk and MoS₂ etched with an Oxford Instruments PlasmaPro NGP80 etcher. The geometric area of the MoS₂ was measured using a Zeiss Lab A1 optical microscope. Images were recorded using a MicroPublisher 3.3 RTV camera. The geometric area of the MoS₂ was calculated by Klion image measurement software.

All electrochemical measurements were performed in a three-electrode electrochemical cell using a PGSTAT128N potentiostat (Metrohm Autolab BV, Utrecht, NL) under a nitrogen atmosphere. The proton reduction experiments were performed in 2 mM perchloric acid (98%, Sigma-Aldrich) electrolyte with 0.1 M sodium perchlorate (98%, Sigma-Aldrich) supporting electrolyte prepared in ultra pure water (MilliQ by Millipore, with resistivity ≥18 MΩ cm) and thoroughly purged with N₂ gas to remove dissolved oxygen. A silver-silver-chloride electrode (saturated KCl) (Sigma-Aldrich) and a bright Pt mesh were used as reference and counter electrodes, respectively. The potential vs SHE was calculated using the following equation:

$$E_{\text{SHE}} = E_{\text{measured}} + E^{\circ}_{\text{Ag/AgCl}} + \left(0.059 \times pH\right)$$

Where $E_{\text{SHE}}$ is the converted potential value versus SHE, $E_{\text{measured}}$ is the voltage reading from the potentiostat, and $E^{\circ}_{\text{Ag/AgCl}}$ is the experimentally determined electrode potential of an Ag/AgCl (Sat. KCl) electrode (0.197 V vs SHE). The pH was 2.7. For ease of comparison all graphs and quoted potentials are given vs SHE.

The sulfidation of MoS₂ crystals was carried out in a solution of 10 mM sodium thiosulfate (99%, Sigma-Aldrich), 1mM sulfuric acid (98%, Sigma-Aldrich), with 0.1 M sodium sulfate (99% Sigma-Aldrich) supporting electrolyte prepared in ultra pure water purged with N₂ gas. A double-junction Ag/AgCl (3M KCl) electrode (Sigma-Aldrich) was used as a reference electrode to prevent interference from sulphide ions. The counter electrode was a bright Pt mesh. PEC measurements were made using an electrochemical cell equipped with a quartz window, and a Lot-Oriel Hg-Xe lamp calibrated to 1000 W m⁻² (A.M 1.5) light source. The graphs for EC and PEC measurements are presented as recorded baseline correction, whereas the values in the text have been adjusted against SHE and corrected for Nernstian shift in order to aid comparison with other published values, and to account for the low concentration of electrolyte used in this study for the purpose of removing the effects of migration from the electrochemical results.

An XL 20 SFEG Scanning Electron Microscope (FEI) was used to image the surfaces. XPS spectra were acquired using a Kratos Axis HSi XP spectrophotometer equipped with a charge neutraliser and a magnesium kα source (1,253.7 eV). Spectra were recorded at normal emission using a pass energy of 160 for survey scans and 20 for high resolution scans under a vacuum of 10⁻¹⁰ Torr. Curve fitting was performed using CasaXPS software version 2.3.16 and energy calibrated to the adventitious carbon 1s peak at 284.6 eV, employing Gaussian-Lorentz peak shapes and a Shirley background.

**Acknowledgments**

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**References**
