Sonochemical edge functionalisation of molybdenum disulfide

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ABSTRACT: Liquid-phase exfoliation (LPE) has been shown to be capable of producing large quantities of high-quality dispersions suitable for processing into subsequent applications. LPE typically requires surfactants for aqueous dispersions or organic solvents with high boiling point. However, they have major drawbacks such as toxicity, aggregation during solvent evaporation or the presence of residues. Here, dispersions of molybdenum disulfide in acetone are prepared and show much higher concentration and stability than predicted by Hansen parameter analysis. Aiming to understand those enhanced properties, the nanosheets were characterised using UV-visible spectroscopy, zeta potential measurements, atomic force microscopy, Raman spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and scanning transmission microscopy combined with spatially-resolved electron energy loss spectroscopy. Also, the performance of the MoS$_2$ nanosheets exfoliated in acetone was compared to those exfoliated in isopropanol as a catalyst for the hydrogen evolution reaction. The conclusion from the chemical characterisation was that MoS$_2$ nanosheets exfoliated in acetone have an oxygen edge-functionalisation, in the form of molybdenum...
oxides, changing its interaction with solvents and explaining the observed high-quality and stability of the resulting dispersion in a low boiling point solvent. Exfoliation in acetone could potentially be applied as a pretreatment to modify the solubility of MoS$_2$ by edge-functionalisation.

INTRODUCTION

Layered materials are composed of two-dimensional (2D) sheets bonded strongly in-plane and stacked weakly through the van der Waals force. The enhanced mechanical$^{1,2}$, electrical$^{1,3}$, optical$^{3,4}$, and thermal$^2$ properties displayed by the two-dimensional materials have attracted the interest of scientists over the past 15 years$^5$. Inorganic materials such as the transition metal dichalcogenides (TMDs) are of particular interest due to their broad range of semiconducting and optical properties.

Liquid-phase exfoliation (LPE) is a simple production technique that provides the highest yields of nanosheets in the shortest timeframes$^6$. Solvent selection for LPE is typically performed using a model based on Hansen solubility parameters. Charles Hansen extended the Hildebrand solubility parameter formalism by hypothesising that the cohesive energy density can be resolved into contributions from three classes of intermolecular interactions.$^7$ This approach was first proposed to understand the solubility of polymers, for which it has proven very effective. However it can also be applied for dispersions of layered materials$^8$. This formalism predicts high exfoliation yields and good dispersion stability if there is close matching of the solubility parameters of the solvent and the layered material.$^9$ As such, Hansen solubility parameter analysis makes it possible to develop liquid phase methods to disperse and process various layered materials in a general and reproducible way.

The most common organic solvents for liquid-phase exfoliation have a high boiling point, based on the correlation between surface tension and solubility parameters through the cohesive energy density. However, aggregation occurs during deposition of thin films due to the slow evaporation of high boiling point solvents$^{10}$. Similarly, for fabrication of polymer composites, heat treatments above the boiling point of the solvent are usually required to remove them, which is impractical for very high boiling point solvents and incompatible with some polymers. Alternatively, surfactants in aqueous dispersions are used to
achieve high concentrations and stable dispersions\textsuperscript{11,12}. While aqueous dispersions provide a lower boiling point alternative, it is difficult to remove any residual surfactant which may influence film or composite properties\textsuperscript{13}. Other approaches such as washing with lower boiling point solvents are wasteful and may impact the properties of the produced structures\textsuperscript{14}. A solvent exchange method has been used as a way of incorporating the advantages of low boiling point dispersions of layered materials with more effective exfoliating solvents\textsuperscript{15}. While this provides a solution, it would be desirable to prepare dispersions in low boiling point solvents by direct exfoliation as a mean of reducing process complexity\textsuperscript{13,16}.

RESULTS AND DISCUSSION

Acetone is an example of a desirable low boiling point solvent for LPE as it is readily available, has low toxicity and is widely used. As such, dispersions of molybdenum disulfide (MoS\textsubscript{2}) in acetone were prepared and found to have concentration and stability much higher than expected, according to the standard Hansen parameter model. Table 1 compares Hansen parameters of acetone and other conventionally used organic solvents\textsuperscript{8} for LPE of MoS\textsubscript{2} (\textit{N}-methyl-pyrrolidone and cyclopentanone), as well as Hansen interaction radius of those solvents with the nanomaterial. While the interaction radius for acetone is only \(\sim 50\%\) greater than NMP and CPO, the attainable concentration exponentially decays with the square of the interaction radius. Isopropanol (IPA) is another low boiling point solvent that has been used before to exfoliate layered materials, despite it being poorly Hansen matched\textsuperscript{8,17,18}, as seen in Table 1. There is also a high mismatch between the surface tension of acetone (23.4 mN/m) and the value for solvents which produced maximum concentration dispersions of layered materials (around 40 mN/m).\textsuperscript{8}
Table 1. Hansen parameters for MoS$_2$ and different organic solvents: N-methylpyrrolidone (NMP), cyclopentanone (CPO), acetone and isopropanol (IPA). The last column contains the respective calculated interaction radius to the layered material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dispersive component (MPa$^{1/2}$)</th>
<th>Polar component (MPa$^{1/2}$)</th>
<th>Hydrogen bonding component (MPa$^{1/2}$)</th>
<th>Interaction radius to MoS$_2$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$</td>
<td>18.0</td>
<td>8.5</td>
<td>7.0</td>
<td>0</td>
</tr>
<tr>
<td>NMP</td>
<td>18.0</td>
<td>12.3</td>
<td>7.2</td>
<td>3.8</td>
</tr>
<tr>
<td>CPO</td>
<td>17.9</td>
<td>11.9</td>
<td>5.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7.0</td>
<td>5.4</td>
</tr>
<tr>
<td>IPA</td>
<td>15.8</td>
<td>6.1</td>
<td>16.4</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Using metrics based on the extinction efficiency and confinement effects, it is possible to analyse the quality of the dispersion by estimating the concentration and the average layer number $\langle N \rangle$. Figure 1a shows a typical extinction spectrum with the position of both A and B exciton absorptions of MoS$_2$ indicated. An inset table contains values of both estimated dispersion properties over one year. Concentration was found to be higher than 0.1 mg/mL and the average layer number was estimated as approximately four. Both values are unexpected results for a low boiling point solvent with such a mismatch in the Hansen solubility parameters. Analysing the concentration and average layer number over a long time scale, it is inferred that the dispersion remains stable and the aggregation is minimal. Zeta potential measurements, shown in Figure 1b, corroborate the observed stability. It is noted that the magnitude decreased by only 6% over more than a year.
Figure 1. a) Representative extinction spectrum versus wavelength. The inset table contains the values for concentration (in mg/ml) and layer number over time. b) Zeta potential data shows that the dispersion is stable ($|\zeta| > 30 \text{ mV}$) for more than one year. A photograph of the high-quality dispersion is shown.

Figure 2. Atomic force microscopy (AFM) data for acetone-exfoliated (a, b and c) and IPA-exfoliated (d, e and f) nanosheets. a and d) Topography. b and e) Nanomechanical
In order to understand the enhanced properties of the acetone-exfoliated MoS$_2$, further characterisation was performed to identify any structural modification to the exfoliated nanosheets. Atomic force micrographs show that the nanosheets have a different morphology (Figure 2a) when comparing with MoS$_2$ exfoliated in isopropanol (IPA) using the same exfoliation parameters (Figure 2d). IPA is chosen as another low boiling point solvent and a molecular structural analogue for acetone. Line sections indicated on the micrographs of the height and adhesion channels (Figures 2a, 2b, 2d, 2e) are plotted separately in Figures 2c and 2f. The values for nanomechanical adhesion were offset to the average value for the substrate for both samples. There is a “halo”, a region of higher adhesion surrounding the nanosheets exfoliated in acetone representing a higher interaction between the tip and nanosheets than tip and substrate. The feature is not observed in the height channel, as seen in Figure 2a. Also, the magnitude of adhesion forces is lower for the acetone-exfoliated nanosheets, which differs from the IPA sample, where adhesion for the flakes is the same as for the substrate.
Figure 3. Raman spectra mapping. a) Peak separation map for resonant excitation. b) Histogram of the peak separation and the corresponding average layer number. c) Typical spectrum from the map is shown. Inset corresponds to mapping image. Colour scheme: green represents the MoS$_2$ peak; grey, silicon and red, molybdenum trioxide. d) Zoomed region from panel c showing additional peaks observed for acetone-exfoliated (black) in contrast with IPA-exfoliated nanosheets (blue).

Resonant Raman mapping was performed to statistically evaluate the degree of exfoliation over a large area. The separation of the two main MoS$_2$ peaks, the in-plane ($E_{2g}^1$) and the out-of-plane ($A_{1g}$) modes$^{22}$, for each pixel is plotted as a colour map (Figure 3a). The associated histogram of the peak separation, which is correlated with layer number distribution$^{23}$, is shown in Figure 3b. The histogram features a narrow asymmetric distribution with average peak separation of 24.2 cm$^{-1}$ (standard deviation of 0.63 cm$^{-1}$).
Indicative values of the mode separation based on measurements of mechanically exfoliated MoS\(_2\) from the literature suggest that the mean layer number in the sample is \(\langle N \rangle \approx 4\), which is consistent with UV-vis measurements made previously. This supports the demonstration of high-quality exfoliation in a low-boiling point solvent.

Non-resonant Raman mapping (Figure 3c) shows the expected MoS\(_2\) modes: the in-plane vibration \((E_{2g}^1)\) at 378 cm\(^{-1}\) and the out-of-plane \((A_{1g})\) at 405 cm\(^{-1}\). Acetone-exfoliated nanosheets shows a broader full width at half maximum for the out-of-plane mode when compared to the IPA-exfoliated material (see Supporting Information). Literature about mechanically cleaved MoS\(_2\) suggests the broadening may be associated with a higher defect density. The peak at 521 cm\(^{-1}\) is the silicon wafer substrate and the peak at 447 cm\(^{-1}\) is silicon oxide. The remaining modes are not present in dispersions of MoS\(_2\) in IPA produced with the same exfoliation parameters (Figure 3d). Peaks at 590 and 776 cm\(^{-1}\) are vibrational modes of acetone. The samples have been treated above the boiling point of acetone before performing the characterisation to remove any residual solvent. The presence of those modes even after the heat treatment suggest a strong interaction between the nanosheets and acetone. The peaks at 283 and 815 cm\(^{-1}\) correspond to known modes of MoO\(_3\), while the peak at 627 cm\(^{-1}\) is associated with hydrates of MoO\(_3\). The peaks at 565 and 744 cm\(^{-1}\) are associated with MoO\(_2\). Mapping of the modes associated with the oxides and disulfide are shown in the inset of Figure 3c (in red and green, respectively). For the agglomerate mapped, the presence of the oxide peak is relatively uniform throughout the disulfide-containing areas, but the two are fundamentally co-localised. This suggests that particles of the oxides do not form in isolation from the disulfide nanosheets.

Following this indication of the presence of other molybdenum compounds in the samples, transmission electron microscopy was performed to evaluate the morphology of these additional components.
Figure 4. a) Representative TEM micrograph of MoS$_2$ exfoliated in isopropanol. b) Zoomed in TEM micrograph of the same dispersion with an inset showing the FFT as a regular hexagonal structure. c) Representative TEM micrograph of MoS$_2$ flake casted from the dispersion in acetone. d) Edge of an acetone-exfoliated MoS$_2$ flake. Inset shows
a different pattern in the highlighted area corresponding to few-layered molydenum trioxide. e) XPS measurement showing binding energy in the range of molybdenum of acetone-exfoliated nanosheets show the expected MoS$_2$ structure with additional molybdenum oxide peaks. f) XPS data for IPA-exfoliated nanosheets in the same range. HAADF-STEM micrographs of two MoS$_2$ flakes from samples of two different MoS$_2$ dispersions: (g) IPA and (i) acetone. In the IPA-exfoliated MoS$_2$ nanosheet (g) an EELS spectrum-line was collected following the green marked line. (h) Two EELS spectra corresponding to the sum of 12 spectra collected in each of the two highlighted areas (red (i) and blue (ii)) of this spectrum-line of g). Sulfur and molybdenum (associated to the MoS$_2$) as well as some carbon are detected in these spectra. j) Two EEL spectra corresponding to the addition of 21 spectra recorded in each of the 2 regions highlighted in red (iii) and blue (iv) in the EELS spectrum-image obtained in the green marked area of i). The inset of this figure shows the O map obtained from this EELS spectrum-image. Oxygen, which is likely associated to molybdenum oxide, is present at the edge of the flake, as clearly observed in this elemental map.

Figure 4 shows transmission electron micrographs comparing MoS$_2$ flakes exfoliated in IPA (a and b) and acetone (c and d) using the same exfoliation process. Analysing various regions of multiple nanosheets (additional micrographs are shown in Supporting Information) with fast Fourier transform (FFT) it is possible to identify different crystallographic structures. The usual hexagonal structure expected for this nanomaterial is observed for the flakes exfoliated in both solvents, as seen in the inset of figure 4b. However, the edges of the acetone-exfoliated nanosheets have an orthorhombic pattern associated with few-layer molybdenum trioxide$^{28,29}$ (Figure 4d).

In order to confirm that the structural modification at the nanosheet edges corresponds to the chemical modification observed in the Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) was employed to characterise the composition. The acetone-exfoliated sample was found to have 11.2 at.% molybdenum, 18.2 at.% sulfur and 16.0 at.% oxygen. This excess of molybdenum atoms in the sample when compared to sulfur atoms (see Supporting Information for data) (the ratio is greater than 1:2) and the significant oxygen presence confirms the formation of other molybdenum-based
compounds including MoO$_2$ and MoO$_3$, as shown in Figure 4e. The atomic percentages when analysing just the compounds containing molybdenum atoms are 70.6% for MoS$_2$, 22.3% for MoO$_3$ and 7.1% for MoO$_2$. For IPA-exfoliated nanosheets, the atomic percentages for molybdenum atoms are assigned to each compound as follows: 87.7% for MoS$_2$, 7.91% for MoO$_3$ and 4.39% for MoO$_2$. Even though some oxidation was observed for this sample, oxide content is significantly higher for acetone-exfoliated nanosheets.

In order to get more detailed chemical and structural information of the effects of the dispersion of MoS$_2$ in different solvents at the local scale, aberration-corrected scanning transmission electron microscopy (STEM) was performed. High-angle annular dark field (HAADF) STEM combined with spatially-resolved electron energy loss spectroscopy (SR-EELS) is a powerful technique for getting this information$^{30}$. Figures 4g and 4i show two HAADF-STEM images of two of these MoS$_2$ nanosheets exfoliated in IPA and acetone, respectively. Different EELS spectrum-lines (SPLI, 1D)-images (SPIM, 2D) were recorded on these flakes. Figures 4g and 4i display the areas where an EELS SPLI and a SPIM have been collected (green highlighted areas). Two different EEL spectra, corresponding to the addition of 12 spectra in the regions marked in Figure 4g, are displayed in Figure 4h. The analysis of these EELS data indicates that the flakes from the IPA dispersion are composed of MoS$_2$ and that their composition is homogenous and uniform, even at the edges of the nanosheets. The C-K feature is visible in these spectra probably from a small carbon contamination. This situation is different in the case of the MoS$_2$ in acetone dispersion sample, as seen in Figure 4i and 4j. The edges present an amorphous layer of less than 1 nm. This layer contains some carbon and oxygen (see the O-map, inset of Figure 4j). The presence of this oxygen at the edge indicates the clear oxidation of this MoS$_2$ flake in this region agreeing with the other characterisation results performed on these samples.

As seen in literature$^{31–33}$, the chemical reaction for oxidation of MoS$_2$ in presence of oxygen gas is:

\[
2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2
\]

\[
MoS_2 + 6MoO_3 \rightarrow 7MoO_2 + 2SO_2
\]
\[2\text{MoO}_2 + \text{O}_2 \rightarrow 2\text{MoO}_3\]

Thermodynamically, the surface of MoS\(_2\) tends to be oxidised when in contact with oxygen by oxygen adsorption or substitution. Density functional theory calculations show that the kinetic energy barrier for oxidation is lowered when sulfur vacancies, which have a high prevalence at edge sites, are produced during exfoliation\(^{34}\).

These equations suggest the formation of sulfur dioxide, which would outgas and prevent observation by the characterisation techniques employed here. However, a pungent, sulfur-like odour, different from acetone, was noticed in the as-produced samples. Sulfur dioxide gas is very soluble (reaching several hundred \text{v/v}) in several organic solvents, including acetone\(^{35}\). This adds some weight, albeit qualitative, to the series of reactions shown above. It suggests that the observed chemical modification to the nanosheets occurs through interaction with atmospheric oxygen rather than with the solvent as acetone has greater propensity to contain or produce dissolved oxygen or oxygen radicals during sonication.\(^{36}\)

**In order to study the timescales involved for the spontaneous functionalisation of MoS\(_2\) during exfoliation in acetone**, an experiment was performed where the sonication time during exfoliation was varied. Lateral size and concentration values were obtained from the metrics\(^{19}\) using UV-vis spectra. Average nanosheets length decays exponentially while concentration increases until a saturation point is reached (Figure 5a). Zeta potential measurements (see Supporting Information) show that the exfoliated nanosheets are stable in dispersion even after short sonication times. It is noted that the high stability and concentration originates from a self-limiting process since each measured property of the dispersions has the tendency to plateau after approximately 3 hours of sonication.

Continuing quantifying how microscopic modification of the nanosheets by edge-functionalisation influence macroscopic properties such as the interaction with the solvent, Hansen and Hildebrand solubility parameters were measured for both supernatant and sediment of the final centrifugation step after the sonication (see Supporting Information). Figure 5b shows the Hildebrand plot for a dispersion of MoS\(_2\) nanosheets. NMP has the highest concentration which could be explained by its high
susceptibility to ambient and sonochemical degradation. The solvent degradation complicates the production of an identical reference sample to the solvent in dispersion for extinction spectroscopy, and may also interfere with the exfoliation and stabilisation processes. Although it is known that good solvents for nanomaterials cannot solely be identified based on Hildebrand parameters, it is therefore interesting to note that this exfoliation in acetone produces materials whose solubility is well described by this model, which is inferred by comparing the width of the Gaussian fitting with literature values. The observed modification in Hansen and Hildebrand solubility parameters reported is a direct result of the edge functionalisation of MoS$_2$ with MoO$_3$. The Hildebrand parameter for the nanosheets is $20.8 \pm 0.6$ MPa$^{1/2}$. The accepted value of the solubility parameter for MoO$_3$ is $20.7$ MPa$^{1/2}$ and MoS$_2$ is $21.1$ MPa$^{1/2}$. The oxidation processes shift the values of the parameters for the MoS$_2$ nanosheets closer to the value for acetone ($19.9$ MPa$^{1/2}$). This functionalisation is responsible for the improved dispersability in acetone and appears to make MoS$_2$ more selective to well Hildebrand matched solvents, as is the case for MoO$_3$.

Hansen parameters for 2-butanone, a linear ketone containing one extra carbon than acetone, are 16.0, 9.0 and 5.1 MPa$^{1/2}$, for dispersive, polar and hydrogen bonding components, respectively. Highly concentrated dispersions of TMDs in 2-butanone using bath sonication was obtained by Lobo et al. A similar degree of exfoliation was obtained by them, as indicated by peak separation of the in-plane and out-of-plane Raman modes for MoS$_2$ (24.2 cm$^{-1}$ for acetone and 24.9 cm$^{-1}$ for 2-butanone). However the sedimentation lifetime is significantly lower for 2-butanone, despite it having a better Hansen matching (smaller interaction radius) and higher viscosity. Chemical characterisation (XPS) and microscopy (HRTEM and AFM micrographs) in that work does not indicate the presence of molybdenum oxides. It is observed that the zeta potential for nanosheets exfoliated in acetone is significantly higher than for those reported in 2-butanone. It is inferred that this is due to edge functionalisation present in the acetone-exfoliated nanosheets, and that this is in turn responsible for the extended sedimentation time. Exfoliation in 2-butanone using the same parameters for acetone was performed and the nanosheets characterised using Raman spectroscopy (see Supporting Information). Oxides peaks were not observed for the sample. The high quality and
stability observed in acetone-exfoliated MoS2 nanosheets due to edge-functionalisation seems to be unique to acetone because of a combination of factors such as dissolved oxygen content, low viscosity and low vapour pressure, independently of surface energy and Hansen parameters matching.

Figure 5. a) Length and concentration from metrics\textsuperscript{19} plotted for different sonication times. b) Hildebrand solubility parameters for exfoliated MoS\textsubscript{2} nanosheets. c) Polarization curves for MoS\textsubscript{2} exfoliated in acetone (red) and IPA (blue). Reference substrate glassy carbon electrode is shown in black. d) Corresponding Tafel plots.

Exfoliated MoS\textsubscript{2} has been proposed as an efficient catalyst for the hydrogen evolution reaction (HER). Hydrogen is an environmentally-friendly alternative energy source to fossil fuel, and catalysts are necessary to increase the reaction efficiency to reach mass production levels. Platinum is known to be the best catalyst\textsuperscript{42}, however its high cost and
unavailability in large quantities limit its use\textsuperscript{43}, and have prompted searches for alternative materials. Recent work has indicated that the edge sites and active site density on the edges of nanosheets are responsible for this catalytic activity\textsuperscript{44,45} In order to investigate the effect of edge oxidation on the performance of MoS\textsubscript{2} nanosheets as HER catalysts, MoS\textsubscript{2} exfoliated in acetone was compared against the same mass of MoS\textsubscript{2} prepared in IPA. The measurement was made by supporting the MoS\textsubscript{2} catalyst on a conductive and inert substrate (glassy carbon). Linear sweep voltammetry was used to measure the current against potential. For the HER, it is useful to offset the potential scale to the reversible hydrogen electrode (RHE), while the current is normalised to the electrode area,\textsuperscript{46} as seen in Figure 5c. A superficial analysis of Figure 5c-d shows that the acetone-exfoliated nanosheets have a higher current density across the entire potential range which indicates its superiority.

Table 2. Hydrogen evolution characteristics of MoS\textsubscript{2} exfoliated in IPA and acetone.

<table>
<thead>
<tr>
<th></th>
<th>Tafel slope (mV/decade)</th>
<th>Onset potential (V vs RHE)</th>
<th>J @ -0.4V (mA/cm\textsuperscript{2})</th>
<th>Size (from UV-vis metrics) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS\textsubscript{2}/IPA</td>
<td>193</td>
<td>-0.38</td>
<td>0.50</td>
<td>172</td>
</tr>
<tr>
<td>MoS\textsubscript{2}/acetone</td>
<td>150</td>
<td>-0.27</td>
<td>2.51</td>
<td>212</td>
</tr>
</tbody>
</table>

Deeper analysis shows an onset potential, the potential value for which catalyst current is first observed, for hydrogen evolution at -0.27 V vs RHE and a current density of 2.51 mA/cm\textsuperscript{2} at -0.4V for the sample prepared in acetone, shown in Table 2. The IPA sample shows a higher onset potential and a lower current density both of which result in an inferior hydrogen evolution catalyst. Figure 5d shows the Tafel curves of the J-V data displayed in Figure 5a. From the linear region of this curve we can extract the Tafel slope which is representative of the effectiveness of a material as a HER catalyst (lower is better) and the mechanism by which the H\textsubscript{3}O\textsuperscript{+} ions are reduced. The Tafel slope recorded is in the range attributed to MoS\textsubscript{2} in literature\textsuperscript{42,43}.
Of primary importance is that across all metrics, shown in Table 2, MoS$_2$ exfoliated in acetone exceeds the performance of that prepared in IPA in terms of hydrogen evolution efficiency. It is also interesting that the MoS$_2$ nanosheets exfoliated in acetone are significantly bigger than those prepared in IPA. The turnover frequency of MoS$_2$ hydrogen evolution has been shown to be inversely proportional to the length and directly to the active site density$^{47}$. This suggests that, while MoS$_2$ prepared in acetone is larger, it has much more active sites that participate in hydrogen evolution. This could be due to oxide groups having preferential energetics to hydrogen ion adsorption, electron transfer or lower steric hindrance. Also, the MoO$_3$ hydrophilic edges allow for better contact with electrolyte.$^{48}$

**CONCLUSIONS**

The high concentration and stability of MoS$_2$ nanosheets dispersed in acetone is not fully explained by the Hansen solubility parameter model. Edge-functionalisation occurs spontaneously during ultrasonic exfoliation and produces molybdenum oxide, which fundamentally changes the main interaction of the nanosheets with the solvent. It is also observed that the edge functionalisation significantly modifies macroscopic properties resulting in an improved performance of acetone-exfoliated MoS$_2$ as a hydrogen evolution reaction catalyst, in comparison with material prepared in the same way using a structural analogue solvent (IPA). Evidence of functionalisation are observed with modification of solubility parameters and HER activity, which are known to be edge sensitive. Microscopic characterisation confirms the presence of oxygen-containing regions at the edges of the nanosheets. The exfoliation in acetone could be generally applied as a pretreatment to modify the solubility of layered materials by edge-functionalisation. In particular it is of interest to investigate whether the same chemistry is observed, under exfoliation conditions, for the other transition metal dichalcogenides, possibly bringing out useful properties.

**EXPERIMENTAL PROCEDURE**

**Liquid-phase exfoliation of MoS$_2$.** The dispersion of MoS$_2$ (Aldrich Chemistry) at initial concentration of 20 mg/mL (80 mL of total volume) was probe sonicated using the Sonics
Vibracell VCX750 and the ½-inch (13 mm) tip for 1h at 60% amplitude. The resulting dispersion was centrifuged for 30 min at 5000g. The supernatant was discarded and the sediment was redispersed into 80 mL of acetone (VWR Chemicals) or IPA (Fisher Chemical), as received. The dispersion was probe sonicated for 5h at 60% amplitude, pulsed 6s on and 2s off. It was then centrifuged for 5 min at 5000g. The supernatant was collected for further characterisation.

**UV-vis spectroscopy.** UV-vis spectra were measured in quartz cuvettes using the Shimadzu UV-3600 Plus spectrophotometer.

**Zeta potential.** Zeta potential was measured in the AntonPaar Litesizer 500 particle analyser. The sample was prepared diluting 10 µL of MoS$_2$/acetone dispersion in 350 ml of deionized water. A Thermo Scientific Barnstead MicroPure purification system was used to prepare ultrapure water (18.2 MΩ resistivity). A potential difference of 200 mV was applied to an Omega cuvette containing the sample.

**Sonication time study.** For this study, a dispersion was prepared at the same initial concentration of 20 mg/mL but with total volume of 50 mL. It was probe sonicated using a Sonics Vibracell VCX130 with ¼-inch (6.3 mm) tip for 1h at 60% amplitude and centrifuged for 30 min at 5000g. The supernatant was discarded and the sediment redispersed into 50 mL of acetone. The dispersion was sonicated at 60% amplitude for times ranging between 30 min and 8h. Samples of 5 mL were collected every 30 min up until 3h and then every hour. Fresh solvent was added to keep the total volume constant during sonication. Every sample was centrifuged for 5 min at 5000g and the resulting supernatant was further characterised.

**Hansen and Hildebrand parameters.** A MoS$_2$ dispersion in acetone was prepared as described above. In order to measure the Hansen and Hildebrand solubility parameters for the material a total of 10 samples were prepared by centrifuging 2 mL of the supernatant of the final centrifugation step using Beckman Coulter’s Optima TLX ultracentrifuge at 70,000 rpm (265,070g) for 20 minutes. Additional 10 samples were prepared by redispersing the sediment from the initial centrifugation step during preparation in fresh acetone and centrifuging them in the ultracentrifuge for 5 minutes at
5,000 rpm (1,350g). For both sets of centrifuge tubes the supernatant was discarded and 2 mL of solvent was added to each tube: N-pentane, ethanol, toluene, tetrahydrofuran, acetone, N-methyl-2-pyrrolidone, methanol (VWR Chemicals), cyclopentanone, 1-cyclohexyl-2-pyrrolidone (Aldrich Chemistry) and isopropanol (Fisher Chemical). Each sample was sonicated for 10 seconds at 30% amplitude using Sonics Vibracell VCX130 with ¼-inch (6.3 mm) tip to redisperse the sediment into each solvent. These samples represent identical dispersions of particles (either exfoliated MoS$_2$ or bulk MoS$_2$) in different solvents of known solubility parameters. The stable concentrations achieved after a period of sedimentation allow the corresponding parameters of the particulates to be estimated. Samples were characterised using UV-vis spectroscopy.

**Atomic force microscopy.** The characterisation technique was employed with the Dimension Icon system from Bruker operating in the Peak Force Tapping mode (Quantitative Nanomechanical property mapping). This mode allows for topographic as well as nanomechanical properties characterisation. The probe used was a ScanAsyst Air tip whose spring constant is 0.4 N/m. The sample was prepared drop casting the MoS$_2$/acetone dispersion on silicon wafer. The wafer was heated above the boiling point of acetone (60°C) to remove any residual solvent in the analysed sample.

**Raman spectroscopy.** A Raman spectra map was measured on the same sample used for AFM characterisation. The non-resonant map was taken with an excitation laser wavelength of 532 nm and a 2400 l/mm grating. For the resonant map a 660nm laser was used with an 1800/mm grating. For both maps, step size was 0.25 µm in a square area of 20 µm side, 1s as integration time per point, power of 5 mV and optical magnification of 100x.

**Transmission Electron Microscopy.** Micrographs were taken using FEI Titan 80 – 300 scanning transmission electron microscope (STEM) operating at 300kV. The samples were deposited onto ultrathin carbon grid (standard lacey with 2 nm film on the top). Fast Fourier transform pattern was created using the ImageJ software.

**X-ray photoelectron spectroscopy.** Analysis was carried out using an ESCALAB 250 Xi system (Thermo Scientific) equipped with a monochromated Al K$_\alpha$ X-ray source.
Uniform charge neutralization was provided by multi-mode electrostatic flood source. The standard analysis spot of ca. 900x900 μm² was defined by the microfocused X-ray source. Full survey scans (step size 1 eV, pass energy 150 eV, dwell time 50 ms and 5 scans) and narrow scans (step size 0.1 eV, pass energy 20 eV, dwell time 100 ms and 15 scans) of the Mo3d (binding energy, BE~229 eV), S2p (binding energy, BE ~162 eV), C1s (BE ~285 eV) and O1s (BE~531 eV) were acquired from four separate regions on each sample. Data were analysed using Thermo Avantage Software (Version 5.952) using a smart background.

**Electron energy loss spectroscopy.** The scanning transmission electron microscopy (STEM) imaging studies were performed on probe-corrected FEI Titan Low-Base 60-300 microscope operating at 200 kV (fitted with a X-FEG® gun, a Cs-probe corrector (CESCOR from CEOS GmbH)). EEL spectra were recorded using the spectrum-imaging (SPIM in 2D or spectrum-line (SPLI) in 1D) mode in a Gatan GIF Tridiem ESR 865 spectrometer. The convergent semi-angle was of 25 mrad, the collection semi-angle was of 80 mrad and the energy resolution ~ 1.0 eV. The EEL spectra were denoised with the open-source program Hyperspy by using principal component analysis routines.

**Electrochemical characterisation.** Measurements were performed in a three-electrode configuration with a Gamry potentiostat. Glassy carbon electrodes were used as the working electrode (3 mm diameter, BASi), while platinum wire and Ag/AgCl (3M KCl) were used as the counter and the reference electrode, respectively. A total mass of 13.4 µg of MoS₂ exfoliated in acetone was deposited onto the glassy carbon electrode with a catalyst loading of 0.2 mg/cm². In comparison, the same mass of MoS₂ exfoliated in IPA was deposited in the same way. Linear sweep voltammetry (LSV) experiments were performed with a scan rate of 5 mV/s from 0 V to -1 V (vs RHE) in 0.5M H₂SO₄ to investigate the hydrogen evolution performance. The measured potential was converted to the RHE scale by adding +0.210 V, measured with respect to a Gaskatel Hydroflex H₂ reference electrode.

**ASSOCIATED CONTENT**

**Supporting Information.** This material is available free of charge via the Internet at http://pubs.acs.org.
FWHM histogram of Raman mode

XPS data for acetone-exfoliated nanosheets in the range of sulfur energy

Raman map for MoS$_2$ nanosheets exfoliated in 2-butanone

Additional TEM micrographs

Zeta potential characterisation for sonication time study

Hansen and Hildebrand solubility parameters results

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**Notes**
The authors declare no competing financial interest.

**Author contributions**
The manuscript was written through contributions of all authors.

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