Supporting Information

Self-expansion, self-exfoliation and self-dispersion: insights into colloidal formation of atomically thin two-dimensional MoO$_{2.5}$(OH)$_{0.5}$

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Experimental section

**Preparation of bulk MoO$_3$ nanobelts:** All chemical reagents were commercial products used without further purification. Firstly, MoO$_3$ nanobelts were prepared via a facile hydrothermal approach, according to reported studies.\(^1\) Typically, 1 g of ammonium molybdate was dissolved in 30 mL of deionized water under continuous stirring. After 30 min, 6 mL of HNO$_3$ was added to the beaker dropwisely and stirred for another 30 min. The homogeneous suspension was formed. Then the resulting suspension was transferred to a Teflon-lined autoclave with a capacity of 50 mL and then kept inside an electric oven at 180 °C for 24 h. The as-prepared MoO$_3$ nanobelts powder was collected by filtration and thoroughly washed with deionized water and ethanol for several times and finally dried in air. The single as-prepared MoO$_3$ nanobelts is consistent with our previously reported work, indicating single crystal structure.\(^2\)

**Preparation of bulk MoO$_{2.5}$(OH)$_{0.5}$ nanobelts:** The two layer fibrous cloth (ca. 30.0mm×30.0 mm×0.5 mm) were placed on the top of Al$_2$O$_3$ crucible. 0.5 g of MoO$_3$ nanobelts powders were placed between two layer cloth. 20 mL of distilled water was poured into the crucible pool. Then all of them were transferred to a 50 mL Teflon-lined autoclave with 20 mL water, and then kept inside an electric oven at 180 °C for 24 h. The crucible with fibrous cloth was carefully taken out of the container. The powders were finally collected between the two layer cloth for further experiments and materials characterizations.

**Preparation of monolayered MoO$_{2.5}$(OH)$_{0.5}$ sheets:** The monolayered MoO$_{2.5}$(OH)$_{0.5}$ sheets were obtained by liquid exfoliating of as-prepared bulk MoO$_{2.5}$(OH)$_{0.5}$ nanosheets in water. In detail, 100 mg of bulk MoO$_{2.5}$(OH)$_{0.5}$ nanosheet powders dispersed in 100 mL water without any ultrasound for about 8 months.

**Material characterizations:** The crystal structure was performed by X-ray diffraction (XRD) analysis with a PANanalytic X’Pert spectrometer using Cu Kα radiation with wavelength of 0.15405 nm. The surface morphologies of the samples were studied using a JEOL JSM6300 (Tokyo, Japan) field emission scanning electron microscope (FESEM). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEM-2010F electron microscope (JEOL, Japan) operating at 200 kV. Atomic force microscopy (AFM) samples were prepared by drop drying the colloidal onto a mica substrate and the characterization was carried out on Veeco dIlInnova with a Si tip. UV-vis absorption spectra were recorded on a UV-4100 (Shimadzu) spectrometer between 200-800 nm. Photoluminescence spectra were collected by FLUOROLOG-3-TAU type spectrometer. The 330 nm exciting wavelength of a krypton ion laser (Coherent Innova) was used, with the nominal output power of the laser kept at 200 mW. All measurements were performed at room temperature. The zeta potential is an important and useful indicator of this charge that can be used to predict the stability of colloidal suspensions. The zeta potential of yellow colloidal particles was determined by a zeta potential analyzer (Zeta PALS, Brookhaven Instruments Co., USA).
**Figure captions**

**Scheme. S1** The comparison of crystal structure of MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$. Noted that the positions of the molybdenum atoms are different within the octahedra. The coordination of oxygen atoms (red spheres) around the molybdenum atoms (grey spheres) is respectively shown below MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$.

**Supplementary Note 1** The discussion of crystal structure of MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$.

**Fig. S1** The comparative XRD patterns of MoO$_3$ nanobelts under different conditions. Black: the MoO$_3$ nanobelts powders on the surface of Aluminum sheet; Red: the MoO$_3$ nanobelts powders on the surface of Nickel foam; Blue: the MoO$_3$ nanobelts powders on the surface of fibrous cloth at atmospheric conditions (room temperature and 1 atm).

**Supplementary Note 2** The discussion of the formation mechanism of the obtained MoO$_{2.5}$(OH)$_{0.5}$.

**Fig. S2** XPS spectras for Mo3d core level (a, b) and oxygen 1s level (c, d) of MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$ nanobelts, respectively.

**Fig. S3** FESEM image of the bulk MoO$_3$ nanobelts (a), the as-prepared MoO$_{2.5}$(OH)$_{0.5}$ nanobelts (b) and the residual unexfoliated MoO$_{2.5}$(OH)$_{0.5}$ nanobelts at the bottom of colloidal solutions (c).

**Fig. S4** Photographs of the color changes of the MoO$_{2.5}$(OH)$_{0.5}$ nanosheets in water with increasing time.

**Fig. S5** The TEM image of yellow colloidal solutions for ca 8 months.

**Fig. S6** The TEM image of yellow colloidal solutions for ca 1 month.

**Fig. S7** The TEM image of broken and tearing MoO$_{2.5}$(OH)$_{0.5}$ nanosheets.

**Fig. S8** TEM image of single particle of yellow colloidal solutions for ca 8 months.

**Fig. S9** (a) pristine MoO$_{2.5}$(OH)$_{0.5}$ colloidal solutions with low concentration; (b) MoO$_{2.5}$(OH)$_{0.5}$ suspension with addition of CTAB. After adding CTAB, the transparent solutions turned opaque, which clearly indicates that the MoO$_{2.5}$(OH)$_{0.5}$ colloidal solutions were negatively charged. The measured zeta potential value for pristine MoO$_{2.5}$(OH)$_{0.5}$ (a) is -28 mV (Fig. S10c) further confirmed that the MoO$_{2.5}$(OH)$_{0.5}$ colloidal solutions were negatively charged.

**Fig. S10** Photographs of the MoO$_{2.5}$(OH)$_{0.5}$ nanosheets in various solvents of water, ethanol, NMP, formamide, IPA., respectively, after storage for 1 days at room temperature. It clearly demonstrates that water is promising solvent to exfoliate and disperse bulk MoO$_{2.5}$(OH)$_{0.5}$ nanosheets.

**Supplementary Note 3** The discussion of why the resultant colloidal solutions are charged negatively and the origin of extra drive force of water molecular insertion into between the layers of MoO$_{2.5}$(OH)$_{0.5}$.

**Table captions**

**Tab. S1.** Comparison between our method and the previous exfoliation methods.

**Tab. S2** Comparative results of the lattice parameters and unit cell volume between orthorhombic MoO$_3$ and orthorhombic MoO$_{2.5}$(OH)$_{0.5}$.

**References**
Supplementary Note 1 | The discussion of crystal structure of MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$.

Based on the comparison of crystal structure of MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$, the MoO$_{2.5}$(OH)$_{0.5}$ is remarkably similar to that of MoO$_3$. Two OH groups in MoO$_{2.5}$(OH)$_{0.5}$ substituted one O atom per unit cell of MoO$_3$. When MoO$_{2.5}$(OH)$_{0.5}$ nanosheets were exfoliated into monolayered nanosheets, the MoO$_6$ monolayer in MoO$_{2.5}$(OH)$_{0.5}$ is also remarkably similar to that of MoO$_3$.

From a large number of exfoliated two-dimensional materials, such as graphene oxide and h-BN, in fact, a stable single-layer sheet is actually not a simple single-layer graphene and h-BN, but the “functionalized” single-layer graphite and single-layer h-BN, such as, graphene with OH groups, and h-BN with surface functionalization groups. Therefore, for as-prepared single-layer MoO$_{2.5}$(OH)$_{0.5}$ in our work, it was considered as MoO$_3$ with “H” functionalization.
**Fig. S1.** The comparative XRD patterns of MoO$_3$ nanobelts under different conditions. Black: the MoO$_3$ nanobelts powders on the surface of Aluminum sheet; Red: the MoO$_3$ nanobelts powders on the surface of Nickel foam; Blue: the MoO$_3$ nanobelts powders on the surface of fibrous cloth at atmospheric conditions (room temperature and 1 atm).

**Supplementary Note 2**

The discussion of the formation mechanism of the obtained MoO$_{2.5}$(OH)$_{0.5}$.

Based on previously reported literature, MoO$_{2.5}$(OH)$_{0.5}$ was formed in a reducing environment. Moreover, our XPS results further confirmed that Mo was a mixed valence state with +4 and +6. For our case, the fibrous cloth acted a double role during the formation of MoO$_{2.5}$(OH)$_{0.5}$, which may accelerate the decomposition of water vapor in high pressure. This may occur in the equation:

$$
H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)
$$

The formation of H$_2$ is very favorable for the formation of MoO$_{2.5}$(OH)$_{0.5}$. In our previously reported literature, we also confirmed that carbon is a catalytic role in the formation of H$_2$MoO$_3$.

Additionally, to validate the necessaries of fibrous cloth and “sauna reaction”, we substituted fibrous cloth by other two different substrates, Aluminum sheet, Nickel foam. Compared to the proposed method, we found that the original MoO$_3$ powders were unchanged. Their corresponding XRD results also confirmed that the MoO$_3$ powders were not transformed into MoO$_{2.5}$(OH)$_{0.5}$. This evidence shows that fibrous cloth are necessary. Further, we also designed fibrous cloth at atmospheric conditions. The MoO$_3$ powders were placed between the two layer fibrous cloth. The color of MoO$_3$ powders were also unchanged under the action of the water vapor. Based on the results mentioned above, we reasonably inferred that both high pressure environment and fibrous cloth are necessary for the formation of MoO$_{2.5}$(OH)$_{0.5}$. 
Fig. S2. XPS spectra for Mo3d core level (a, b) and oxygen 1s level (c, d) of MoO$_3$ and MoO$_{2.5}$(OH)$_{0.5}$ nanobelts, respectively.

The arrows indicate that both the highest peak at 532.23 eV and a weak peak at 531 eV in MoO$_{2.5}$(OH)$_{0.5}$ originated from the OH group.\textsuperscript{7} Compared to MoO$_3$, the intensity of oxide lattice began to decrease, which may be the introduction of OH group. The effect of the break of oxygen bonds during “sauna reaction” may be a critical for hydrogen injection into the bulk MoO$_3$ nanobelts.\textsuperscript{8}
**Fig. S3.** FESEM image of the bulk MoO$_3$ nanobelts (a), the as-prepared MoO$_{2.5}$(OH)$_{0.5}$ nanobelts (b) and the residual unexfoliated MoO$_{2.5}$(OH)$_{0.5}$ nanobelts at the bottom of colloidal solutions (c).

**Fig. S4.** Photographs of the color changes of the MoO$_{2.5}$(OH)$_{0.5}$ nanosheets in water with increasing time.
Fig. S5. The TEM image of yellow colloidal solutions for ca 8 months.

Fig. S6. The TEM image of yellow colloidal solutions for ca 1 month.

Fig. S7. The TEM image of broken and tearing MoO$_{2.5}$(OH)$_{0.5}$ nanosheets.
Fig. S8. TEM image of single particle of yellow colloidal solutions for ca 8 months.

It is curious that the crystalline lattice pattern from TEM is unstable at high-energy electron beams at 200 keV. An electron beam can adversely affect an organic or inorganic sample during examination in a high-energy electron microscope, such as, 200 Kev. F. Egerton et al had discussed this issue of radiation damage in the TEM and SEM.\(^9\) Similarly, Laruelle, S et al also found similar phenomena during the TEM observation.\(^10\)

Fig. S9. (a) pristine MoO\(_{2.5}(\text{OH})_{0.5}\) colloidal solutions with low concentration; (b) MoO\(_{2.5}(\text{OH})_{0.5}\) suspension with addition of CTAB. After adding CTAB, the transparent solutions turned opaque, which clearly indicated that the MoO\(_{2.5}(\text{OH})_{0.5}\) colloidal solutions were negatively charged. The measured zeta potential value for pristine MoO\(_{2.5}(\text{OH})_{0.5}\) (a) was -28 mV (Fig. S10c) further confirmed that the MoO\(_{2.5}(\text{OH})_{0.5}\) colloidal solutions were negatively charged.
Fig. S10. Photographs of the MoO$_{2.5}$(OH)$_{0.5}$ nanosheets in various solvents of water, ethanol, NMP, formamide, IPA, respectively, after storage for 1 days at room temperature. It clearly demonstrates that water is promising solvent to exfoliate and disperse bulk MoO$_{2.5}$(OH)$_{0.5}$ nanosheets.
Tab. S1. Comparison between our method and the previous exfoliation methods

<table>
<thead>
<tr>
<th>Colloidal solutions</th>
<th>Methods</th>
<th>functionalization</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Few-layer boron nitride</td>
<td>one-step mechano-chemical process, complex</td>
<td>amino groups</td>
<td>5</td>
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<tr>
<td>Single-layered graphitic-C$_3$N$_4$</td>
<td>Three steps including acid treatment, NH$_3$-H$_2$O treatment and ultrasonication, complex</td>
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<td>11</td>
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<td></td>
<td>ultrasonication, complex</td>
<td>dangling hydrogens</td>
<td>12</td>
</tr>
<tr>
<td>Atomically thick g-C$_3$N$_4$-NSs</td>
<td>sulphuric acid, complex</td>
<td>oxygen functional groups</td>
<td>13</td>
</tr>
<tr>
<td>Exfoliated graphene-like carbon nitride</td>
<td>organic solvents, complex</td>
<td>dangling hydrogens</td>
<td>14</td>
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<tr>
<td>WS$_2$, MoS$_2$, MoSe$_2$, h-BN</td>
<td>Temperature assisted by ultrasonication, complex</td>
<td>edge functionalization</td>
<td>15</td>
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<tr>
<td>transition metal dichalcogenides</td>
<td>Cosolvent, complex</td>
<td>-CH$_3$ et al</td>
<td>16</td>
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<tr>
<td>graphene</td>
<td>intercalation, oxidation or functionalization, complex</td>
<td>-OH</td>
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<td>MoS$_2$</td>
<td>solvent-assisted exfoliation via sonication, complex</td>
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<td>MgB$_2$</td>
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<td>Fewer layered MoS$_2$</td>
<td>Combined grinding and sonication</td>
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<td></td>
<td>Solvent N-methyl-pyrrolidine and sonication, complex</td>
<td>Unknown, assisted by solvent</td>
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<td>Biocompatible block copolymers, complex</td>
<td>Unknown, assisted by biocompatible block copolymers</td>
<td>27</td>
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<td>Graphene oxide nanosheets</td>
<td>Acoustic cavitation, complex</td>
<td>Unknown, assisted by K$^+$</td>
<td>28</td>
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<td>MoO$<em>{2.5}$(OH)$</em>{0.5}$</td>
<td>Direct exfoliation and dispersion, simple</td>
<td>unnecessary</td>
<td>Our work</td>
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Tab. S2 Comparative results of the lattice parameters and unit cell volume between orthorhombic MoO$_3$ and orthorhombic MoO$_{2.5}$(OH)$_{0.5}$.

<table>
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<tr>
<th>Sample phase</th>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
<th>d$_{020}$ (Å)</th>
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<td>35-0609</td>
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<tr>
<td>MoO$<em>{2.5}$(OH)$</em>{0.5}$</td>
<td>Orthorhombic</td>
<td>3.888</td>
<td>14.082</td>
<td>3.734</td>
<td>204.44</td>
<td>7.05</td>
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<td>14-0041</td>
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</table>
Supplementary Note 3 | The discussion of why the resultant colloidal solutions are charged negatively and the origin of extra drive force of water molecular insertion into between the layers of \( \text{MoO}_{2.5}(\text{OH})_{0.5} \).

Before the final summary of the mechanism of colloidal formation of atomically thin two-dimensional \( \text{MoO}_{2.5}(\text{OH})_{0.5} \), we need to address two issues: (1) why are the resultant colloidal solutions charged negatively? (2) what is the origin of extra drive force of water molecular insertion into between the layers of \( \text{MoO}_{2.5}(\text{OH})_{0.5} \)?

Based on analysis of XPS (Fig. S3), \( \text{MoO}_{2.5}(\text{OH})_{0.5} \) contained a mixture valence of Mo\(^{5+}\) and Mo\(^{6+}\). Partially substitution of Mo\(^{5+}\) for Mo\(^{6+}\) in the octahedral sheet leads to negative charge, therefore, \( \text{MoO}_{2.5}(\text{OH})_{0.5} \) colloidal solutions are negatively charged. Polar water molecules can easily move into the space between negatively charged layers of \( \text{MoO}_{2.5}(\text{OH})_{0.5} \), thus leading to its full expansion.

References:


