

Supplementary Information

Generic solvent exchange avenue to disperse MoS₂ in organic solvents for the ease solution process

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Materials

Butyllithium solution in hexane (1.6 M) and molybdenum disulfide (MoS₂, 99.0% purity) with an average diameter of about 1 μm were purchased from Aladdin. Nitrile rubber (NBR) with acrylonitrile content 40%, was manufactured by Jilin Chemical Industry Company, Jilin, China. 1-butyl-3-methylimidazolium chloride ionic liquid was supplied by Henan Lihua pharmaceutical Co., Ltd. The chemicals including dodecanethiol, dimethyl formamide (DMF), methanol, ethanol, tetrahydrofuran (THF), N-methyl pyrrolidone (NMP), hexane, acetone, ethyl acetate (EA), N-imidazole were analytically pure and used as received.

Preparation of chemically exfoliated MoS₂ (ce-MoS₂)

ce-MoS₂ was synthesized by lithium intercalation and exfoliation method according to the procedure reported before.¹ Briefly, 1.0 g of natural MoS₂ powder was dispersed in 10 mL of 1.6 M butyllithium solution in hexane for 72 hours in a flask under nitrogen. The intercalated Li_xMoS₂ was retrieved by filtration and washed with hexane (120 mL) to remove excess lithium and organic residues. Exfoliation of MoS₂ was accomplished by sonication the as-prepared Li_xMoS₂ slurry in 1 L DI-water for 1 h. The MoS₂ aqueous dispersion was then centrifuged and re-dispersed in DI water for at least 3 times to remove excess lithium in the form of Li(OH).

Dispersion of ce-MoS₂ in organic solvents through solvent exchange method

To disperse the ce-MoS₂ in organic solvents, a simple solvent exchange method was explored. Typically, ce-MoS₂ aqueous dispersion (1.0 mg/mL) was subjected to centrifugation and the wet sediment was dispersed in corresponding organic solvent (~1.0 mg/mL). The centrifugation-dispersion process was repeated for 5 times, and then the ce-MoS₂ dispersion in organic solvent was obtained. For comparison, ce-MoS₂ aqueous dispersion was first dried, and then the dried ce-MoS₂ was dispersed into organic solvents by sonication.

Phase transformation of ce-MoS₂ under solvothermal condition

The ce-MoS₂/DMF dispersion was first obtained by the solvent exchange method. Subsequently, the dispersion was heated and refluxed at 160 °C under nitrogen atmosphere. The supernatant was then filtered and rinsed with ethanol, and allowed to dry under ambient conditions.

Modification of ce-MoS₂ (m-MoS₂)

Dodecanethiol was added into MoS₂/acetone dispersion (1 mg/mL) with the dodecanethiol/MoS₂ mass ratio of 4/1. The mixture solution was incubated at room temperature for 36 hours. The mixture was then subjected to several cycles of centrifugation and washing with acetone and methanol to remove the excessive and physically adsorbed dodecanethiol.

Preparation of NBR/MoS₂ composites

In the preparation of NBR/MoS₂ composite, a desired amount of NBR was added into the as-prepared ce-MoS₂/acetone suspension, followed by stirring at room temperature overnight. After that, the above mixture was coagulated with plenty of water under vigorous stirring. The resulting black solid products were filtered and vacuum-dried at 60 °C overnight. Lastly, the dried compounds were compounded with rubber ingredients with a two-roll mill and subjected to compression at 150 °C for the optimum curing time determined by the U-CAN UR-2030

vulcameter. The NBR/m-MoS₂ composite was prepared by adding m-MoS₂ into NBR, following the similar protocol as that for the preparation of NBR/MoS₂ composite. The composites contain 3 phr MoS₂ or m-MoS₂. The formulation of the composite is listed as follow, NBR 100 g; zinc oxide 5 g; stearic acid 1.5 g; dibenzothiazole disulfide 1.0 g; N-cyclohexyl-2-benzothiazole sulfenamide 1.5 g; sulfur 1.5 g.

Characterizations

Atomic force microscopy (AFM) was conducted on a Bruker Multi Mode8 operated in a tapping mode. For the AFM measurements, the samples were prepared by dropping ce-MoS₂/water, ce-MoS₂/acetone, and ce-MoS₂/DMF dispersions onto freshly delaminated mica sheets followed by drying. Transmission electron microscopy (TEM) was conducted on JEOL2100. Fourier transform infrared spectra (FTIR) were collected on a Bruker Vertex 70 FTIR spectrometer. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a NETZSCH TG 209F1 at a heating rate of 10 °C min⁻¹. UV-vis spectra were collected on a Scinco S-3150 spectrometer. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Axis Ultra DLD with Al K α radiation (1486.6 eV). Tensile tests were performed on U-CAN UT-2060 following ISO 37-2005. To determine the concentration of ce-MoS₂ in various solvents, ce-MoS₂ suspension is settled for 72 h, and then a precisely measured volume of the supernatant is decanted and dried. The mass of ce-MoS₂ in the stock dispersion is then determined using a microbalance.

As shown in Fig. S1, the directly dried ce-MoS₂ cannot be wetted or re-dispersed in water or organic solvents under sonication. It can be explained by the fact that the ce-MoS₂ sheets are stacked upon drying, and the solvent molecules/ce-MoS₂ sheet interaction is not sufficiently strong to overcome the van der Waals attractive interactions that operate between ce-MoS₂ sheets.



Fig. S1 Photos of the dried MoS₂ dispersed in solvents under sonication

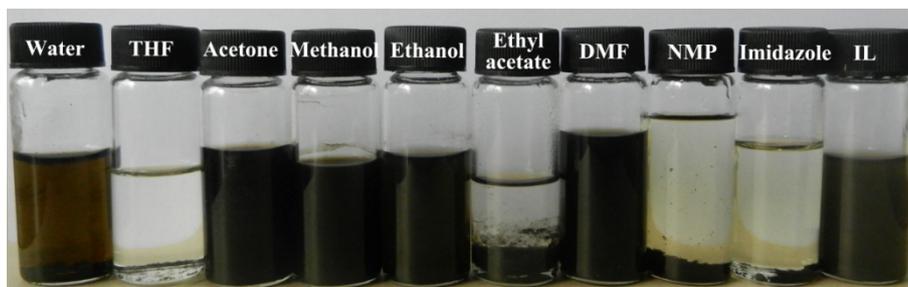


Fig. S2 Photos of ce-MoS₂ dispersed in solvents after settling for one month

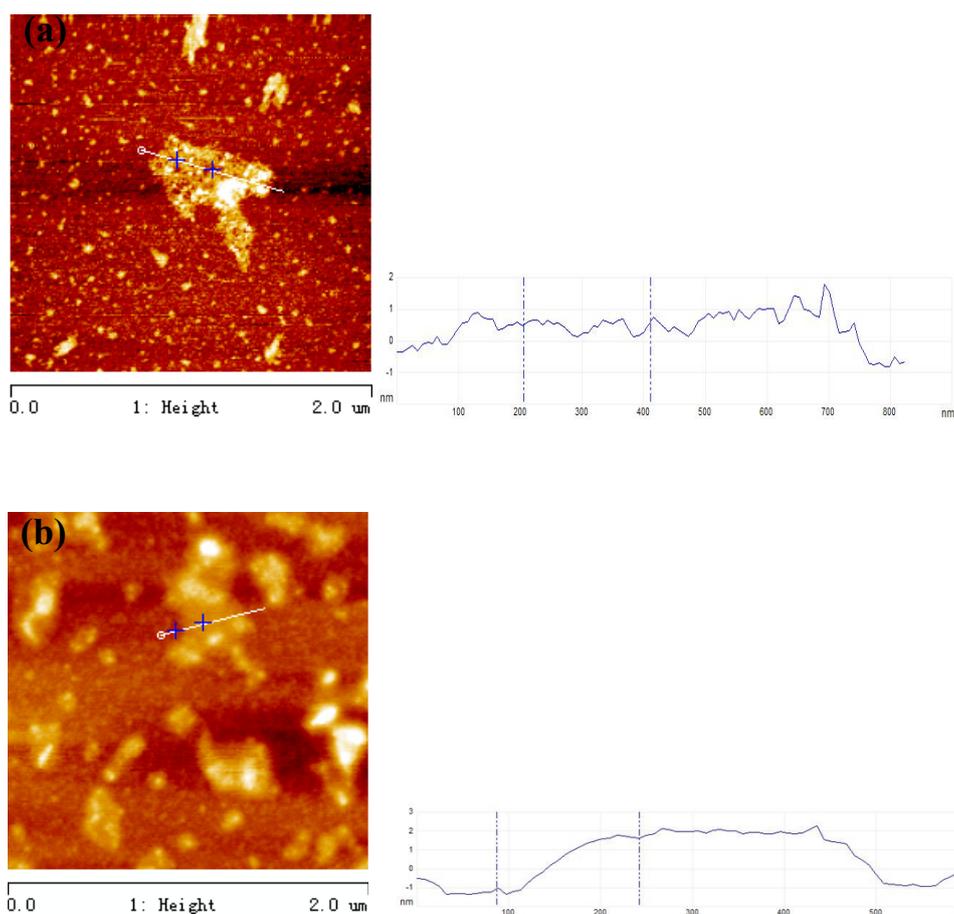


Fig. S3 AFM images and height profiles of ce-MoS₂ dispersed in (a) water and (b) methanol

The evolution of phase structure is further studied by measuring the UV-vis spectra of ce-MoS₂/DMF suspension as a function of heating time. As shown in Fig. S4, the as-prepared ce-MoS₂ exhibits no distinct characteristic peaks in the whole range, while three prominent peaks at 420, 656 and 603 nm are observed upon heating. The absorption at 420 nm associated with the convoluted C and D excitonic peaks increases with prolonged heating time. Besides, the heated ce-MoS₂ also shows two well-resolved excitonic peaks, that is, peak A1 at 656 nm and peak B1 at 603 nm. These peaks are related to the direct excitonic transitions at the κ point of the Brillouin zone with the energy difference arising due to spin-orbital splitting of the valence band. These observations are well consistent with others studies and suggest the restoration of the semiconducting properties of MoS₂.²

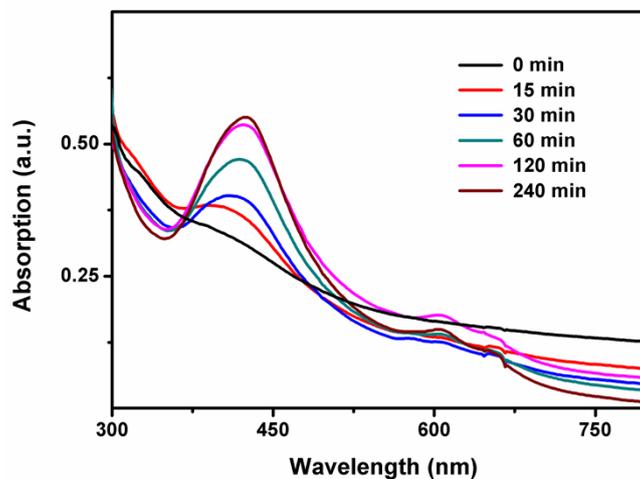


Fig. S4 UV-vis spectra of ce-MoS₂/DMF suspension versus different heating time

The ligand conjugation of ce-MoS₂ is investigated by FTIR. As shown in Fig. S5, in the spectroscopy of m-MoS₂, the absorptions at 2960 and 2870 cm⁻¹ are due to the stretching variation of -CH₂-, indicating that dodecanethiol ligand has been coupled onto ce-MoS₂ sheet. Besides, in the spectroscopy of the free dodecanethiol, the absorption at 2563 cm⁻¹ is ascribed to S-H. While this peak is absent in m-MoS₂ after conjugation with ce-MoS₂, evidencing the formation of ligand conjugation through thiol chemistry.

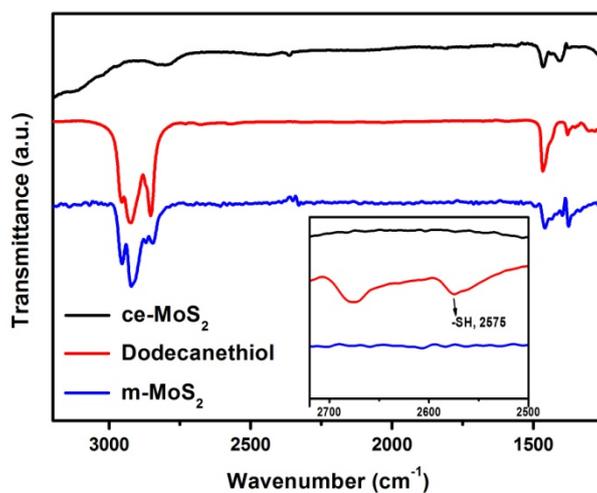


Fig. S5 IR spectra of ce-MoS₂, dedecanethiol and m-MoS₂

In the TGA curve of ce-MoS₂, the weight loss in the range of 150-350 °C is due to the removal of physisorbed and chemisorbed water. For m-MoS₂, there are two major weight loss stages at 150-350 and 400-550 °C. The former stage is due to the evaporation of adsorbed water, and the latter stage above 400 °C is mainly attributed to the degradation of the coupled dodecanethiol. Compared with ce-MoS₂, the adsorbed water in m-MoS₂ is significantly reduced due to the increasing hydrophobic properties of m-MoS₂ with the conjugation of dodecanethiol. In addition, the onset decomposition temperature of dodecanethiol in m-MoS₂ is greatly improved from 280°C (the boiling point of free dodecanethiol) to 420 °C, indicating that dodecanethiol is strongly bonded onto MoS₂ sheets. Furthermore, taking into account of the residue at 600 °C, the quantity of grafted dodecanethiol in m-MoS₂ is calculated to be ca. 22 wt %.

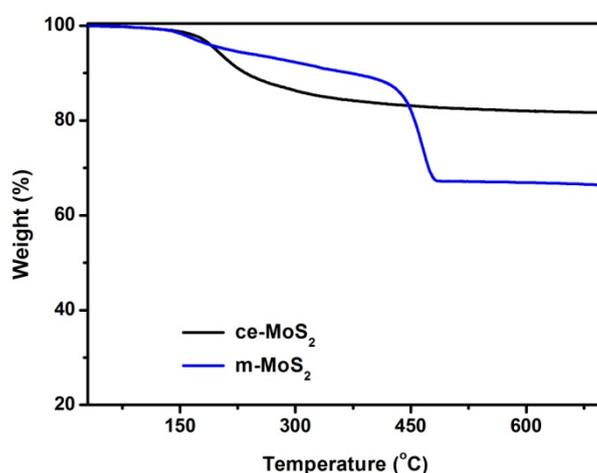


Fig. S6 TGA curves of ce-MoS₂ and m-MoS₂

Solubility experiment is conducted by adding ce-MoS₂ and m-MoS₂ into water/chloroform biphasic system. It shows that ce-MoS₂ is dispersed in the aqueous phase, while m-MoS₂ is remained in the chloroform phase. It demonstrates that the surface properties of m-MoS₂ are altered by the grafted dodecanethiol, thereby imparting m-MoS₂ solubility in chloroform.

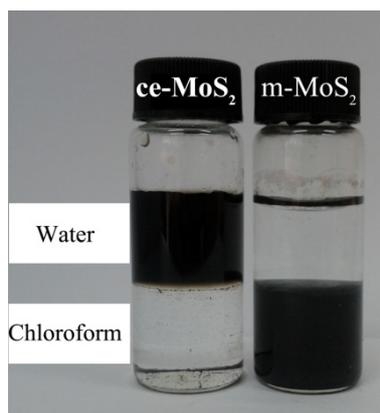


Fig. S7 Dispersion of ce-MoS₂ and m-MoS₂ in water/chloroform biphasic system

References

- 1 S. S. Chou, B. Kaehr, J. Kim, B. M. Foley, M. De, P. E. Hopkins, J. Huang, C. J. Brinker and V. P. Dravid, *Angew. Chem., Int. Ed.*, 2013, **52**, 4160-4164.
- 2 G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen and M. Chhowalla, *Nano Lett*, 2011, **11**, 5111-5116.