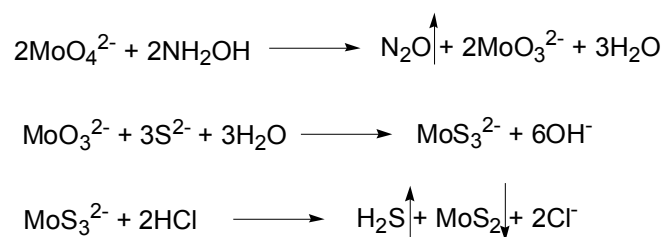


Supporting Information

Preparation of Solvent-Free Ionic MoS₂ Nanofluids

Hydrothermal synthesis was used to synthesize nanoscale amorphous MoS₂. Analytically pure hydroxylamine hydrochloride ammonia (NH₂OH·HCl, Sinopharm Chemical Reagent Co., Ltd, ≥ 98.5%) was used as a reductant to turn Mo⁺⁶ in the form of sodium molybdate (Na₂MoO₄, Sinopharm Chemical Reagent Co., Ltd, ≥ 99.0%) into Mo⁺⁴, which was followed by adding sodium sulfide (Na₂S, Sinopharm Chemical Reagent Co., Ltd, AR) to conduct sulfonation reaction. Eventually, nanoscale MoS₂ was precipitated after the addition of hydrochloric acid as shown in

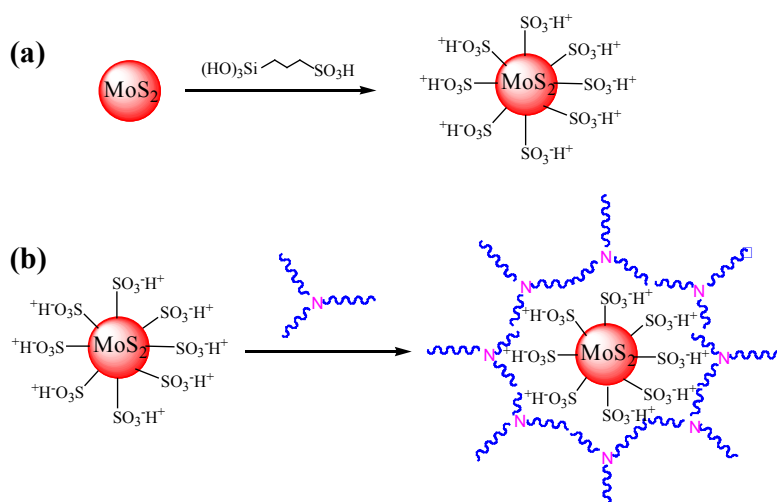
Scheme 1.



Scheme 1 Synthesis of nanoscale MoS₂ by hydrothermal synthesis.

Solvent-free ionic MoS₂ nanofluids were prepared by acid-base reaction. **Scheme 2a** shows an outline of the procedure of covalently bound organic corona to the surface of as-synthesized nanoscale MoS₂. The surface modifier (corona in this case) 3-(trihydroxysilyl)-1-propane sulfonic acid (SIT, 30-35 wt% solution in H₂O) was purchased from Fluorochem Ltd. and used as received. The PEG-substituted tertiary amine ((C₁₈H₃₇)N(CH₂CH₂O)_mH)-(CH₂CH₂O)_nH) (*M_w* = 930 g/mol) was brought from Haishihua Inc. and used as received. 3-(trihydroxysilyl)-1-propane

sulfonic acid (SIT) was diluted to a concentration of 8 wt% using deionized water. The MoS₂ suspension was slowly added to the SIT solution dropwise under vigorous stirring. 1 M NaOH was slowly added until the solution pH was about 5. The weakly acidic solution was then stirred vigorously for 24 h at 70 °C. The suspension was then cooled to room temperature and dialyzed in deionized water for 2 days (water changed every two or three hours) to remove free SIT and ionic impurities. The functionalized nanoparticles were passed through an ion-exchange column (732, Sinopharm Chemical Reagent Co., Ltd) four times to ensure complete replacement of Na⁺ ions by protons. Afterwards, functionalized nanoscale MoS₂ was ionically tethered with oligomeric chains as canopy to balance the charges as shown in **Scheme 2b**. An appropriate amount of tertiary amine ((C₁₈H₃₇)N(CH₂CH₂O)_mH)(CH₂CH₂O)_nH) in deionized water was added to the functionalized nanoparticle suspension while stirring and closely monitoring the solution pH. Once the reaction of the corona and canopy was completed, the resulting mixture was dialyzed. Then, the solvent was slowly removed under vacuum at 50 °C for 4 days to obtain the resulting solvent-free ionic MoS₂ nanofluids.



Scheme 2. Typical schematic for synthesis of solvent-free nanofluids. (a) Covalently bound organic corona to the surface of as-synthesized nanoscale MoS₂. (b) Ionically tethered with oligomeric chains as canopy to balance the charges.

Characterization

X-ray fluorescence spectroscopy (XRF, SRS3400, BRUKER, Germany) was used to measure the chemical composition of inorganic nanoparticles. X-ray diffractometer (XRD, D/max2550VB3+/PC, Rigaku International Corporation, USA) was used to determine the structure of inorganic nanoparticles with CuK α radiation ($\lambda = 1.542$ nm). The spectra were recorded at a scanning rate of 10 ° per minute in the range of 2θ between 10 ° and 80 °. High resolution transmission electron microscope (HRTEM, JEM 2010F, JEOL, Japan) was used to analyze the structure and distribution of inorganic cores. Dispersability and hydrodynamic diameters of the modified MoS₂ were determined by dynamic light scattering (DLS, Zetasizer Nano ZS90, Malvern Instruments). Measurements were carried out at constant temperature $T = 25$ °C after sonicating for 30 min. DSC traces were recorded on a Q100 TA

instrument at a heating and cooling rate of 10 °C/min. TGA measurements were taken under N₂ using STA 449 C (NETZSCH) at a heating rate of 20 °C/min. Rheological properties were measured using ARES Rheometer (TA instruments) by dynamic strain frequency sweep mode at a fixed temperature of 20 °C and a strain of 1%. Nanotribological properties were measured using an in-situ nanomechanical test system (Tribo Indenter, Hysitron Inc.) with constant normal loads of 200 μN, 400 μN and 600 μN at room temperature (22 °C). The tip used for the scratch experiments was a 60° conical diamond tip on fused quartz with a tip end radius of curvature of 1 μm in length. Solvent-free MoS₂ nanofluids thin films were prepared by spin-coating technology on polished silicon substrates. The scratching was conducted at a sliding speed of 1 μm/s for three cycles with a constant length of 5 μm. In-situ images of scratches were taken by scanning probe microscope (SPM) equipped with the tester.

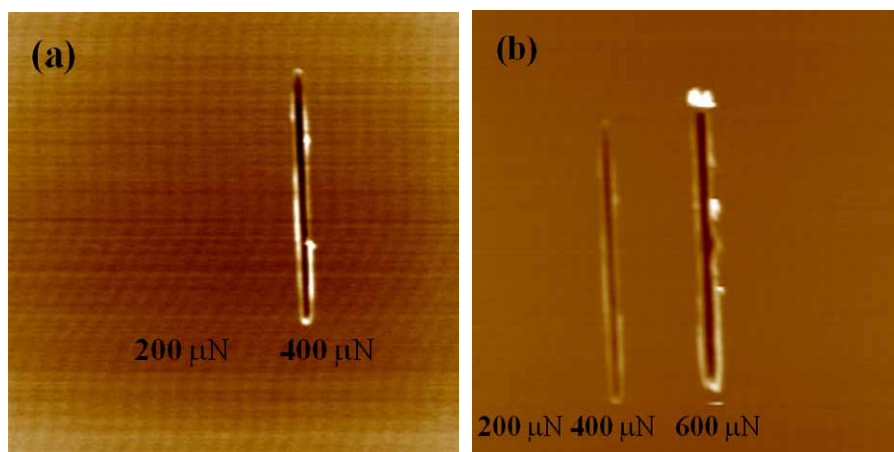


Figure 1S. Images of scratches at different applied normal loads. (a) 200 μN; 400 μN. (b) 200 μN; 400 μN (200 seconds after scratching); 600 μN. Scratches under 200 μN are invisible. Capture area is 10 μm × 10 μm, and the scratch length is 5 μm.