Electronic Supplementary Information (ESI)

MoS_2 armored polystyrene particles with a narrow size distribution via membrane-assisted Pickering emulsions for monolayer-shelled liquid marbles

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Materials

MoS_2 was achieved from Afar Sally chemical co., LTD, Tianjing, China. C_4H_9Li, AIBN, hexadecane were supplied from lark technology co., LTD, Beijing, China. Liquid paraffin and n-hexane were purchased from Qiangsheng chemical co., LTD, Jiangsu, China. Styrene was purchased from Damao chemical co., LTD, Tianjing, China. $BaCl_2{\cdot}2H_2O$ was obtained from Fuchen chemical co., LTD, Tianjing, China. Water used in all experiments was purified with a resistivity higher than 18.0 MΩ cm by deionization and filtration with a Millipore purification apparatus.

Preparation of MoS_2 aqueous dispersion

Chemical exfoliated MoS_2 was synthesized by lithium intercalation and exfoliation method. Briefly, 1.0 g of natural MoS_2 powder was dispersed in 10 mL of 1.6 M butyllithium solution in hexane for 72 hours in a flask under nitrogen. Li-intercalating MoS_2 ($LixMoS_2$) was retrieved by filtration and washed with hexane (120 mL) to remove excess lithium and organic residues. Exfoliation of MoS_2 was accomplished by sonication the as-prepared $LixMoS_2$ slurry in 1 L water for 1 h. The MoS_2 aqueous dispersion was then centrifuged and re-dispersed in water for at least 3 times to remove excess lithium in the form of Li(OH).

Preparation of MoS_2-stabilized Pickering emulsion

A typical MoS_2-stabilized Pickering emulsion was fabricated as follows. To enhance the stability of the droplet, $BaCl_2{\cdot}2H_2O$ (45 mg) was added to a MoS_2 aqueous dispersion (4 mg/mL). Then 2.5 mL of styrene with 1 wt% AIBN was added. Emulsification was performed by vigorous agitation of water and oil phase for 3 min using IKA Ultra Turrax t25 basic instrument at 10 000 rpm, and a MoS_2-stabilized Pickering emulsion was obtained.

Fabrication of MoS_2 armored polystyrene (PS) particles with a narrow size distribution

To preparation of MoS_2 armored PS particles with a narrow size distribution, emulsion droplets with a narrow size distribution were prepared by a membrane-assisted re-emulsification based on a hand-driven mini-extruder (Avanti Polar Lipids, Inc.) containing two 1 mL syringes. The two poly(vinylidene fluoride) filtering membranes (Shanghai Xingya Scavenging-Materials Inc., China) used in this study had opening pores with 7.5 μm in diameter. 1 mL of the emulsions prepared by vigorous agitation were drawn into the syringes and pushed back and forth through the membranes, exchanging between the syringes on either side of the device. After a certain passing times (such as 100 times), the emulsions were transferred to a glass bottle and polymerized in an oven at 60 ^{o}C for 8 h. the resulting MoS_2 armored PS particles were purified by three centrifugation/re-dispersion cycles, replacing each decanted supernatant with deionized water., followed by drying overnight in a vacuum at 45 ^{o}C for 12 h. the final product obtained was a gray powder.

Preparation of liquid marbles with a monolayer shell

To prepare of liquid marbles with a monolayer shell, water droplets were deposited onto the dried MoS_2 armored PS particle powder bed using a syringe. By gently rolling the droplet on the powder bed, the liquid was entirely encapsulated by the MoS_2 armored PS particles, resulting in a liquid marble. Then, the liquid marble was transferred to a polypropylene mesh which was placed on an M-shaped rigid aluminum foil. Then, the obtained sample was placed in a closed glass bottle containing 2 mL of toluene. After 20 sec, the liquid marbles was taken out and liquid marbles with monolayer-shelled were obtained.

Characterization

Pickering emulsions were observed with a microscope (Carl Zeiss, Germany). The zeta potential was measured using a Malvern Zeta Sizer Nano ZS90. Atomic force microscopy (AFM) was conducted on a Bruker Multi Mode 8 operated in a tapping mode. Transmission electron microscopy (TEM) was conducted on JEOL2100. The average diameter of the emulsion droplets and particles were determined with a laser scattering particle size distribution analyzer (Malvern Mastersizer 2000). The confocal micrographs were taken with a Leica TCS-SP2 confocal laser scanning microscope. Morphologies of the particles and liquid marbles were analyzed using a Zeiss EVO 18 scanning electron microscope (SEM) equipped with a field emission electron gun and energy dispersive spectrometer (EDS). For the SEM observation of the shell of liquid marbles, the specimen was first scattered onto a conductive tap, then sliced using a sharp razor blade, and afterwards sputter coated with gold.

Table S1. Elemental analysis of the MoS_2-armored PS particles.

Element	C	O	Mo	S
Weight %	84.27	13.1	1.12	1.29

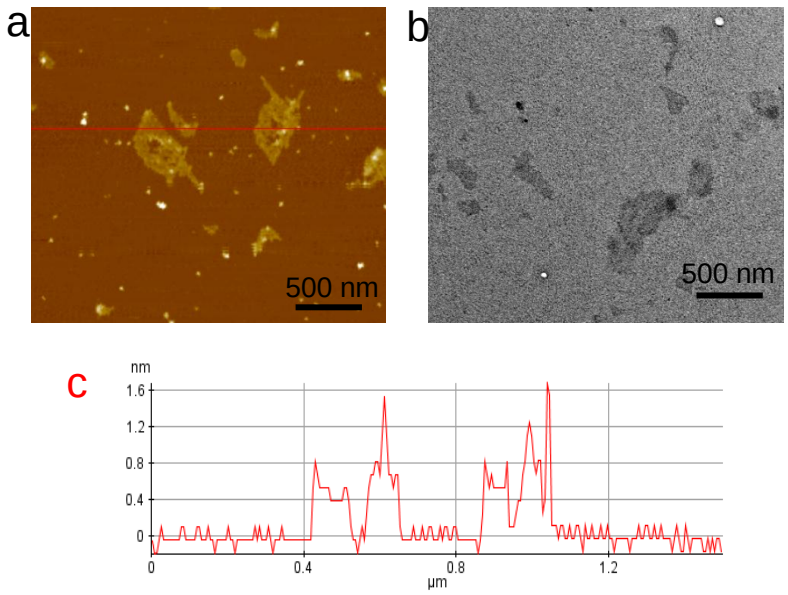

Fig. S1. (a) AFM and (b) TEM images of ce-MoS_2, (c) the height profile of the red line in a.

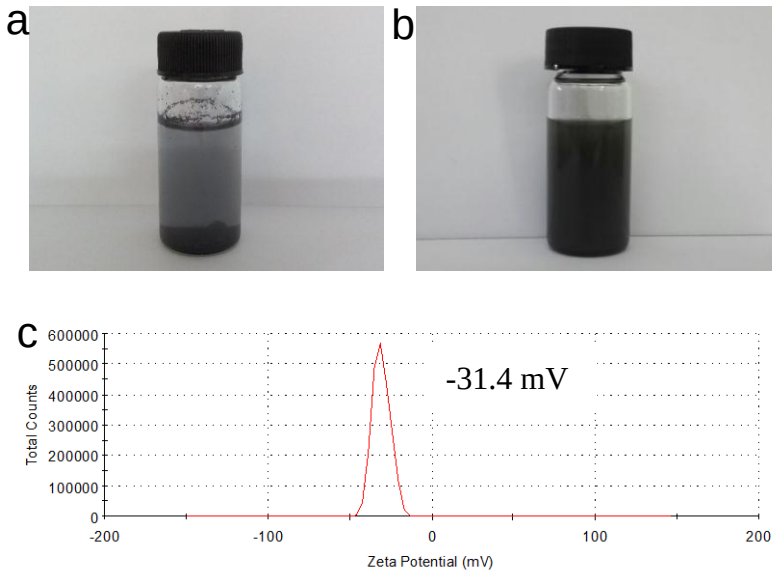

Fig. S2. Photos of (a) bulk MoS_2 and (b) ce-MoS_2 dispersed in water. (c) The zeta potential of ce-MoS_2 with a concentration of 4mg/mL in water.

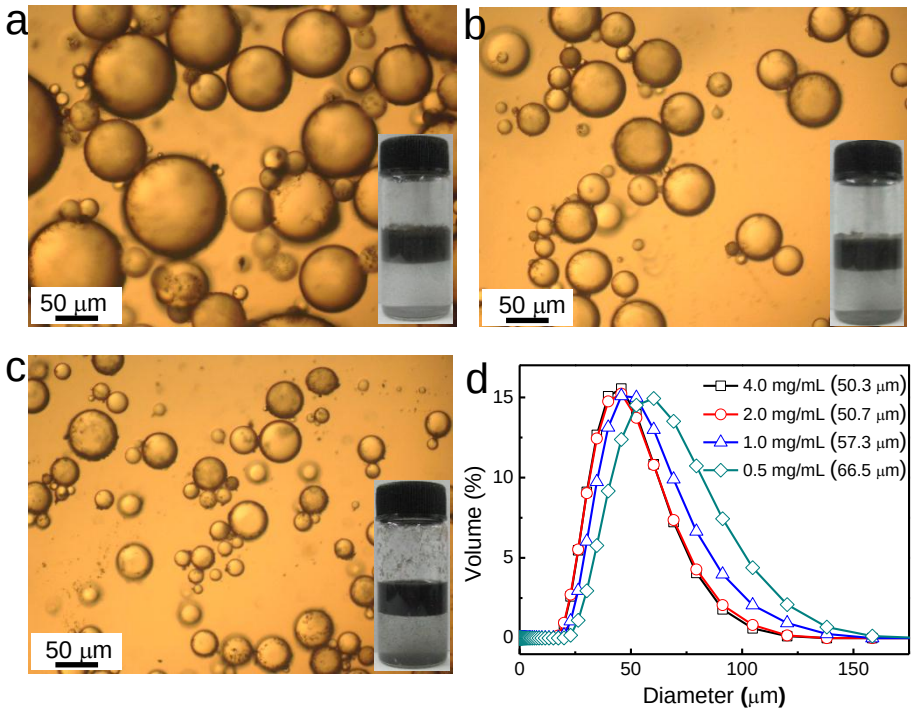

Fig. S3. Optical microscopy images of styrene-in-water Pickering emulsions stabilized by different ce-MoS_2 concentrations: (a) 0.5, (b) 1.0, and (c) 2.0 mg/mL. The insets of a-c are the photos of their corresponding emulsions. (d) The corresponding size distribution curves of the Pickering emulsions. The styrene to water ratio is 1:3.

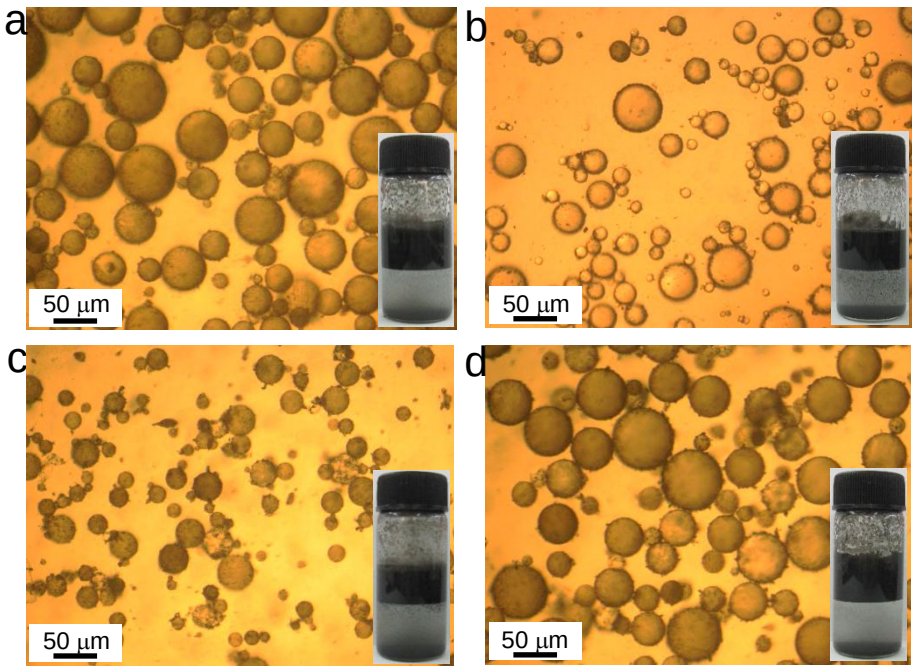

Fig. S4. Optical microscopy images of MoS_2 nanosheet-stabilized O/W Pickering emulsions with different oil phases: (a) liquid paraffin, (b) toluene, (c) n-hexane, and (d) hexadecane. The insets of a-d are the photos of their corresponding emulsions. The oil to water ratio is 1:3, and the MoS_2 concentration is 4mg/mL.

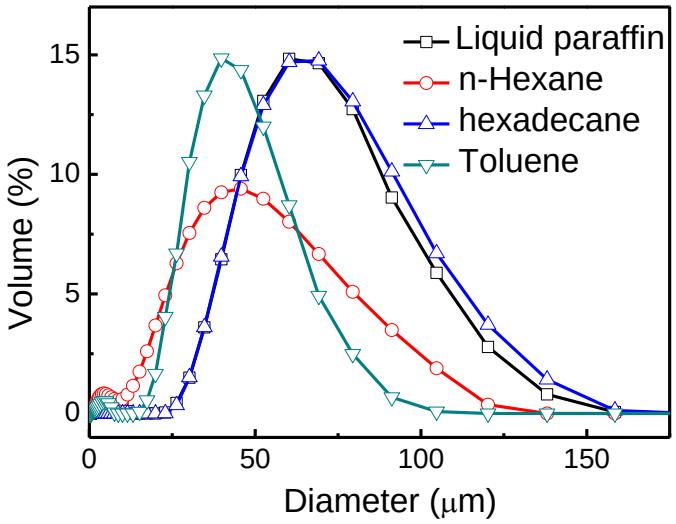

Fig. S5. The size distribution curves of the Pickering emulsions in Fig. S4.

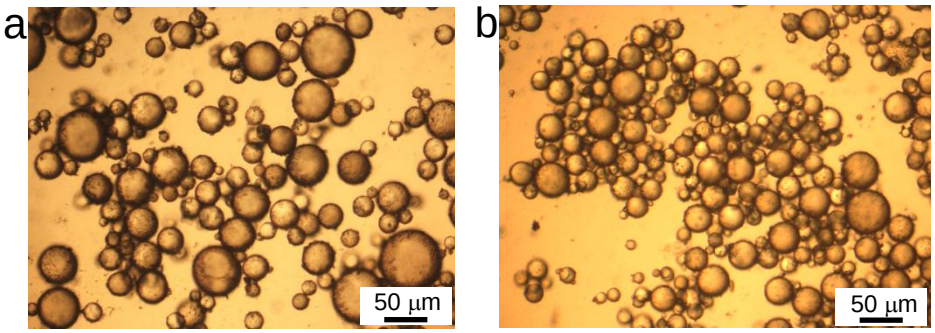

Fig. S6. Optical microscopy images of MoS_2 nanosheet-stabilized styrene/water Pickering emulsion droplets by membrane extrusion after (a) 25 passing times and (b) 50 passing times. The styrene to water ratio is 1:3, and the MoS_2 concentration is 4 mg/mL.