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

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We report an effective method to fabricate MoS_2 armored polystyrene particles with a narrow size distribution based on membrane-assisted Pickering emulsions. These prepared hybrid particles can be served as stabilizers to form monolayer-shelled liquid marbles by rolling water droplets on their powder bed and then a solvent vapor treatment.

One interesting class of nanocomposite (NC) polymer latexes is those with morphologies that are armored or multilayered in nature.[1-3] They are widely applied in various fields such as biomedicine, catalysis, and optics, and are also important for fundamental studies in colloid and interface science.[4-6] The traditional path to produce these complex NC colloids is a layer-by-layer approach, which involves first preparing a core, and subsequent depositing multi-shells.[7-9] Disadvantages of this approach are time-consuming, requires of specifically designed for the coupling shell materials, intermediate purification or separation, and the limitation of large-scale production.[4-9]

Recently, self-assembly of solid particles at the liquid-liquid interface to stabilize so-called Pickering emulsions has been well documented and offers a straightforward pathway for the production of organized nanostructures.[10-14] The solid particles first self-assemble at the liquid-liquid interface and act as effective stabilizers during the polymerization process. By polymerizing the inner monomer phase, the particle stabilizers are captured on the surface of the resultant polymer beads, resulting in the final product with a polymer core with nanoparticles armoring on the core surface.[15-18] Several successful examples were conducted that using Pickering emulsion polymerization to produce armored polymer latexes: Armes et al. described the synthesis of poly(methyl methacrylate)-silica NC particles in aqueous alcoholic media using silica nanoparticles as stabilizer;[19] Bon et al. used clay discs as stabilizer to produce a variety of armored "soft" polymer latexes.[20] However, only particles with suitable surface wettability could be served as Pickering emulsion stabilizers.[21-23] Particles with too hydrophobic or hydrophilic should be preferred to be modified with suitable wettability.[24-28] Moreover, as the conventional preparation of the Pickering emulsion is based on a droplet breakup method by disrupting the large droplets of the pre-emulsion into smaller ones and the obtained emulsion droplets exhibit highly polydisperse which limits their practical applications.[14-22]

MoS_2, as a type of transition metal dichalcogenides, has drawn much attention due to its unusual physical properties, especially for its complementary electronic properties compared to graphene.[29,30] For example, a monolayer of MoS_2 is a semiconductor and shows an intrinsic band gap and high mobility, making it useful for potential applications in sensors, optoelectronics, and electroluminescent devices.[31-33] MoS_2/organic nanocomposites have recently received extensive attention,[34,35] while there are few reports about the research on the fabrication of MoS_2-armored polymer latexes. In this work, MoS_2 was firstly introduced as Pickering stabilizers to stabilize oil-in-water (O/W) emulsions. Under a membrane emulsification process and polymerization of inner phase, MoS_2 armored polymeric particles with a narrow size distribution were obtained. Liquid marbles were then achieved by rolling water droplets on a powder bed of the dried obtained particles. Moreover, MoS_2 hybrid polymeric capsules were prepared from the liquid marble via a solvent vapor treatment.

Monolayer MoS_2 (mo-MoS_2) were produced by a chemically exploitation method, which involved intercalating Li into the bulk MoS_2 and followed by exposing the $LixMoS_2$ to water. AFM measurement revealed mean longest diagonals of 0.7 μm and a thickness of about 0.8 nm, which was consistent with the reported values for monolayer chemically exploited MoS_2 (Fig. S1).[36] The obtained mo-MoS_2 could be homogeneously dispersed in water as its zeta potential value of -31.4 mV (Fig. S2). However, such a large zeta potential value was not beneficial to stabilize oil-in-water emulsion droplets. Because too large mutual repulsion of nanosheets led to an insufficient nanosheet coating on the droplet surface, and it could not provide significant prevention to the droplets from coalescence. To our best knowledge, an electrolyte of $BaCl_2$ was applied for the first time to the MoS_2 aqueous suspension to screen part of the charges to enhance its emulsifying ability.

As shown in **Fig. 1**a, styrene was rapidly emulsified in mo-MoS_2/$BaCl_2$ aqueous mixture to produce O/W Pickering emulsions by shear agitation, with the nanosheet self-assembled at the liquid-

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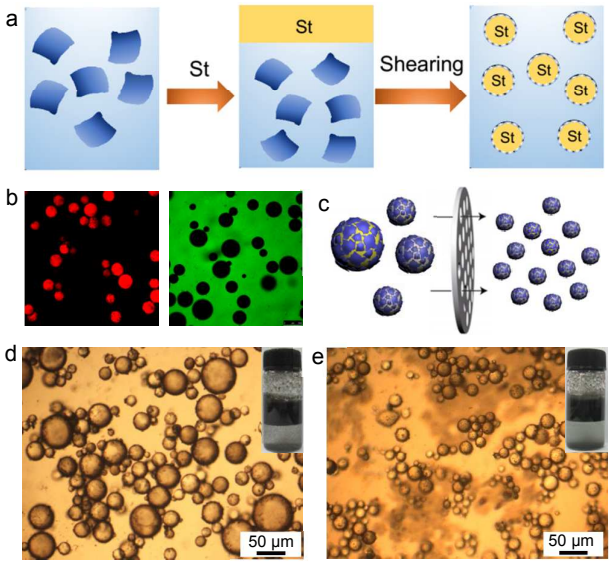

Fig. 1. (a) Schematic of formation of MoS_2 nanosheet-stabilized styrene (St)-in-water Pickering emulsions. (b) Confocal laser scanning microscopy images of the obtained emulsion droplets: Nile red-marked oil phase on the left, and Rhodamine B-stained water phase on the right. (c) Schematic illustration of the membrane-extrusion emulsification processing. The optical microscopy images of the MoS_2 nanosheet-stabilized styrene-in-water emulsions (d) before and (e) after membrane extrusion of 100 passing times. The styrene to water ratio is 1:3, and the MoS_2 concentration is 4 mg/mL.

liquid interfaces. The obtained droplets appeared as a typical Pickering emulsion with spherical shape, and the average size devoted to about 47 μm. With increasing MoS_2 concentration, the size of emulsions would decrease slightly (Fig. S3). By confocal microscope, both markers were imaged in the emulsion droplets (Fig. 1b). Firstly, the styrene phase was labeled with Nile red appearing as red and the water phase appeared as black; then, the water phase was stained with Rhodamine B appearing as green, and the styrene phase appeared as black. It revealed that the water phase acted as the continuous phase with styrene being the disperse phase, demonstrating an O/W Pickering emulsion system.

In practical applications, MoS_2 armored particles with different core components are needed under varied situations. Therefore, besides styrene, various kinds of organic solvents, including liquid paraffin, toluene, n-hexane, and hexadecane, were applied as oil phases to exam the generalizability of the MoS_2 nanosheet-stabilized O/W Pickering emulsion system (Fig. S4). It was revealed that most of the water-insoluble liquids could be successfully emulsified by this surfactant-free system. The obtained emulsions exhibited as traditional Pickering types, whilst their sizes and size distributions varied with their different density, viscosity, and surface tension (Fig. S5). Moreover, increasing the nanosheet concentration decreased the mean droplet diameter, until a plateau at ca. 50 μm was reached. Higher nanosheet concentrations did not led to any further reduction in droplet size, but merely to excess latex nanosheets in solution. This observation was consistent with those reported previously.[14-17]

Even though the sizes of the obtained emulsion droplets could be tuned by adjusting the nanosheet concentrations, they exhibited fairly polydisperse. It was described to the conventional pre-emulsion/droplet breakup method which could not easily control the mean droplet sizes.[21-24] In order to obtain particles with a narrow size distribution to satisfy the practical requirements, many microengineering techniques, such as microchannel emulsification based microfluidic devices and membrane emulsification by Shirasu porous glass membranes,[37-39] have been developed to further treatment of the Pickering emulsions. However, the requirement of complex devices brings barriers when applying for practical productions. Recently, Zhu et al. utilized membrane-extrusion emulsification-assisted approach to generate microcapsules with uniform sizes.[40] Inspired by that, the MoS_2 nanosheet-stabilized O/W Pickering pre-emulsions were re-emulsified by a hand-driven mini-extruder containing two syringes (Fig. 1c). The poly(vinylidene fluoride) filtering membrane used in this study consisted opening pores of 7.5 μm in diameter. As shown in Fig. 1d, the sizes of emulsion droplets fabricated by shear agitation are large and polydisperse, ranging from 20 to 120 μm with an average diameter of 50 μm. It was clear to see that the droplet sizes were significantly reduced and the size distribution became much narrower after the extrusion process (Fig. 1e and Fig. S6).

Moreover, the droplet sizes and size distributions were found to strongly depend on the number of passes through the membrane. As shown in **Fig. 2**a,b, with the increasing of the passing times, the average sizes of the obtained droplets decreased from 47 to 25 μm. More importantly, the polydispersity index (PDI) significantly decreased from o.199 to 0.078 over 100 passing times, resulting in relatively uniform emulsion droplets (Fig. 2b). It is almost able to comparable to the value of the uniform particles.[41]

By polymerization the styrene phase, MoS_2 armored polystyrene (PS) particles were achieved (Figure 2c,d). Compared with the surfactant-stabilized emulsion polymerization, the nanoparticle-stabilized Pickering emulsion polymerization could be classified as a type of suspension polymerization without any stirring saving much energy. Moreover, the adhesion between the neighboring particles could be avoided as the MoS_2 nanosheets absorbed at the oil-water

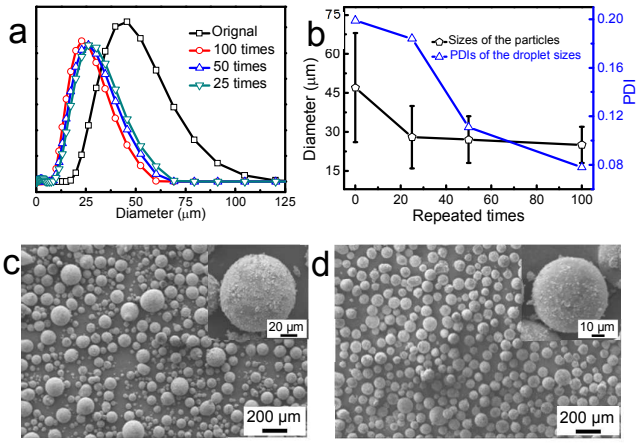

Fig. 2. (a) Size distribution curves of MoS_2 nanosheet-stabilized styrene-in-water emulsions after different membrane extrusion passing times. (b) The average size and PDI of the emulsions from (a). SEM images of the MoS_2 armored PS particles fabricated based on emulsions (c) before and (d) after membrane extrusion of 100 passing times. The insets of (c,d) are the corresponding amplifying images of the particles.

interfaces being the physical barriers. As shown in Fig. 2d, the MoS_2 armored PS particles were spherical and size monodisperse and the surface was rough. EDS test revealed that there was about 3 wt% of MoS_2 in the obtained hybrid particles (Table S1). Such uniform particles which consisted of a MoS_2 coating on the surface and polymeric cores could be found great potentials in sensors, transistors, optoelectronics, and many other fields.

Liquid marbles are liquid droplets with liquid-repellent particles irreversibly adsorbed at liquid-air interfaces that decreases the apparent surface tension of the liquid, and maintains their spherical shape.[42,43] Because of their unique surface properties, the liquid marbles move smoothly over any substrate without leakage, having been exploited in a wide range of applications ranging from, but no limited to, cosmetics, micropumps, water surface pollution detection, gas storage, gas-liquid reactions, and preparation of microreactors.[44] In this work, the obtained MoS_2 armored PS particles were applied to stabilize liquid marbles, producing capsules with MoS_2/PS hybrid shells (**Fig. 3**a). Firstly, a water droplet was rolled on a powder bed of monodisperse particles, and the latex particles immediately coated the water droplet. These liquid marbles remained intact after transfer onto a polypropylene mesh (Fig. 3b). However, the stability of the obtained liquid marbles remained challenges in the practical applications, and a solvent vapor treatment was applied to enhance the marble mechanical strength. The liquid marble-contained polypropylene mesh was placed on an M-shaped rigid aluminum foil, which was placed in a closed glass bottle containing 2 mL of toluene. After 20 seconds, the liquid marbles were taken out and MoS_2/PS hybrid walled capsules were obtained. The hybrid particles adhesive each other by swelling to form a polymer film, which could largely enhance the obtained liquid marbles' stabilities. Interestingly, unlike the previous liquid marbles,[45-53] the liquid marbles obtained in this work consisted of a monolayer shell, which could be identified in Fig. 3c. It could be ascribed to the fact that the liquid marble stabilizers were particles with a narrow size distribution, and these relatively uniform stabilizers resulted in a two-dimensional close packing on the surface of the water droplet without any space for the other layer particles adsorbed at the water-air interfaces.

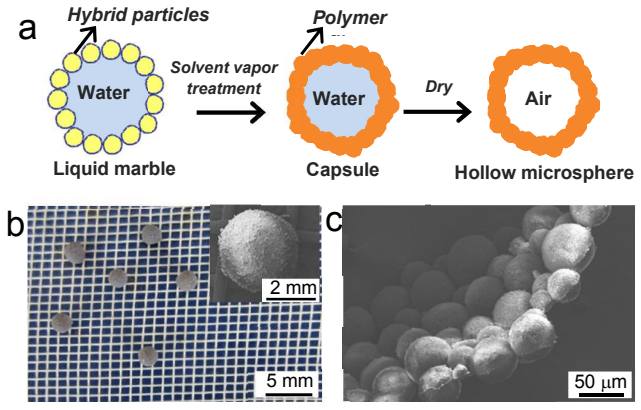

Fig. 3. (a) Fabrication of the monolayer-shelled liquid marbles via a rolling and solvent vapor treatment. (b) Digital photograph of the obtained liquid marbles. The inset of (b) is the SEM image of the obtained liquid marble. (c) SEM image of the monolayer shell of the obtained liquid marbles

In conclusion, we demonstrated, for the first time, the chemical exploited MoS_2 could be served as solid surfactant for producing O/W Pickering emulsion without any molecule surfactants. Followed by a membrane-extrusion process and suspension polymerization, MoS_2 armored PS particles with a narrow size distribution were successfully achieved. Furthermore, these hybrid particles could be served as stabilizers to form liquid marbles by rolling water droplets on a powder bed of the particles and followed by a solvent vapor treatment. It was demonstrated that the obtained liquid marbles exhibited good mechanical strength and consisted of a monolayer MoS_2/PS hybrid shell, having great potential applications in microcapsulation and surface chemistry.

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