

# Fabrication of covalently-bonded polystyrene/SiO<sub>2</sub> composites by Pickering emulsion polymerization

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**Abstract** Pickering emulsion polymerization has attracted considerable attention in material fabrication due to its unique surfactant-free character and versatile association of oil, water and particles for a large set of materials. In this study, SiO<sub>2</sub> modified with Methacryloxypropyltrimethoxysilane (MPTMS) was employed to prepare Pickering emulsion, and subsequently covalently-bonded polystyrene/SiO<sub>2</sub>(PS/SiO<sub>2</sub>) composites were synthesized by Oil-in-water Pickering emulsion polymerization. Optical micrograph, contact angle, thermogravimetric analysis (TGA), Fourier transform infrared spectra (FT-IR), scanning electron microscope (SEM) and dynamic laser scattering (DLS) were employed to characterize the modified SiO<sub>2</sub>, Pickering emulsion and prepared composites. It was found that prepared composites possess ragged surface morphology and SiO<sub>2</sub> concentration has an important effect on the morphology of as-prepared composites. In addition, covalent bond between PS core and SiO<sub>2</sub> shell was evidenced by FT-IR.

**Keywords** Pickering emulsion · Hybrid composites · Surfactant-free polymerization

## Introduction

Emulsion polymerization possesses distinguished advantages such as facilitate controlling and high degree of polymerization. Surface-active agent, typically as surfactant

with low molar mass, is essential in emulsion to stabilize droplet from coalescence. However, it has been recognized that recycling the surfactant after polymerization is rather tedious and the surfactant has negative effect on the products and potential crisis to the environment.

Besides surfactants, colloidal particles can also be used to protect droplets from coalescence and stabilize Pickering emulsion, as summarized systematically by Robert Aveyard in 2003 [1]. Subsequently extensive interests and studies have been focused on it due to its surfactant-free character [2–6]. Using solid particles, conventional emulsifying agents can be reduced and hazardous surfactants may be replaced by less harmful materials. In some cases, organic emulsifying agents can even be completely avoided. This is the dominant reason that Pickering emulsion is of growing interest in food engineering [7, 8] and pharmaceutical fields [9, 10].

Recently, arising interesting and efforts have been focused on fabrication of materials by Pickering emulsion. It have demonstrated theoretically and experimentally that Pickering emulsion polymerization is a feasible way for the preparation of organic (core)-inorganic (shell) hybrid composites. In Pickering emulsion, solid particles anchor irreversibly on the surface of droplet. After polymerization, solid particles form a spherical inorganic shell while polymerizable monomer droplet forms an organic core. The versatile association of monomer droplet, water and solid particles in Pickering emulsion allows a large set of composites to be prepared, e.g. polyaniline(PANI)/CeO<sub>2</sub> [11], PANI/SiO<sub>2</sub> [12], PANI/ Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub> [13], polystyrene(PS)/ZnO [14], poly(vinyl acetate)/SiO<sub>2</sub> [15]. However, no strong covalent bond exists between the inorganic shell and organic core of the obtained composites, because solid particles employed in the literatures are inert in chemical reaction, i.e., have no polymerizable groups on their surfaces.

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Herein, nano-SiO<sub>2</sub> particles modified by methacryloxypropyltrimethoxysilane (MPTMS) were employed to prepare Pickering emulsion, followed by radical polymerization initiated by Azobisisobutyronitrile (AIBN) to fabricate PS/SiO<sub>2</sub> hybrid composites. By variety of MPTMS amount, wettability of SiO<sub>2</sub> particles was tuned significantly. Furthermore, SiO<sub>2</sub> particles were functionalized with reactive C = C groups which can copolymerize with styrene during polymerization. As a result, the interaction between SiO<sub>2</sub> shell and PS core was enhanced.

## Experimental

### Materials

Nano-SiO<sub>2</sub> particles with an average diameter of 20 nm were provided by GuangzhouYixin New Material Co. (Guangzhou, China). MPTMS and AIBN were obtained from Beijing Chemical Reagent Co.LTD (Beijing, China). Styrene was supplied by Shanghai Shanpu Chemical Reagent Co. (Shanghai, China). 10% NaOH solution was used to eliminate inhibitor in styrene, followed by rinse with distilled water to pH 5.0. Other reagents are analytical grade and used as received.

### Modification of SiO<sub>2</sub> particles

The modification of SiO<sub>2</sub> was carried out in ethanol/water media based on the hydrolysis/condensation between Si-OH of SiO<sub>2</sub> surface and hydrolyzed MPTMS. In a typical procedure, 3 g of SiO<sub>2</sub> particles was added to 100 mL of ethanol/ammonia (1 M) mixture (3/1, *V/V*) and dispersed using a Nankun 250-SW ultrasonic processor (Kunshan Experimental Instrument, China) for 15 min. A definite amount of MPTMS was added into the suspension under vigorous magnetic agitation and reacted at room temperature under moderate agitation for 8 h or 24 h. After reaction, the suspension was centrifuged at 6,000 rpm and the collected SiO<sub>2</sub> particles were washed by dispersion into ethanol and centrifugation for three times. Finally, the SiO<sub>2</sub> particles were ultrasonically dispersed in distilled water.

### Preparation of PS/SiO<sub>2</sub> composites by Pickering emulsion polymerization

PS/SiO<sub>2</sub> composites were synthesized by Pickering emulsion polymerization initiated by AIBN. A typical preparation procedure is detailed as follows: 1.0 wt% of AIBN was dissolved in styrene to form oil phase, and subsequently the oil phase was mixed with the SiO<sub>2</sub> suspension described above. A stable Pickering emulsion was generated by

means of an Ultrasonic processor (Kunshan,China) for 5 min. The emulsion obtained was subsequently discharged into a reactor to conduct polymerization under mildly stirring (30 rpm) at 55 °C for 4 h and 65 °C for another 4 h. The obtained PS/SiO<sub>2</sub> composites were filtrated and washed with water and ethanol respectively, followed by dried in vacuum at 45 °C.

### Characterization

The type of Pickering emulsion was inferred by observing what happened when a drop of emulsion was added into pure water or styrene. Styrene-in-water emulsions were dispersed in water and remained as drops in styrene, while water-in-styrene emulsions were dispersed in styrene and remained as drops in water [16]. The contact angle of particles was determined by a JY-82 contact angle goniometer (Chengde, China). Optical micrographs were obtained using a DMM-330C microscope (CAIKON, Shanghai) equipped with a high speed digital camera and a super scale-demarcation software. TGA analysis was carried out with a HTG-1/2 thermogravimetric analyzer (HenJiu, China). SEM images were collected by a Hitachi S-2700 electron microscopy (Hitachi, Japan). FTIR spectra were obtained using a BRUKER Tensor27 FTIR spectrometer (Bruker, Germany). The diameter of the composites were detected using a LS13321 Laser Diffraction Particle Size Analyzer (Berckman, USA).

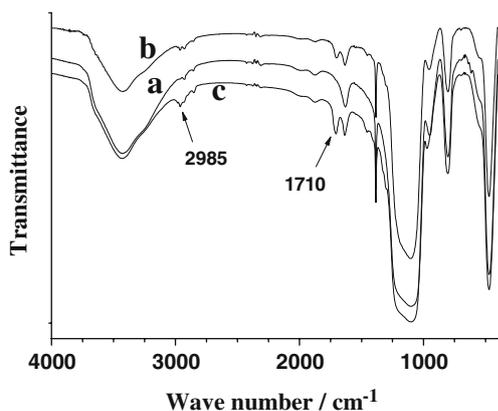
## Results and discuss

### Distribution of SiO<sub>2</sub> particles on Styrene/water interface

By variety of amount of MPTMS and modification time, SiO<sub>2</sub> particles modified with different wettability were prepared, denoted as Si-10a (MPTMS employed equal to 10 wt% of SiO<sub>2</sub> amount and the modification lasted for 8 h),



**Fig. 1** Distribution in dual-phase system of SiO<sub>2</sub> particles. The SiO<sub>2</sub> used from left to right are original SiO<sub>2</sub>, Si-10a, Si-10b, Si-15 and Si-30 respectively

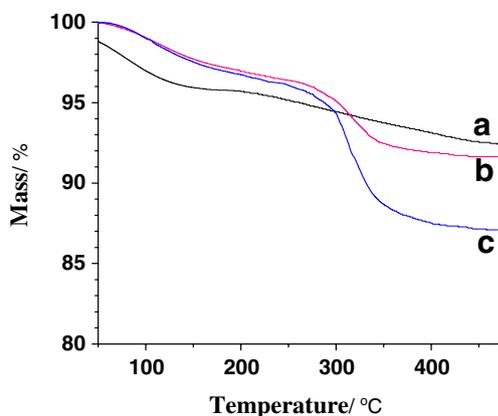


**Fig. 2** FT-IR Spectra of original SiO<sub>2</sub> (a), Si-10b (b) and Si-30 (c)

Si-10b (10%, 24 h), Si-15 (15%, 24 h) and Si-30 (30%, 24 h).

The adsorption of colloidal particles at oil/water interface is a crucial factor for preparing stable Pickering emulsions [3, 17]. In order to probe into the wettability of the particles, their behavior when they are suspended in a styrene/water dual-phase mixture was observed. Three drops of SiO<sub>2</sub> suspension were dropped into styrene/water mixture, followed by violent shaking and settling undisturbed. Particles with different modified procedures present different behavior as shown in Fig. 1. Original silica particles disperse only in water due to hydrophilic Si-OH groups on their surface, while Si-30 particles disperse preferentially in styrene due to their hydrophobicity caused by modified MPTMS. Particles with middle degree of modification (Si-10a, Si-10b and Si-15) assemble spontaneously at the water-styrene interface.

The difference of distribution behavior is originated from the difference of MPTMS amount on the particle surface, as evidenced straightly by FTIR spectra in Fig. 2 and TGA in Fig. 3. In FTIR spectra, besides the characteristic bands of

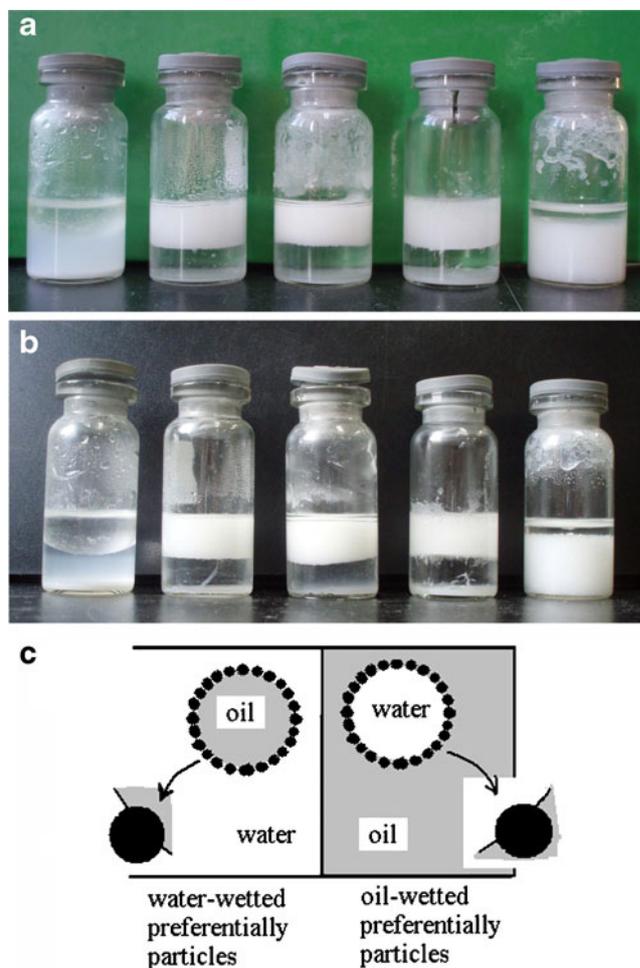


**Fig. 3** TGA curves of (a) original SiO<sub>2</sub>, (b) Si-10b, (c) Si-30

**Table 1** Contact angle of modified SiO<sub>2</sub> particles

Sample	Water contact angle	Oil contact angle	Type of emulsion
Original SiO <sub>2</sub>	0	53	No emulsion
Si-10a	No analysis	No analysis	O/W
Si-10b	35	27	O/W
Si-15	42	15	O/W
Si-30	75	10	W/O

SiO<sub>2</sub> at 3,549 cm<sup>-1</sup> (-OH stretching), 1,106 cm<sup>-1</sup> (Si-O stretching) and 476 cm<sup>-1</sup> (Si-O bending vibration), the modified SiO<sub>2</sub> present characteristic bands of MPTMS at 2,985 cm<sup>-1</sup> (C-H stretching) and 1,710 cm<sup>-1</sup> (C = O



**Fig. 4** Pickering emulsion stabilized by SiO<sub>2</sub>. **a** Digital photograph of emulsion 2 h after preparation. **b** Digital photograph of emulsion one month after preparation. **c** Formation mechanism of O/W and W/O emulsion. SiO<sub>2</sub> used and emulsion type from left to right are original SiO<sub>2</sub> (no emulsion), Si-10a (O/W), Si-10b (O/W), Si-15 (O/W) and Si-30 (W/O), respectively. Oil volume fraction was 0.5 and SiO<sub>2</sub> concentration in SiO<sub>2</sub> suspension was 2.0 wt%

stretching), which indicates that reactive MPTMS molecules have bonded to the surface of SiO<sub>2</sub> particles. In Fig. 3, the weight loss observed between 50 °C and 150 °C is attributed to the elimination of adsorbed water. The weight loss of 3.8% (Fig. 3, b) and 7.7% (Fig. 3, c) from 300 °C to 350 °C is assigned to the decomposition of MPTMS. It can be inferred that the grafted ratio of added MPTMS was approximately 51.6% and 34.9% for Si-10b and Si-30, respectively.

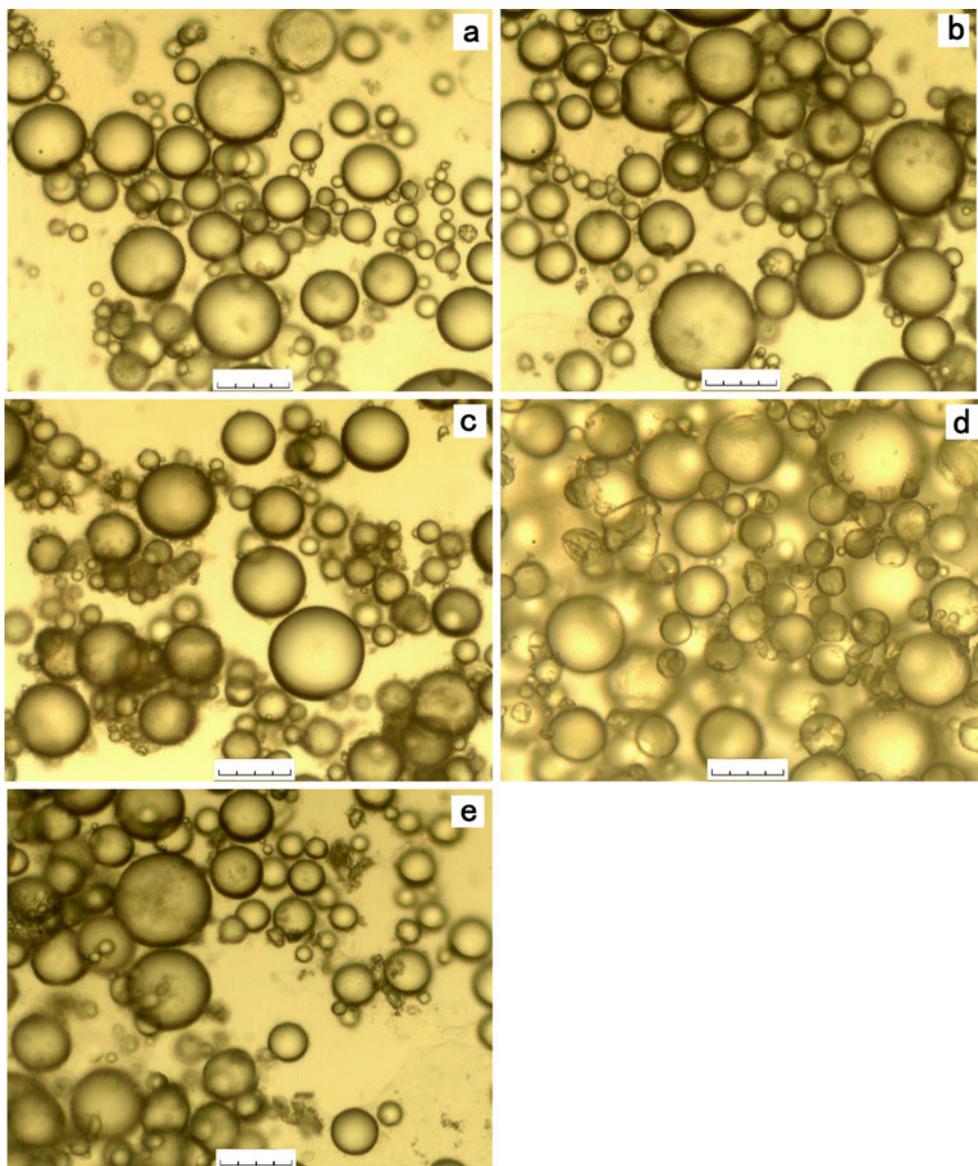
#### Formation of Pickering emulsion

It is well established that the effective stabilization of Pickering emulsion is originated from a dense monolayer or multiplayer film formed by particles adsorbed irreversibly

on the interface [17–20]. Many factors, such as character of particles, ratio of phases, pH value and particle concentration, have effect on stabilizing efficiency of particles. In case of spherical particle, the crucial parameter is its contact angle  $\theta$  which indicates the wettability or hydrophilic-hydrophobic balance of the particle [7, 17, 21]. It has been empirically proved that the phase that preferentially wets the particles becomes the continuous phase of Pickering emulsion.

In this paper, contact angle of SiO<sub>2</sub> particle was determined directly by a contact angle goniometer using water (denoted as  $\theta_{aq}$ ) and 1-dodecanol (denoted as  $\theta_{oil}$ ) respectively. 2  $\mu$ L of water or 1-dodecanol (heated to 40 °C) was putted on a SiO<sub>2</sub> flake obtained by 30 Mpa compressor. The results were shown in Table 1. As the

**Fig. 5** Optical micrographs of droplets stabilized by **a** Si-10a, O/W, **b** Si-10b, O/W, **c** Si-15, O/W, **d** Si-30, W/O, **e** Si-10b 1 month after preparation. The scale bars correspond to 50  $\mu$ m



increase of MPTMS amount,  $\theta_{aq}$  increases while  $\theta_{oil}$  decreases. The results confirmed that the wettability of nano-SiO<sub>2</sub> particles was tuned significantly by modification of MPTMS. It is worthy noting that relative value of  $\theta_{aq}$  and  $\theta_{oil}$  is unqualified to evaluate the hydrophilic or hydrophobic character, because the method employed to detect  $\theta$  is a relative method and the surface tension of water (72.8 mN/m) is much larger than that of 1-dodecanol (26.9 mN/m) [22].

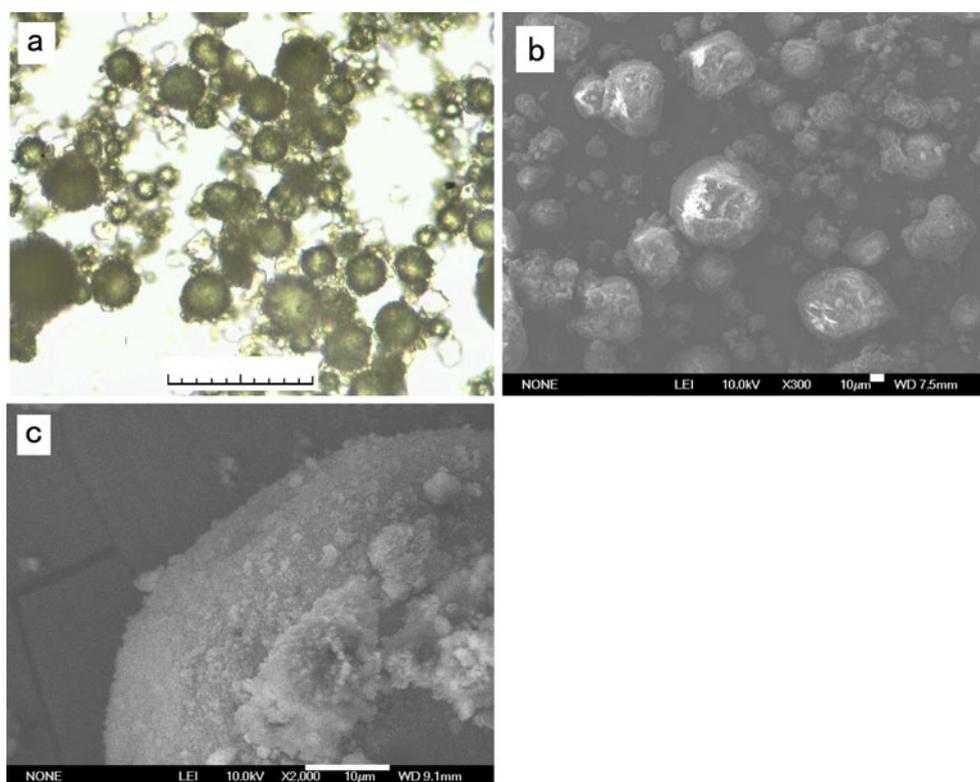
Using different SiO<sub>2</sub> particles, O/W type and W/O type emulsions were prepared as shown in Fig. 4a. No emulsion formed when original SiO<sub>2</sub> employed as stabilizing particles due to its high hydrophilicity. W/O type emulsion formed when Si-30 was used because Si-30 particles are wetted preferentially by styrene while O/W type emulsions obtained when Si-10a, Si-10b and Si-15 was used individually. The formation mechanism of Pickering emulsion was illustrated in Fig. 4c. When water-wetted preferentially particles were used, a larger region of particle immerses in water and the curve line deflects alongside styrene droplets. As a result, O/W emulsion forms. When oil-wetted preferentially particles were used, the curve line deflects alongside water droplets and W/O emulsion forms. The emulsion cream quickly after preparation because the droplets are so big as to 20~50  $\mu\text{m}$  (see Fig. 5 below) and density of styrene is much lower than that of water.

The morphology of droplets was examined by optical microscopy with a high performance digital camera. The diameter of droplets was demarcated by a scale-mark software. The droplets of both O/W and W/O emulsions are spherical with similar size distribution from 20 to 50  $\mu\text{m}$  (Fig. 5). However, the droplets present different clustering character. Droplets stabilized by Si-10a is well dispersed (Fig. 5a), while most of the droplets stabilized by Si-15 (Fig. 5c) cluster together in a disordered fashion. All emulsions are very stable to coalescence and Ostward ripening. Even one month after preparation, the appearance and droplet size have no appreciable change as shown in contrast by Fig. 4a to Fig. 4b and Fig. 5b to Fig. 5e), respectively.

#### Morphology of polystyrene/SiO<sub>2</sub> composites

In this study, O/W emulsion was employed to prepare PS/SiO<sub>2</sub> composites by radical polymerization initiated by oil-soluble AIBN. The suspension obtained after polymerization was diluted and dropped onto a glass slide, followed by volatilizing to dry and being characterized by optical microscope. The optical micrograph of composites using 2.0 wt% of Si-10b as stabilizer was shown in Fig. 6a. The composites are spherical with the diameter of 20~50  $\mu\text{m}$ , which is consistent with the droplet template. SEM micrograph in Fig. 6b and c indicates that the composites

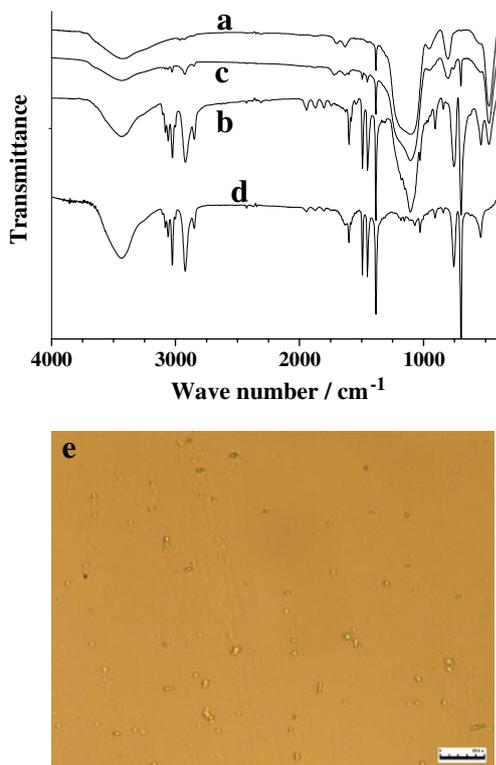
**Fig. 6** PS/SiO<sub>2</sub> composites obtained by O/W Pickering emulsion polymerization. **a** Optical micrograph with scale bar of 100  $\mu\text{m}$ . **b** SEM micrograph with scale bar of 10  $\mu\text{m}$ . **c** SEM micrograph with scale bar of 10  $\mu\text{m}$



have rugged surface. This morphology may be attributed to two mechanisms. Firstly, SiO<sub>2</sub> aggregations form during polymerization and locate on the surface. Secondly, PS particles formed by secondary nuclei assemble on the surface of composites. Although most of hydrophobic AIBN decomposes and initiates polymerization inside the droplets, a small amount of decomposed initiator diffuses into the aqueous phase because of its slight solubility in water, and initiates the monomer dissolved in aqueous phase [23]. After the oligomer reaches a critical length, it no longer dissolves in water, but precipitates to form secondary nuclei. SiO<sub>2</sub> particles are too large in quantity to move as free as low molecular surfactant employed in traditional emulsion, so the secondary nuclei cannot enter the droplet as freely as those in traditional emulsion polymerization. The secondary nuclei absorb monomer and polymerize on the droplet surface, resulting in the formation of micron-sized PS particle on the surface of prepared composites.

#### FTIR spectra of prepared composites

In order to verify that chemical bonds exist between PS core and SiO<sub>2</sub> shell, FTIR spectra were employed. The



**Fig. 7** FTIR spectra of (a) Si-10b, (b) PS/SiO<sub>2</sub> composites, (c) precipitated SiO<sub>2</sub> separated from composites, (d) PS separated from composites and optical micrograph of SiO<sub>2</sub> separated from composites with scale bar of 10 μm (e)

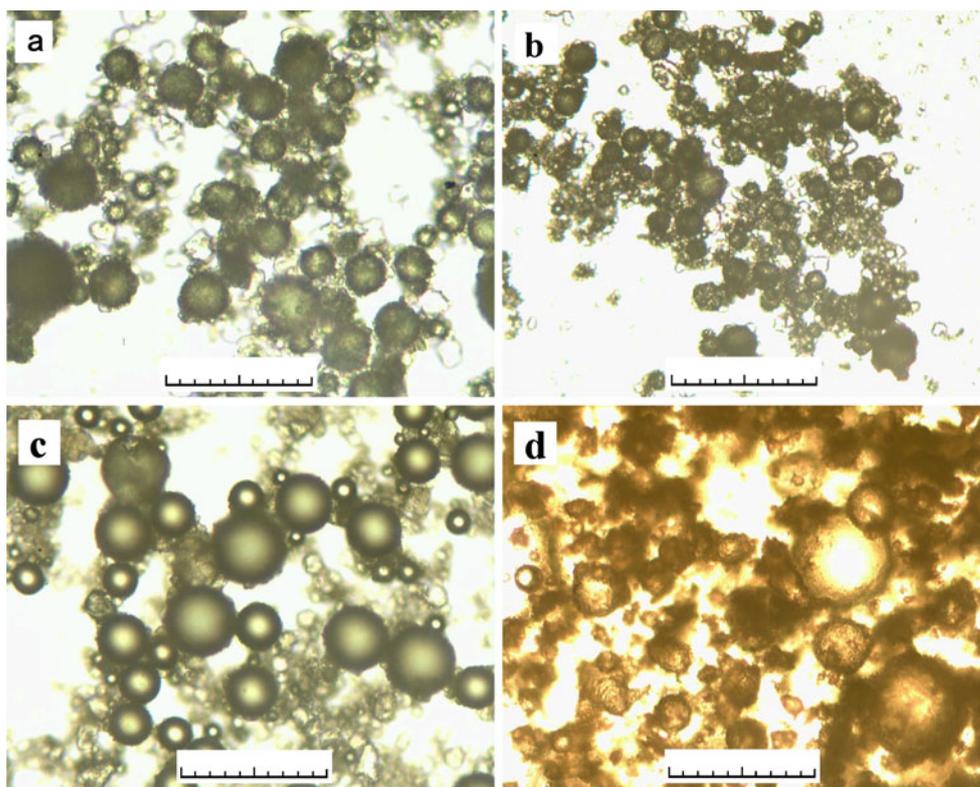
composites were dissolved in toluene, followed by centrifugation to separate SiO<sub>2</sub> precipitation and PS solution. The PS solution was diluted into ethanol to precipitate PS and the precipitation SiO<sub>2</sub> was redispensed in toluene and separated by centrifugation twice to remove residual PS. FTIR spectra of Si-10b, PS/SiO<sub>2</sub> composites, PS and SiO<sub>2</sub> separated from composites were shown in Fig. 7. No particle larger than 1 μm presents in the optical micrograph of precipitated SiO<sub>2</sub> (shown in Fig. 7, e), from which we can infer that all composites were destroyed by toluene and PS ungrafted on SiO<sub>2</sub> was removed entirely from the precipitation SiO<sub>2</sub>. Both the characteristic bands of SiO<sub>2</sub> (3,549, 1,106 and 476 cm<sup>-1</sup>) and polystyrene (1,650~1,400, 760 and 693 cm<sup>-1</sup>) present in spectrum of composite (Fig. 7, b), verifying that PS/SiO<sub>2</sub> composites were successfully synthesized. Furthermore, the characteristic bands of PS also present in the spectrum of precipitated SiO<sub>2</sub> (Fig. 7, c), from which it can be inferred that the C = C bands on SiO<sub>2</sub> particle surface have polymerized with styrene, thus PS core and SiO<sub>2</sub> shell were covalently bonded in the prepared composites.

#### Effect of SiO<sub>2</sub> concentration on polymerization

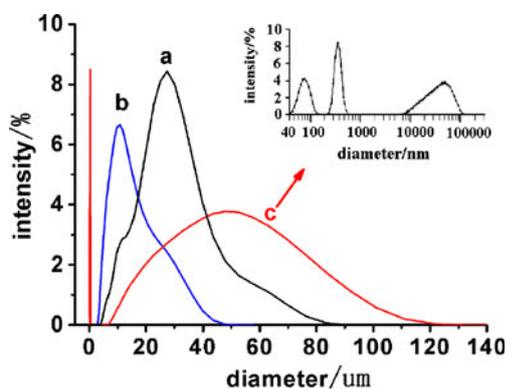
It has been verified that particle concentration has an important effect on the properties of Pickering emulsion. In this work, the effect of SiO<sub>2</sub> concentration on polymerization and morphologies of PS/SiO<sub>2</sub> composites were studied. After polymerization, the appearance of emulsion changed from cream to suspension of individual composites in case of SiO<sub>2</sub> concentration as 4% and 2% or conglomerating blocks in case of SiO<sub>2</sub> concentration as 1% and 0.5%. Figure 8 shows the morphologies of composites prepared with different concentration of Si-10b. The difference of result originates from the difference of particle coverage, defined as the percent of droplet surface covered by particles. Large amount of stabilizing particles results in a denser layer to protect droplets against coalescence and high stability during polymerization. Consequently, individual composites form when SiO<sub>2</sub> concentration is larger than 2.0%. When SiO<sub>2</sub> concentration is 1.0%, the stability of emulsion decline during polymerization and some SiO<sub>2</sub> particles detach away from the droplet surface to the continuous phase, which results in the formation of SiO<sub>2</sub> aggregation as shown in Fig. 8c. When SiO<sub>2</sub> concentration is 0.5%, the emulsion changed to conglomerating blocks containing aggregated SiO<sub>2</sub> and composites.

The average diameter of emulsion droplets increases as the particle concentration decreases [24, 25]. In this study, size distribution of prepared composites at different SiO<sub>2</sub> concentration was illustrated in Fig. 9. The average diameter of composites obtained at SiO<sub>2</sub> concentration of

**Fig. 8** Optical micrographs of PS/SiO<sub>2</sub> composites obtained from emulsion stabilized by different concentration of Si-10b. **a** 2.0%, **b** 4.0%, **c** 1.0%, **d** 0.5%. The scale bars correspond to 100  $\mu\text{m}$



4%, 2% and 1.0% was 13.6  $\mu\text{m}$ , 26.4  $\mu\text{m}$  and 48.1  $\mu\text{m}$ , respectively. Especially, size distribution of composites obtained at SiO<sub>2</sub> concentration of 1.0% is shown exponentially in the inset graph in Fig. 9. Three kinds of different particle with average diameter of 70 nm, 420 nm and 48.1  $\mu\text{m}$  may be corresponded to original Si-10b particles, aggregations of Si-10b particles and composites respectively. This is consistent with the optical micrographs as shown in Fig. 8c.



**Fig. 9** Size distribution of PS/SiO<sub>2</sub> composites obtained from emulsion stabilized by different concentration of Si-10b. (a) 2.0% (average diameter 26.4  $\mu\text{m}$ ), (b) 4.0% (average diameter 13.6  $\mu\text{m}$ ), (c) 1.0% (average diameter 48.1  $\mu\text{m}$ , three peaks were illustrated as inset graph)

## Conclusions

We have modified SiO<sub>2</sub> with MPTMS to change its surface wettability. By modification, the wettability of particles can be tuned significantly, hence, the modified SiO<sub>2</sub> particles can assemble spontaneously on the oil/water interface and can be used to stabilize Pickering emulsion.

By Pickering emulsion polymerization, covalently-bonded PS/SiO<sub>2</sub> composites were successfully synthesized in a surfactant-free emulsion system. Low molecular surfactant was replaced completely by organically modified SiO<sub>2</sub> particles. SiO<sub>2</sub> concentration has an important effect on the polymerization and morphology of composites. Individual composites formed when SiO<sub>2</sub> concentration in suspension is above 2.0 wt%, while conglutinated block obtained when SiO<sub>2</sub> concentration in suspension is below 1.0 wt%. By grafting reactive C = C group on the particles, covalent bonds formed between stabilizing particles and polymer core. The research puts forward a simple and robust way to fabricate other inorganic-organic hybrid composites based on covalent bonds.

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