



Styrene-in-Water Emulsions Stabilized Solely by SiO₂ Nanoparticles with Tunable Wettability

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Hydrophilic SiO₂ nanoparticles were modified by ethacryloxypropyltrimethoxysilane (MPTMS). The surface wettability was tuned by controlling the grafting extent of MPTMS and the surface element content was confirmed by XPS. Through measuring the contact angle, the surface wettability was investigated. The results showed that when the mass ratio of MPTMS to SiO₂ was 5 %, the contact angle was about 85° and the SiO₂ nanoparticles could be partly wetted by both phases. The modified SiO₂ nanoparticles were applied to stabilize styrene-in-water Pickering emulsion. The effect of surface wettability, particles concentrations on the stability and morphology of the Pickering emulsions was systematically studied. It was found that only SiO₂ nanoparticles partly wetted by both phases were suitable to form Pickering emulsion and stable emulsion could not be obtained until the SiO₂ nanoparticles concentrations were above 2 %.

Key Words: SiO₂ nanoparticles, Pickering emulsions, Surface wettability.

INTRODUCTION

About a century ago, Pickering discovered that colloidal particles could stabilize emulsions instead of conventional emulsifiers¹. The emulsions stabilized by colloidal particles, so called Pickering emulsions had aroused intensively interest in recent years because of its advantages over conventional emulsions²⁻⁵. In Pickering emulsion, solid particles were adsorbed at the oil-water interface and impede the coalescence when two droplets approach each other⁶. Due to the nearly irreversible adsorption of the particles at the interface, Pickering emulsions were often super-stable with shelf life stability of months or even years⁷ and it was generally difficult to break a Pickering emulsion by changing the surrounding chemical or physical parameters, such as the pH value of the aqueous phase, temperature and the composition of the oil phase⁸. These characteristics made Pickering emulsions attractive in many field such as the pharmaceutical, food and petroleum industries⁹⁻¹².

Various kinds of solid particles have been applied to stabilize Pickering emulsion, such as clay¹³, ZnO¹⁴, TiO₂¹⁵, carbon black¹⁶, etc. The most popular stabilizing particles were SiO₂ micro- or nanoparticles, because SiO₂ particles had high surface activity and could be functionalized to form a functional shell on the core-shell structured composites. According to the pioneering work of Binks and coworkers^{17,18}, a crucial factor to provide stabilization for a Pickering emulsion was that the stabilizing solid particles need to be partly wetted by

both phases. But the commonly used SiO₂ particles were hydrophilic, due to the abundant silanol-groups on the surface, so the SiO₂ particles used to stabilize Pickering emulsions need to be modified first. Such modification of SiO₂ particles was usually processed by grafting non-polar organic groups on the surface¹⁹⁻²³. In this paper, SiO₂ nanoparticles with tunable surface wettability were fabricated by grafting MPTMS *via* sol-gel reaction (Fig. 1). The partial wetting conditions by oil and water of the SiO₂ nanoparticles was tuned by controlling the extent of grafting to the surface. Subsequently the modified SiO₂ nanoparticles were applied to stabilize styrene-in-water Pickering emulsion. The effect of partial wettability, partial concentrations on the stability and morphology of the Pickering emulsions was systematically studied and the optimum conditions for the stabilization of the Pickering emulsion was ensured too.

EXPERIMENTAL

Tetraethoxysilane (TEOS), methanol, ethanol, isopropanol and styrene (St) were obtained from Sinopharm Chemical Reagent Co.,Ltd (China). Ethacryloxypropyltrimethoxysilane (MPTMS) was purchased from Tianjing Damao Chemical Reagent Co. Ltd. (China). All the reagents used were analytical grade and used as received. Deionized water was used throughout the work.

Preparation and modification of silica nanoparticles: SiO₂ nanoparticles were fabricated through the hydrolysis and

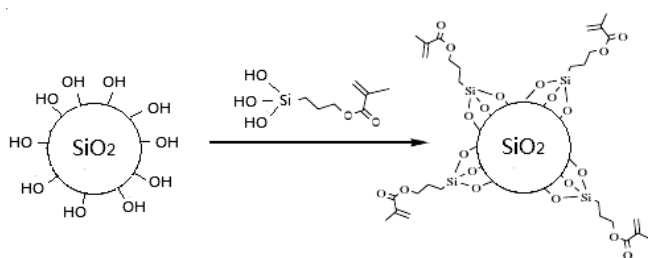


Fig. 1. Surface-configuration of SiO₂ nanoparticles modified by MPTMS

condensation of tetraethoxysilane. A typical preparation procedure was detailed as follows: 60 mL methanol, 8 mL water and 7.5 mL ammonium hydroxide (NH₃ 25 %) were mixed together to form a solution. 20 mL tetraethoxysilane and 60 mL methanol were also mixed together. Subsequently, two solutions were rapidly mixed and stirred for 8 h at 40 °C. Then the mixture of a definite amount of MPTMS and 10 mL methanol was added dropwise into the reactor to modify the SiO₂ nanoparticles. The modification lasted for 24 h and the recipe was shown as Table-1. The white turbid suspension obtained was centrifuged to separate the SiO₂ nanoparticles and the collection was washed with water and ethanol, respectively. After being dried at 50 °C for 24 h, MPTMS modified SiO₂ nanoparticles were obtained.

TABLE-1

RECIPE AND ZETA POTENTIAL OF SiO₂ NANOPARTICLES MODIFIED BY DIFFERENT AMOUNT OF MPTMS

Entry	SM1	SM2	SM3	SM4	SM5
Mass ratio of MPTMS (%)	0	5	10	15	20
Zeta potential of SiO ₂ nanoparticles (mV)	-37.1	-32.7	-29.9	-27.1	-22.1

Preparation of styrene/SiO₂ Pickering emulsion polymerization: Pickering emulsion stabilized by MPTMS modified SiO₂ nanoparticles were prepared subsequently. In a typical procedure, a certain amount of SiO₂ nanoparticles were dispersed in water by an ultrasonic processor. Subsequently, oil was dispersed in the aqueous silica suspension. A coarse emulsion was first prepared by mixing the oil and water phases by magnetic stirring and the dispersion was applied with ultrasonic processor while being cooled in an ice bath.

Characterization: The type of Pickering emulsion was confirmed by observing the phenomenon when a drop of emulsion was added into water or oil. Optical micrographs (OM) were collected with the optical microscope (Beijing TECH Instrument Co. Ltd., China) equipped with a digital camera (Panasonic WV-CP460/G) and an image analysis software (Beijing TECH Instrument co. Ltd, China). The three-phase contact angle of the SiO₂ nanoparticles was measured by the method of compressed disk²⁴ SiO₂ nanoparticles were compressed into 2 mm thick circular disk (pressure, 400 kgf/cm²). Then the disk was put on the bottom of an open, transparent glass vessel. Styrene was first poured into the vessel and then a drop of water was placed on the disk surface. The appearance of the water drop on the SiO₂ disk was immediately photographed and the contact angle was directly measured with a protractor. Fourier transform infrared spectra was obtained in transmission mode on spectrophotometer (Thermo Nicole, Nicolette-6700) with KBr as reference. X-Ray photoelectron

spectra (XPS) was recorded by employing Thermo ESCALAB 250 system with AlK_α (hν = 1486.6 eV) as X-ray source. Field emission electron microscope (FE-SEM) observations were conducted on a FEI Sirion200 system with an accelerating voltage of 5 kV. Translate electron microscope (TEM) observations were conducted on a Hitachi H-800 system.

RESULTS AND DISCUSSION

Effect of solvent on morphology of SiO₂ nanoparticles:

Fig. 2 is a representative SEM image of SiO₂ nanoparticles fabricated in methanol, ethanol and isopropanol, respectively. The molal concentrations of solvent in each recipe was identical. It was shown that when methanol was used as solvent, the particle size of SiO₂ nanoparticles was *ca.* 50 nm and distributed in a narrow size range (Fig. 2a). As the molecular weight of the alcohol increased, the size of SiO₂ nanoparticles prepared in ethanol increased to 150 nm (Fig. 2b) and the products obtained in isopropanol even aggregated (Fig. 2c). It was because methanol had the lowest viscosity and the highest dielectric constant in lower alcohol, which were helpful for tetraethoxysilane to form a large number of nucleus and disperse instantly. If not mentioned, the SiO₂ nanoparticles used hereinafter was all fabricated in methanol.

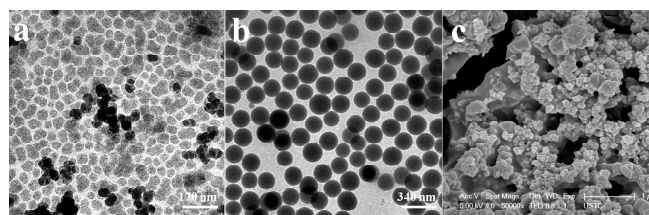


Fig. 2. SEM image of SiO₂ nanoparticles fabricated in (a) methanol, (b) ethanol and (c) isopropanol

FTIR spectra of SiO₂ nanoparticles: SiO₂ particles were subsequently modified by MPTMS *via* the condensation between the hydroxy formed from hydrolysis of MPTMS and the hydroxy on SiO₂. The FTIR spectra of SiO₂ and SiO₂ modified were shown in Fig. 3, demonstrating that for modified SiO₂ (Fig. 3b), besides the characteristic absorption peaks of Si-O at about 1096 cm⁻¹ and the surface -OH at about 3360 cm⁻¹, there were absorption peaks at 2970 and 2880 cm⁻¹, which were the characteristic peak of the C-H bond in -CH₂-, verifying that the surface of SiO₂ nanoparticles was successfully modified.

X-Ray photoelectron spectra of SiO₂ nanoparticles:

The XPS spectra of SiO₂ nanoparticles and SiO₂ nanoparticles modified with different amounts of MPTMS was shown in Fig. 3. The curve for SiO₂ nanoparticles confirmed a substantial amount of Si and O existence and no C existence (Fig. 4a). For SM2, the appearance of the peak belonging to the C element indicated the existence of organic groups on SiO₂ surface, as shown in Fig. 4b and the curve for SM5 in Fig. 4c indicated a larger amount of C, which demonstrated that more areas of the nanoparticles surface of SM5 was grafted by organic groups. The deconvoluted XPS C1s spectra of SM2 (Fig. 5) exhibited three components: C-C (284.6 eV), C-Si (283.9 eV), C=O (288.5 eV), which further confirmed MPTPS was grafted to the surface of the SiO₂ nanoparticles.

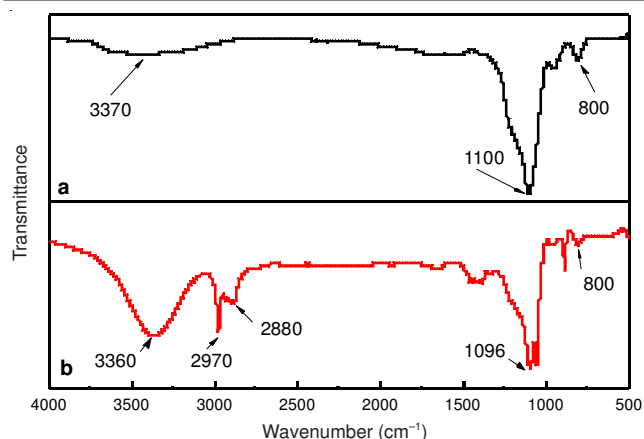


Fig. 3. FTIR spectra of (a) SiO₂ nanoparticles and (b) SiO₂ nanoparticles modified by MPTMS

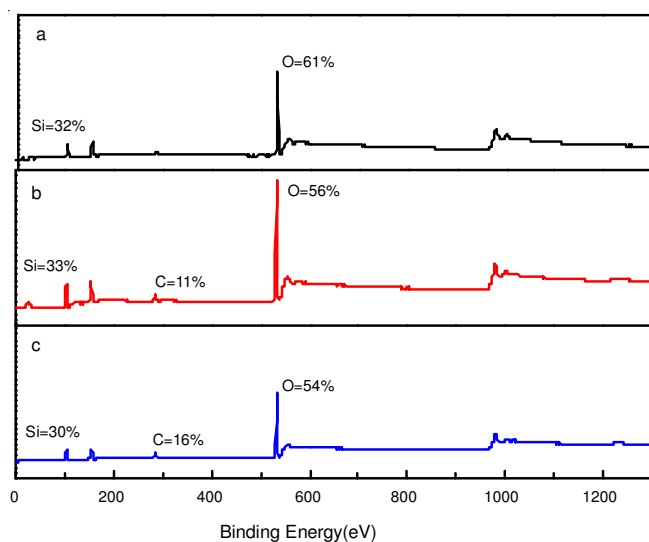


Fig. 4. XPS of (a) SiO₂, (b) SM2, (c) SM5

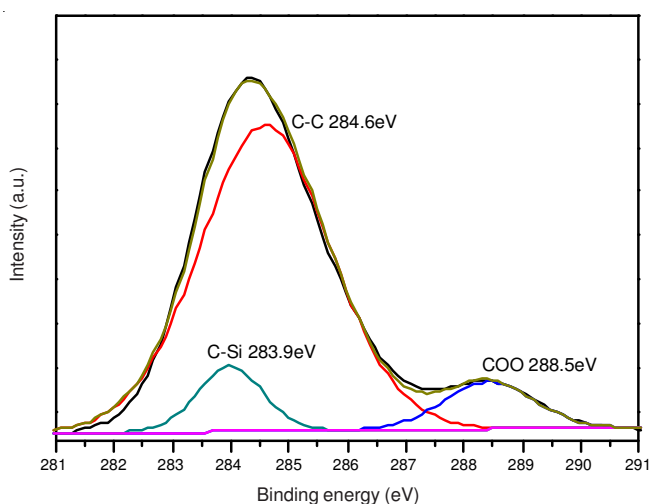


Fig. 5. Deconvoluted XPS C1s spectra of SM2

Zeta potential of SiO₂ nanoparticles: The variations of zeta potential of SiO₂ nanoparticles modified with different amount of MPTMS were shown in Table-1. Because SiO₂ nanoparticles fabricated *via* sol-gel reaction had abundant silanol-groups on the surface, the zeta potential was negative in aqueous phase. When organic groups were grafted to the

surface of SiO₂ nanoparticles, the zeta potential gradually rose with the amount of MPTMS added increased.

According to Yang *et al.*²⁵, colloidal particles must overcome the energy barrier between the particles dispersed in water and the oil-water interface in order to be adsorbed at the interface. The decrease of surface charge density of modified SiO₂ nanoparticles would lead the weakness of electrostatic repulsion between the particles adsorbed at the oil-water interface and the particles in aqueous phase and reduce the energy barrier as a result.

Three-phase contact angle of SiO₂ nanoparticles: The three-phase contact angle θ which the oil-water interface makes with the solid could indicate the wetting condition of SiO₂ nanoparticles surface and was important for the type and stability of the Pickering emulsion. Fig. 6 is a representative three-phase contact angle image of SiO₂ nanoparticles modified with different amounts of MPTMS. Because of the abundant hydroxyl on surface, pure SiO₂ particles was hydrophilic and the contact angle was *ca.* 30° (Fig. 6a). After modified by MPTMS, SiO₂ nanoparticles changed to be hydrophobic and the contact angle was increased. It showed that the three-phase contact angle of SM2 was about 85° (Fig. 6b), which was suitable to stabilize O/W Pickering emulsion and the three-phase contact angle of SM5 was *ca.* 175° (Fig. 6c), which indicated that the SiO₂ nanoparticles turned almost hydrophobic.



Fig. 6. Three-phase contact angle determination photograph of (a) SiO₂, (b) SM2, (c) SM5

Effect of SiO₂ nanoparticles wettability on Pickering emulsion: The Pickering emulsion stabilized by SiO₂ nanoparticles with different surface wettability was prepared. The photos of the emulsion were shown in Fig. 7. It was shown that SiO₂ nanoparticles which were completely wetted by water (Fig. 7a) or oil (Fig. 7c) were incapable of stabilizing emulsions and dispersed in either phase. When SiO₂ nanoparticles were partly wetted by both phases, the nanoparticles were held at the interface and stable emulsion was obtained (Fig. 7b).

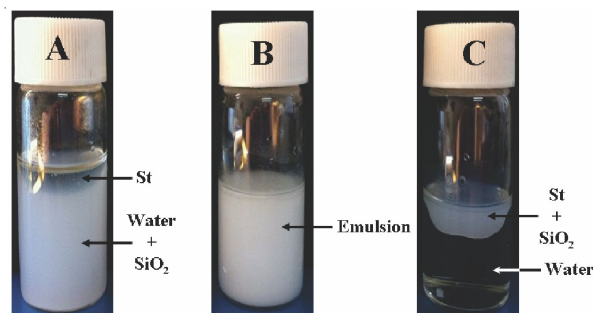


Fig. 7. Photograph of Pickering emulsion stabilized by (A) SiO₂, (B) SM2, (C) SM5

Effect of SiO₂ nanoparticles concentrations on Pickering emulsion: Pickering emulsion stabilized by different amount

of SM2-SiO₂ was prepared and the formation and stability of the Pickering emulsion was shown in Table-2 and Fig. 8. The stabilization of Pickering emulsion depended largely on the formation of a densely packed film at the oil-water interface, which prevented the droplets from coalescence¹⁹. Herein, at low particles concentrations (lower than 2 %), the droplets were sparsely covered by particles and rapid coalescence among the droplets occurred, resulting in phase separation within a short period of time (Fig. 8a). When SiO₂ nanoparticles concentration was above 2 %, stable emulsion was obtained and dispersive droplets were formed (Fig. 8b-d). Then the droplet size gradually decreased with the increase of SiO₂ nanoparticles concentration until the particles concentrations reached 8 %. Further increasing the particles concentration could not continually decrease the particle size.

Fomulation	1	2	3	4	5
SiO ₂ nanoparticles concentration (%)	1	2	6	8	12
Stability	Water and O/W	Water and O/W	O/W	O/W	O/W

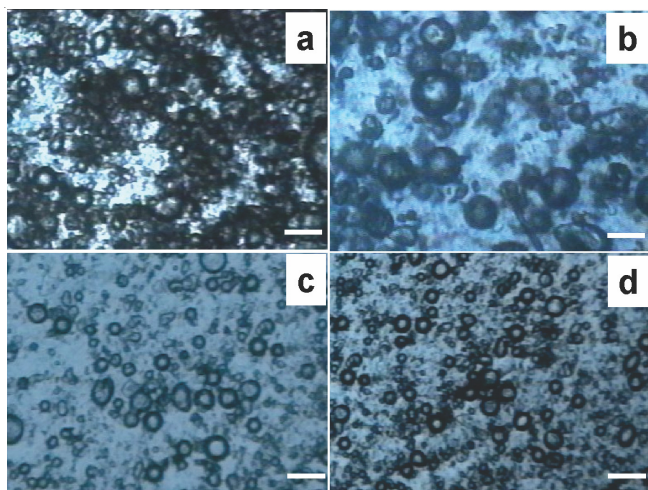


Fig. 8. OM image of Pickering emulsion droplet prepared at different SiO₂ concentrations. The scale bars correspond to 100 μ m. (a) 1 %, (b) 4 %, (c) 8 %, (d) 12 %

Conclusion

In summery, SiO₂ nanoparticles were successfully fabricated by sol-gel reaction, the wettability of which was tuned by grafting different amount of MPTMS. When the MPTMS to TEOS ratio was 5 %, SiO₂ nanoparticles partly wetted by oil and aqueous phases (three-phase contact angle $\theta = 85^\circ$) were obtained, which were suitable for the stabilization of O-W Pickering emulsion. Subsequently, styrene-water

Pickering emulsion stabilized solely by the modified SiO₂ nanoparticles was prepared and the effect of partial wettability, partial concentrations on the stability and morphology of Pickering emulsions was systematically studied. The result showed that stable emulsion could not be formed unless the SiO₂ nanoparticles concentrations increased to 2 %. Then the size of emulsion droplets gradually decreased with the increase of particles concentrations until the value reached 8 % and further increasing the particles concentration could not continually decrease the particle size.

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