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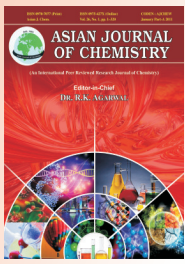

# Fabrication and Inversion of Pickering High Internal Phase Emulsions Stabilized by $SiO_2$ Nanoparticles†

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Silicon dioxide nanoparticles were fabricated *via* sol-gel reaction and modified by ethacryloxypropyltrimethoxysilane (MPTMS) subsequently. The surface grafting degree of the functionalized $SiO_2$ nanoparticles was determined by thermogravimetric analysis and the surface wettablity was investigated through measuring the contact angle. Subsequently W/O pickering emulsion was prepared by using the modified $SiO_2$ nanoparticles. We studied the effect of particle wettability and concentrations on the emulsion stability, the droplet size and the upper limit of the internal phase volume fraction. Pickering high internal phase emulsions with volume fractions of up to 0.90 was obtained and phase inversion was observed above this value.

**Keywords: High internal phase emulsions, $SiO_2$, Pickering emulsion.**

## INTRODUCTION

High internal phase emulsions (HIPEs) characterized by a minimum internal phase volume ratio of 0.74[1] have attracted extensive interest due to their wide applications such as cosmetic, pharmaceutical, food and petroleum industries[2-6]. Conventional high internal phase emulsions are stabilized by large amounts of surfactants[7-9] which probably cause adverse effects in some cases. Particle-stabilized emulsions, so called Pickering emulsions have aroused considerable interest recently[10-12]. In pickering emulsion, solid particles self-assem-ble at the oil-water interface and prevent the droplets from coalescing instead of conventional surfactants[13]. However, most of the reports about Pickering emulsions concern the emulsions that have internal phase levels below 70 vol %. Binks and Lumsdon[14] have observed the phase invert of pickering emulsions between volume fractions of 0.65 and 0.70. In this paper, we prepared Pickering high internal phase emulsions stabilized by $SiO_2$ nanoparticles and the effect of particle wettability and concentrations on the emulsion stability, the droplet size and the upper limit of the internal phase volume fraction was studied.

## EXPERIMENTAL

The fabrication of $SiO_2$ nanoparticles: 60 mL methanol, 7.5 mL ammonium hydroxide ($NH_3$ 25 %) and 8 mL water were mixed together. 20 mL of TEOS and 60 mL of methanol were mixed too. Then two solutions were mixed rapidly and stirred for 8 h at 40 ºC. Subsequently the mixture of 10 mL methanol and a definite amount of ethacryloxy propyltrimethoxy silane (MPTMS) was added dropwise the modification last for 24 h. Then $SiO_2$ nanoparticles were separated through centrifugation and the collection was washed with water and ethanol, respectively. MPTMS modified $SiO_2$ nanoparticles was obtained after 24 h of drying at 50 ºC.

**Preperation of emulsion:** A certain amount of $SiO_2$ nanoparticles was dispersed in liquid paraffin by an ultrasonic processor. Then water was dispersed in the silica suspension by magnetic bar stirring and the coarse emulsion was applied with ultrasonic processor to form water-in-liquid paraffin pickering emulsion and the recipe is shown in Table-1.

**Detection method:** Optical micrographs (OM) was collected with the optical microscope (Beijing TECH Instrument Co. Ltd., China). The contact angle of the $SiO_2$ nanoparticles was measured by contact angle tester (DSA20). Field emission electron microscope (FE-SEM) observations was conducted on a FEI Sirion200 system with an accelerating voltage of 5 kV. Thermogravimetric analysis (TGA) curves were collected with a thermoanalyzer (TG209F3 NETZSCH) within a temperature range of 20-800 ºC and with the rate of increasing temperature of 10 ºC/min.

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TABLE-1
RECIPE OF PICKERING-HIPES

| Sample | Internal phase volume (vol %) | Amount of modified $SiO_2$ (wt %) | Emulsion state |
|---|---|---|---|
| 1 | 65 | 1 | Sedimentation |
| 2 | 75 | 1 | Stable emulsion |
| 3 | 85 | 1 | Slight phase separation |
| 4 | 90 | 1 | Phase separation |
| 5 | 70 | 4 | Stable emulsion |
| 6 | 75 | 4 | Stable emulsion |
| 7 | 80 | 4 | Stable emulsion |
| 8 | 85 | 4 | Stable emulsion |
| 9 | 90 | 4 | Stable emulsion |
| 10 | 92 | 4 | Stable emulsion |
| 11 | 90 | 6 | – |

## RESULTS AND DISCUSSION

**Surface modification of $SiO_2$ nanoparticles:** In this study, we prepared hydrophilic $SiO_2$ nanoparticles *via* hydrolysis-condensation of TEOS. Subsequently, the $SiO_2$ nanoparticles were functionalized by MPTMS and the surface wettability was tuned by controlling the surface grafting degree. SEM (Fig. 1) showed the diameter of functionalized $SiO_2$ nanoparticles ranges from 30 to 60 nm and the surface grafting degree of the functionalized $SiO_2$ nanoparticles was determined by thermogravimetric analysis. The TGA curves and contact angle photos of $SiO_2$ nanoparticles modified by different amount of MPTMS are shown in Fig. 2. As shown in Fig. 2, the weight loss at 100 ºC in all curves is due to the loss of water, which is bound to the surface hydroxyl on $SiO_2$ nanoparticles. The weight loss from 300 to 450 ºC is obvious because of the degradation of the organic groups bonded to the surface of $SiO_2$ nanoparticles. For curve a, b and c, the surface grafting degree of the functionalized $SiO_2$ nanoparticles is calculated to be 4.5, 5.4 and 6.1 wt %, respectively. It is seen that the contact angle of functionalized $SiO_2$ nanoparticles increases from 30 to 100º with the increase of surface grafting degree. According to the work of Binks and Lumsdon[14], 100º is a favourable value to stabilize W/O pickering emulsion, so we choose $SiO_2$-c as the stabilizer in this work.

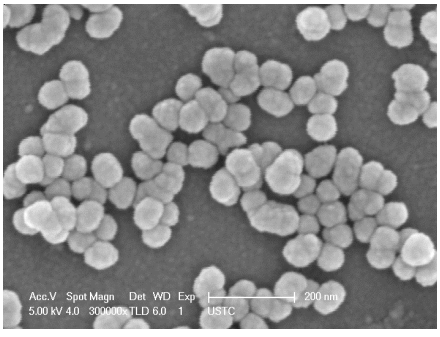


Fig. 1. SEM of functionalized $SiO_2$ nanoparticles

The liquid paraffin-in-water pickering emulsion stabilized by $SiO_2$-a and $SiO_2$-c was prepared, respectively. The optical micrographs of the emulsions are shown in Fig. 3. As shown in Fig. 3a, when the contact angle is 30º, most $SiO_2$ nanoparticles are dispersed in water phase because of their extreme hydrophilicity. When the contact angle is 100º, $SiO_2$ nanoparticles can be partly wetted by both Phases, we can see that most $SiO_2$ nanoparticles are adsorbed at the o/w interface (Fig. 3 a), which is conducive to the formation of stable emulsion.

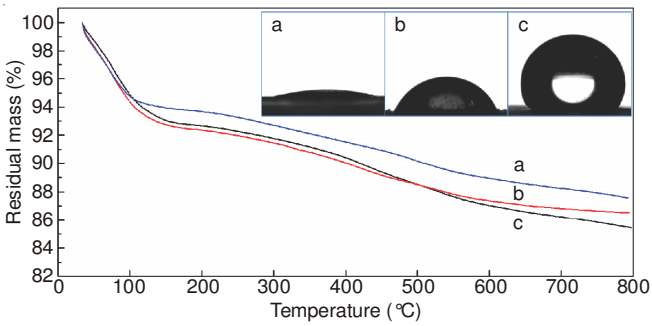


Fig. 2. TGA curves and the contact angle determination photos of functionalized $SiO_2$ nanoparticles

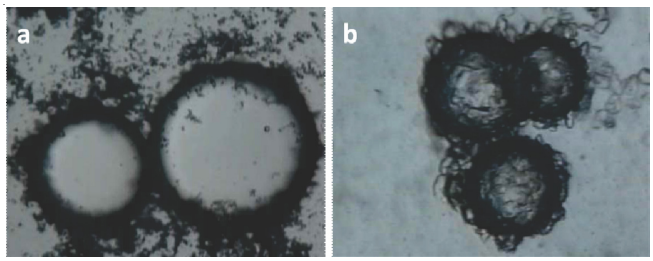


Fig. 3. Optical micrograph of liquid paraffin-in-water pickering emulsion stabilized by $SiO_2$ particles with different contact angle

**Formation of pickering HIPEs:** We prepared HIPEs 1-10 according to the formula in Table-1 (entries 1-10). The appearance of HIPEs 1-4, 9 after 24 h is shown in Fig. 4. It is observed that under the same $SiO_2$ nanoparticles concentration (1 % with respect to liquid paraffin), HIPE 1 containing 65 % internal aqueous phase experienced significant sedimentation (Fig. 4a) while HIPE 2 containing 75 % internal aqueous phase is stable (Fig. 4b). It is probably ascribed to the closely packing of droplets at higher internal phase volumes. When the internal phase volumes in the HIPEs increases, the droplets enlarge extremely and crowd each other. As a result, the droplets are deformed and compressed. The closely packed structure and the particle layer surrounding the droplet make the emulsion more stable and sedimentation caused by gravity is less likely to occur. When the emulsion of HIPE 3 processes the same particles concentration to HIPE 1 but higher internal aqueous phase of 85 %, slight phase separation can be observed (Fig. 4c). As far as HIPE 4, the internal aqueous phase of which is further increased to 90 %, the emulsion experiences obvious water phase separation (Fig. 4d). This trend is probably because that when the internal aqueous phase increases, the interface area increases too, which make particles insufficient to cover the o/w interface and form effective barrier to prevent droplet coalescence. As an evidence, when the particle concentration is increased to 4 %, HIPE 9 containing 90 % internal aqueous phase keeps stable (Fig. 4e). However, when the particle concentration is further increased to 6 %, HIPE 11 resulted in a highly viscous floater surrounded by water, because high particles concentration causes extreme high viscosity in the continuous phase, which make water dispersion difficult.

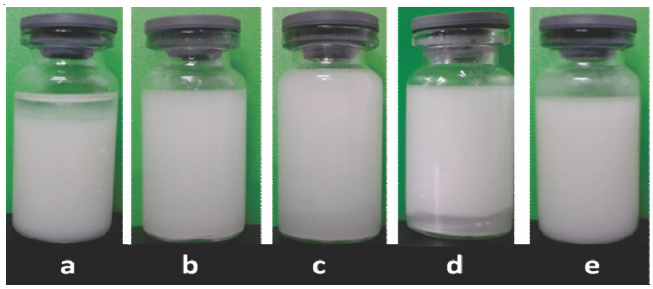


Fig. 4. Photos of (a) HIPEs-1; (b) HIPEs-2; (c) HIPEs-3; (d) HIPEs-4; (e) HIPEs-9

**Phase invert of pickering HIPEs:** To realize the effect of internal aqueous phase fraction on the morphology of emulsion, we prepared HIPEs 5-10 containing the same $SiO_2$ nanoparticles concentration (4 % with respect to liquid paraffin) with 70, 75, 80, 85 and 90 vol % internal aqueous phase and the optical micrographs of the emulsions are shown in Fig. 5. When the internal aqueous phase fraction is 70 %, the size of droplets in HIPEs 5 is *ca.* 200-400 μm and the droplets are close to each other. When the internal aqueous phase fraction is increased to 75 %, the droplets enlarge obviously and pack tighter. It can be observed that there are smaller droplets wrapped in the big droplets, which are probably the aqueous droplets. With the increase of the internal aqueous phase fraction, there are more aqueous droplets wrapped in and the droplets enlarged and packed more densely so that the interface became fuzzy. At last, when the internal aqueous phase fraction reaches 92 %, the interface disappears and the emulsion is inverted.

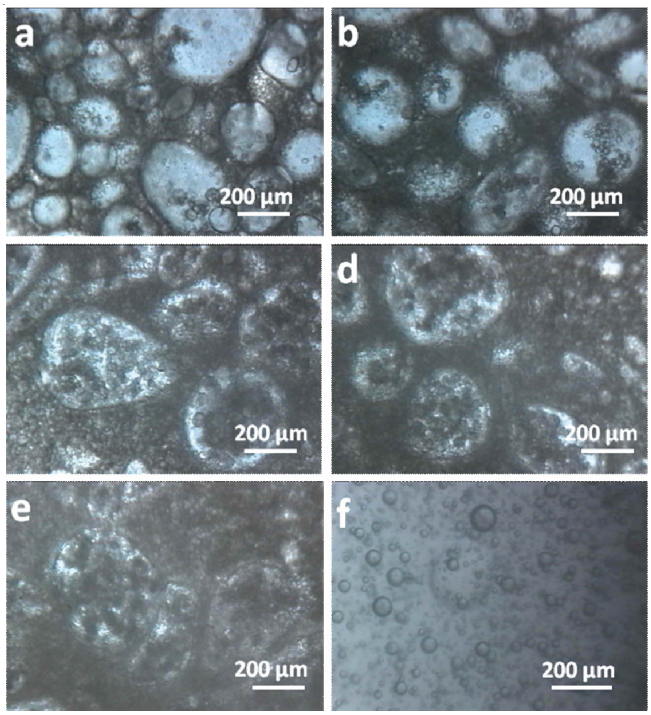


Fig. 5. Optical micrographs images of (a) HIPEs-5; (b) HIPEs-6; (c) HIPEs-7; (d) HIPEs-8; (e) HIPEs-9 and photo of (f) HIPEs-10

## Conclusion

We have successfully fabricated water-in-liquid paraffin HIPEs stabilized by functionalized $SiO_2$ nanoparticles. It is found that the aqueous phase fraction in HIPEs increases with the increase of the concentration of functionalized $SiO_2$ nanoparticles. But too high particles concentration will result in a highly viscous floater surrounded by water. Under the concentration of 4 % HIPEs with 90 % aqueous phase is prepared and phase inversion is observed above this value. If the continuous oil phase is polymerizable, the pickering-HIPEs can be used a templates for the manufacturing of highly porous polymer materials without surfactants, which might have many potential applications.

## ACKNOWLEDGEMENTS

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