

Stimuli-Responsive Composite Particles as Solid-Stabilizers for Effective Oil Harvesting

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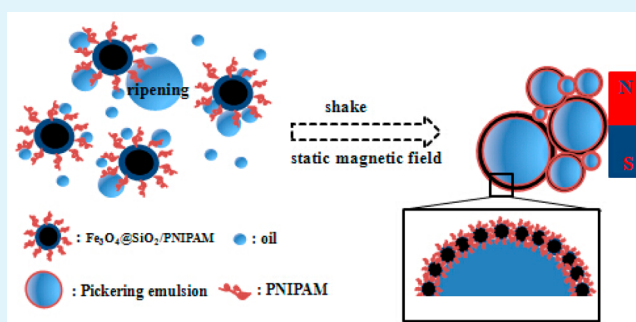
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S Supporting Information

ABSTRACT: The polymer-grafted magnetic composite particles have been synthesized and developed to harvest oil by use of their special wettability. Different from gravity-driven oil–water separation, the prepared polymer brushes-grafted magnetic composite particles can act as solid-stabilizers that diffuse to the oil–water interfacial region and effectively minimize the direct oil–water interfacial area by volume exclusion, whereas the magnetic Fe_3O_4 core allows easy separation of Pickering emulsions from oil–water mixture under an external magnetic field. When the emulsions were heated from room temperature to $50\text{ }^\circ\text{C}$, the coil-to-globule transition of poly(*N*-isopropylacrylamide) (PNIPAM) acts as the driving force for the destabilization of the emulsion, thereby achieving the release of oil. The novel materials can be used in aspects of oil–water separation, inducing oil droplet transport and release of lipophilic substrates.

KEYWORDS: stimuli-responsive, oil harvesting, poly(*N*-isopropylacrylamide), Pickering emulsion, drop transport, polymer brushes



With the increasing industrial oily wastewater and the frequent oil spill accidents, advanced materials or techniques that can effectively separate oil and water have attracted extensive attention in recent years. Because of a relatively simple process and acceptable discharge quality, membrane or meshes with special wettability have been acknowledged as an effective and facile way for oil/water separation.^{1–6} In spite of these advantages, such “oil-removing” materials have suffered some problems, such as serious fouling or secondary pollution. In addition, the core–shell structured particles show more flexible features in oil/water separation. For example, the magnetic nanoparticles with superhydrophobic/superoleophilic property are reported to achieve oil/water separation and induce droplet transport.⁷ However, their separation efficiency is far less than applicable requirements. Furthermore, the superhydrophobic nanoparticles are not suitable for the separation of microemulsion because of their poor dispersion in water. Although the reasonable design endows those composite particles with attractive features, this above-mentioned method is not able to reflect the advantage of nanoparticles with high specific surface area.

Pickering emulsions or solid-stabilized emulsions were described for the first time by Pickering and Ramsden in the early 20th century.⁸ Stabilization is achieved as long as particle surface has the right wettability. When nano- to micrometer-sized particles diffuse to the interfacial region, those particles can effectively minimize the direct liquid–liquid interfacial area

by volume exclusion.^{9,10} In recent years, although there has been increasing interest in the use of inorganic/organic particles to stabilize emulsion,^{11–15} Pickering emulsion acting as the encapsulation of lipophilic substances for the separation of oil-in-water emulsion have rarely been reported. On the other hand, although Pickering emulsion can be formed as long as particle surface has the right wettability, controlled breaking of Pickering emulsions is desirable in practical applications. In this communication, we demonstrate that magnetic composite particles grafted polymer brushes can be a wonderful candidate for oil harvesting, allowing for oil/water separation, inducing droplet transport and release of lipophilic substances.

The stimuli-responsive composite particles consist of a magnetic $\text{Fe}_3\text{O}_4@SiO_2$ core and an outmost PNIPAM polymer brushes (a detailed method is provided in the Supporting Information). The water dispersible Fe_3O_4 microspheres were prepared according to the method previously reported by Liu et al. (Figure 1a).¹⁶ The magnetite exhibits polycrystalline features that were confirmed by spotty diffraction rings of selected area electron diffraction pattern shown in inset. A modified Stöber method was carried out to obtain monodisperse $\text{Fe}_3\text{O}_4@SiO_2$ composite particles (Figure 1b). The silica–polymer interface is

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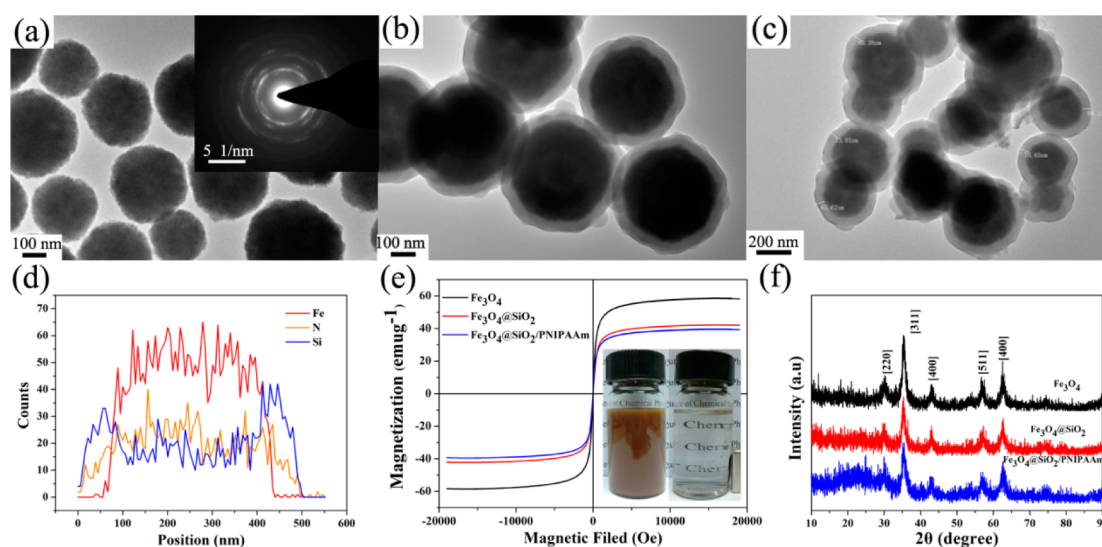


Figure 1. (a) TEM image of Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and (c) $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{PNIPAM}$ composite particles; (d) STEM-EDS line scan of a single $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{PNIPAM}$; (e) magnetization curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{PNIPAM}$; (f) their corresponding XRD patterns.

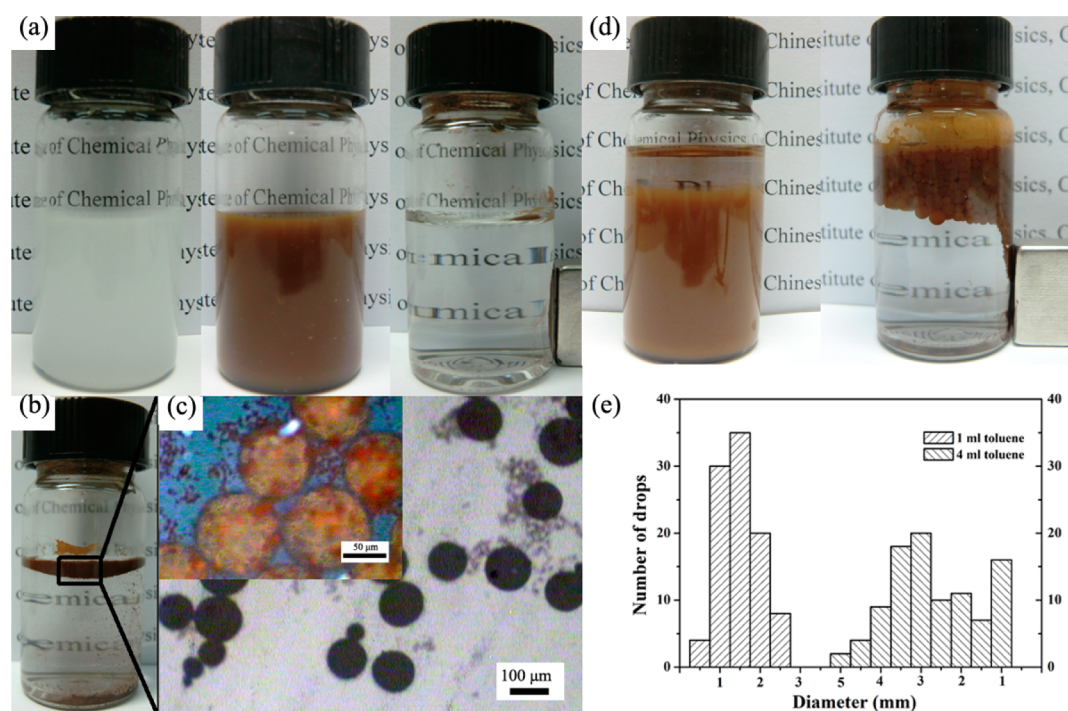


Figure 2. (a) Process of the separation of oil-in-water emulsion and transmittance of the separated water. (b) Emulsion float above an aqueous phase. (c) Microscopic images of the resulting emulsions and their high-magnification images. (d) Photographs of 4 mL of toluene on water surface and oil/water separation. (e) Drop-size distribution when 1 and 4 mL of oil was added, respectively.

not very clear owing to mixing at the interface (Figure 1c). Observed from the change of the thickness of shell, the PNIPAM layer thickness is of about ~ 10 nm. Figure 1d displays an STEM-EDS line scan across a single particle. The result reflects the higher atomic number of Fe in the center and the higher atomic number of Si and N in the outer shell that consistent with the designed structure. Fourier transform infrared (FTIR) analysis were carried out to further confirm the designed structure (see Figure S1 in the Supporting Information). Two adsorption peaks appearing at 1645 cm^{-1} (C=O stretching) and 1552 cm^{-1} (N–H bending) are both

the exact proofs that PNIPAM has grown from the initiator particles successfully.

Three samples all exhibit ferromagnetic behavior shown in Figure 1e. The saturation magnetization are 59.8, 41.5, and 39.7 emu g^{-1} , respectively. Compared with the bare Fe_3O_4 particles, $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{PNIPAM}$ exhibit lower saturation magnetization values because of the existence of the silica coating. To determine the crystallographic structure of the iron oxide nanoparticles before and after coating, we carried out XRD experiments to investigate the crystal structures of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{PNIPAM}$. As shown in Figure 1f, diffraction peaks at 2θ values of 30.4, 35.8, 43.4, 57.4, and

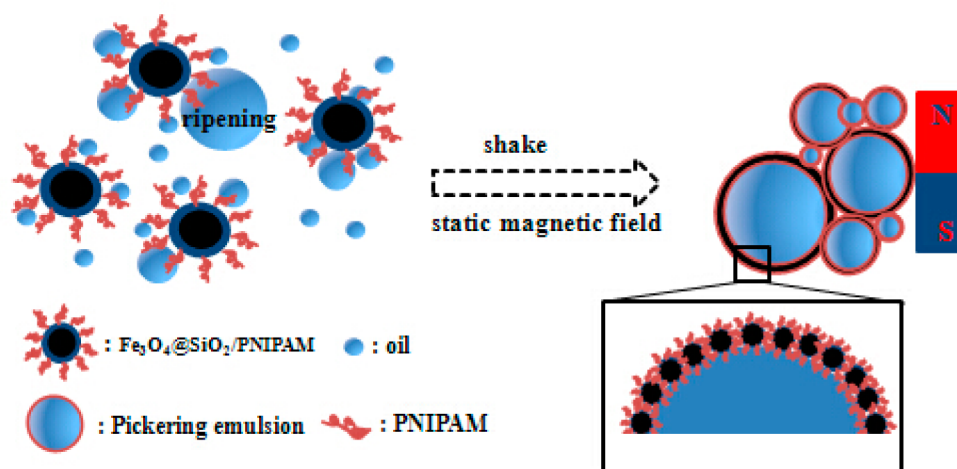


Figure 3. Schematic illustration of the proposed mechanism of the separation of oil-in-water emulsion by PNIPAM-carrying magnetoresponsive particles.

62.9°. These diffraction peaks could be easily indexed to the reflections of standard Fe_3O_4 , which confirm that the magnetite particles were successfully synthesized. Similar diffraction peaks are also found for the samples of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{PNIPAM}$, which suggest that the Fe_3O_4 were well-retained after coating. In addition, a broad diffraction band between 20 and 24° was observed when the iron oxide nanoparticles were coated with a layer of silica, confirming the existence of amorphous silica shell on iron oxide.

In previous reports, membrane or meshes with special wettability were used for gravity-driven oil–water separation. Herein, we try to achieve the goal through different forms by use of the special wettability of polymer brushes. The amide groups of PNIPAM make it water-solution when the solution temperature is lower than LCST.^{17,18} In addition, the amphiphilic nature of PNIPAM, which has both amide groups and isopropyl groups, makes it surface-active.^{19–21} To test oil absorption capacity of the composite particles, we prepared a surfactant-free toluene-in-water emulsion (see Figure S2 in the Supporting Information). When 0.2 mL of aqueous solution containing composite particles was added into the oil-in-water microemulsion, the composite particles were well-dispersed in mixture. After shaking for 10 s, those particles were collected when external magnetic field was applied, then achieve oil harvesting as shown in Figure 2a. Interestingly, when the magnet was removed, the emulsion phase float up (Figure 2b). To get much information on the type of the obtained emulsion phase, we present microscopic images of the obtained emulsions in Figure 2c. The images show that the emulsion phase consist of different sizes of droplets. Observed from the high-magnification images, the image clearly indicate that the obtained emulsion are of the so-called Pickering emulsion. In other words, the prepared magnic composite particles acting as solid-stabilizer diffuse to the interfacial region and reside at the interface between the dispersed and continuous phases, thus making a stable mechanical equilibrium.

To further study the oil absorption capacity, we added 1 and 4 mL of toluene, respectively. As shown in Figure 2d, 4 mL of toluene was added into 12 mL of aqueous solution containing 0.02 g of composite particles. The two separated phases are mixed by shaking for 10 s. Then, droplets of different sizes were collected on one side of the bottle when a static magnetic field is applied (Figure 2d). In previous report, 0.01 g of functional

particles can remove 0.029 mL of hexane.⁷ In our experiment, 0.02 g of stimuli-responsive composite particles can effectively remove 4 mL of toluene. It is worth noting that although this method makes full use of the advantage of nanoparticles with high specific surface area, the separating as a emulsion phase seems to be disadvantageous for much achieving higher separation efficiency comparing with the conventional methods. The drop-size distribution in Pickering emulsions can be effectively varied by adjusting the relative proportion of oil and water while keeping the mass of the particles constant (Figure 2e).

On the basis of these results, a mechanism proposed to account for the above observation as shown in Figure 3. Three important process are involved in oil harvesting: (1) when the composite particles were exposed to the oil droplets in oil-in-water mixture, the amphiphilic nature of PNIPAM cause them to adsorb oil; (2) magnetic force make them gather together to accelerate Ostwald ripening of oil drops thereby getting bigger oil drops; (3) polymer-grafted magnetic composite particles act as solid-stabilizer and finally obtain Pickering emulsion to minimize coalescence when droplets approach one another. The conventional superhydrophobic/superoleophilic particles utilize the special wettability to achive oil/water separation. In contrast, the prepared polymer-grafted magnetic composite particles can take advantage of large specific surface area of nanoparticles and greatly improve the oil adsorption capacity. This high separation efficiency matches well with the practical requirements for oil/water separation.

The obtained Pickering emulsions are very stable over time and maintain their appearance for at least 3 months as long as they were stored at room temperature. When the emulsion were heated from room temperature to 50 °C, PNIPAM shows coil-to-globule transition in water. As a result, the energy,²² E , required to remove a particle from the interface and the coverage of the surface of the oil droplet reduce along with the reduction of the radius, leading to destabilization of the interface. E is given by

$$E = \pi r^2 \gamma_{ow} (1 \pm \cos \theta)^2$$

in which the sign inside the bracket is negative for removal into the water phase, and positive for removal into oil. The hydrodynamic diameters of stimuli-responsive particles in

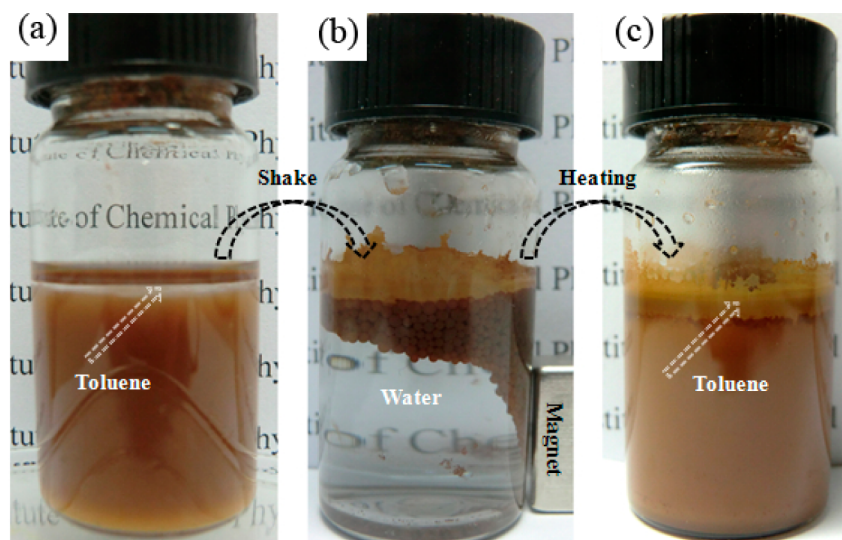


Figure 4. (a) Photographs of 1 mL of toluene on brown solution surface, (b) oil/water separation when a static magnetic field on the Pickering emulsion, (c) phase separation of toluene emulsions stabilized by stimuli-responsive particles when temperature goes above LCST.

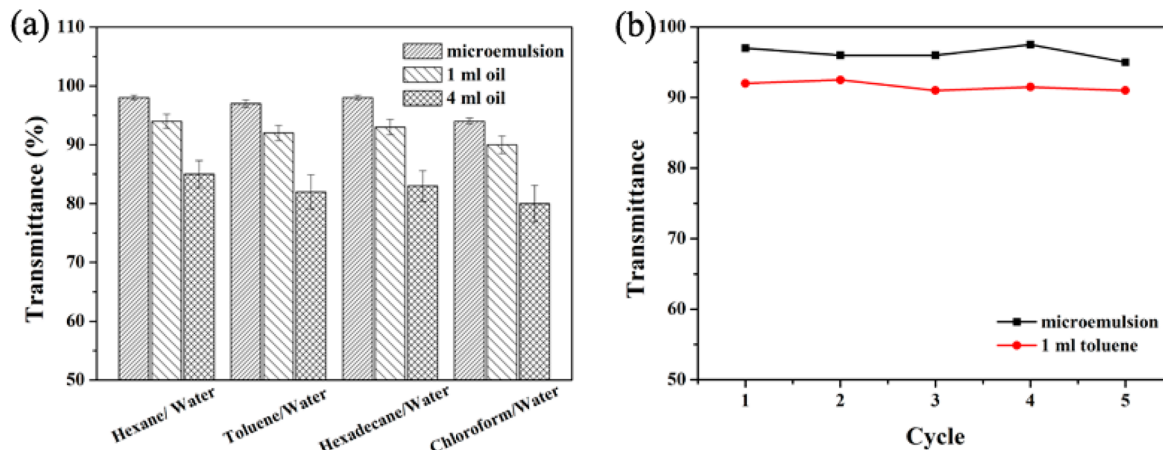


Figure 5. (a) Separation efficiency of the PNIPAM-carrying magnetoresponsive particles for various oils. (b) Study of antifouling ability of the stimuli-responsive composite particles.

swollen state (25 °C) and shrunken state (40 °C) are different (see Figure S3 in the Supporting Information). Meanwhile, the hydrophobicity of the surface of NIPAM polymer will change dramatically as temperature goes up. Those changes act as the driving force for the destabilization of the emulsion. Then, oil droplet starts to ripen and coalesce to compensate for the insufficient coverage by the reduction of the total interfacial area, resulting in the occurrence of phase separation (Figure 4c). In addition, we speculate that the grafting density of PNIPAM, particle size, and shape have an important impact on the stability of Pickering emulsion, which will be studied in more detail in our future work.

Different from gravity-driven oil–water separation, the prepared polymer brushes-grafted magnetic composite particles acting as solid-stabilizers diffuse to the oil–water interfacial region and finally obtain Pickering emulsions. Therefore, the concentration of composite particles in the mixture greatly affect the efficiency of oil/water separation. To study the relationship between particle concentration and separation efficiency, a series of experiments were carried out. The $T_{\text{separation}}/T_{\text{initial}}$ was used to assess the separation efficiency, where $T_{\text{separation}}$ is the transmittance of water after oil

separation and T_{initial} is the transmittance of water before mixing. The results observed from Figure 5a show that the transmittance of water after oil separation are all above 95% in the cases of the separation of microemulsion. However, the transmittance decrease gradually along with increasing the relative proportion of oil while keeping the mass of the particles and water constant. When the oil volume is increased to 4 mL, the transmittance is reduced to 80%. On the basis of these results, we confirm that the separation efficiency improve with increasing particle concentration. Furthermore, the cycle characteristics of stimuli-responsive composite particles was tested as shown in Figure 5b. Toluene was taken as example. After 5 cycles, the stimuli-responsive composite particles still maintain high separation efficiency, which demonstrates their good resistance to fouling.

In summary, the polymer-grafted magnetic composite particles have been synthesized and developed to harvest oil by use of their special wettability. The novel materials can not only act as solid-stabilizers for oil harvesting, but also the magnetic Fe_3O_4 core allow easy separation of Pickering emulsions from oil/water mixture under an external magnetic field. The coil-to-globule transition of PNIPAM act as the

driving force for the destabilization of the emulsion, thereby achieving the release of oil, which matches well with the requirements in practical applications. We anticipate that Pickering emulsion stabilized by stimuli-responsive composite particles will provide a new method for practical application in oil harvesting and microfluidic devices.

■ ASSOCIATED CONTENT

● Supporting Information

Experiment in detail; FT-IR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@/\text{SiO}_2$, $\text{Fe}_3\text{O}_4@/\text{SiO}_2/\text{PNIPAM}$; photograph of surfactant-free toluene-in-water emulsion; hydrodynamic diameters of PNIPAM-carrying particles at given temperature. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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