Supporting Information

Magnetic-responsive switchable emulsions based on $Fe_3O_4@SiO_2-NH_2$ nanoparticles

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Experimental

Preparation of unmodified and modified Fe_3O_4 MNPs. They were prepared by co-precipitation of aqueous ferrous and ferric ions.[25] 0.5 M $FeSO_4$ solution with 0.2 M HCl, 1 M $FeCl_3$ solution with 0.2 M HCl and 1.5 M NaOH solution were prepared, respectively. 100 mL NaOH solution was added into a flask and heated to 80 °C. Then the mixture of 10 mL $FeSO_4$ solution and 10 mL $FeCl_3$ solution was added into the flask dropwise in an N_2 atmosphere and at the temperature of 80 °C. The black product was obtained after 30 min and the system was cooled down with continuous stirring. The Fe_3O_4 nanoparticles were washed more than three times with water and ethanol, respectively.

The prepared Fe_3O_4 nanoparticles were dispersed in 50 mL ethanol by a S04H ultrasonic cleaning machine (Zhiwei Instrument Co., Ltd., China) for 5 min, and then poured into a flask. 100 mL toluene and 3-aminopropyltriethoxy silane (Meryer Chemical Technology Co., Ltd., AR, 98%) were added into the flask which was heated to 110 °C in N_2 atmosphere. The reaction process is described as shown in Figure S9 a~c. The modified particles were obtained after 8 h and the system was separated with a hand magnet. The product was washed more than three times with ethanol and water, respectively, and then dried in a LGJ-10 freeze dryer (Beijing Songyuanhuaxing Technology Development Co., Ltd., China). Other chemicals (AR, 99%) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.

Characterization of MNPs. The composition of Fe_3O_4 and $Fe_3O_4@SiO_2\text{-}NH_2$ nanoparticles was determined by a TENSOR-27 fourier transform infrared spectroscopy (FTIR, Bruker, Germany) spectra ranging from 400 to 4000 cm^{-1}, and the disk shaped samples were obtained by compression molding with KBr. The weight change of nanoparticles was examined by a TG-DTA6300 thermogravimetric analyzer (NSK, Japan) from 30 to 1000 °C at a heating rate of 10 °C/min in N_2 atmosphere. The magnetic properties of MNPs before and after modification were measured with a PPMS-9 magnetometer/susceptometer (Quantum Design Inc., America). The measurements were conducted at room temperature with a magnetization field strength cycling from -10000 Oe to 10000 Oe and back to -10000 Oe. Nanoparticles were dispersed in water at a concentration of 0.4 wt.% using an ultrasonic cleaning machine for 1 h, and then added one drop onto a carbon-coated copper grid. After drying, the samples were imaged under a JEM-2100F transmission electron microscope (TEM) at a working voltage of 200 kV (JEOL, Japan). The elemental surface component of MNPs was determined by X-ray photoelectron spectroscopy (XPS) using ESCALab 250Xi with 200 W monochromated Al Ka radiation. The base pressure in the analysis chamber was about 3×10^{-10} mbar and the hydrocarbon C1s line at 284.8 eV from adventitious carbon was used for energy referencing. Size distribution of MNPs was measured using a Zetasizer (Malvern, England) at room temperature. Water contact angle (CA) of surfaces pressed by nanoparticles was measured by the CA goniometer (OCA 20L, Dataphysics Inc.) with a sessile-drop method. During the experiment, 2 μL water drop gradually approached and remained on the surfaces with an aging time of about 5 min. The CA values were obtained from video snapshots using a tangent-fitting method in data analysis software (SCA 22).

Preparation and characterization of Pickering emulsions. Emulsions were prepared using the mixture of n-dodecane (J&K Scientific Ltd., AR, 98%) and water in a 2:1 volume ratio, and stabilized by MNPs at the particle concentration of 0~1 wt% which was initially dispersed in n-dodecane. The mixture was vibrated using a DMT-2500 multitube vortex mixer (Hangzhou Mio Instrument Co., Ltd., China) at a speed of 2,500 rpm for 30 s. There is an obvious oil-water separation after 17 h in the presence of 0.05 wt% of magnetic NPs (Figure S10) and a quick complete separation under external response (Movie S8) and, therefore, we selected the low concentration from 0.1 wt% in which case the emulsion system performs a good stability without external response. In the case of higher concentrations such as 1 wt%, the emulsion performs such a strong stability that the system needs longer time (≥1 h) to be demulsified under external response (Movie S9) and, therefore, we selected the high concentrations of 0.2 and 0.4 wt% as control experiments. The morphology of emulsion droplets was performed on a B011 stereo microscope (Shenzhen Super Eye Technology Co., Ltd., China). The size distribution of emulsion droplets has been measured through a particle size analyzer (Microtrac S3500SI, America). The emulsion type was determined by measuring the conductivity of the emulsion phase through 4320 conductivity meter (Jenway, England), in which the cell constant is 0.930 cm^{-1}. Millipore Milli-Q grade water (18.2 MΩ·cm) was used in all our experiments and all the measurements were carried out under room temperature.

Demulsification Process. The emulsions were poured into a beaker and placed onto a hand magnet of 0.4 T on surface (Figure S9 d~f). To squeeze the emulsion drops and assist the demulsification, a mechanical stirring was also applied at a very low speed of 30 rpm as shown in Movie S1~S3. In comparison, only the mechanical stirring without magnet field was applied at the same speed in the emulsion systems as shown in Movie S4~S6.

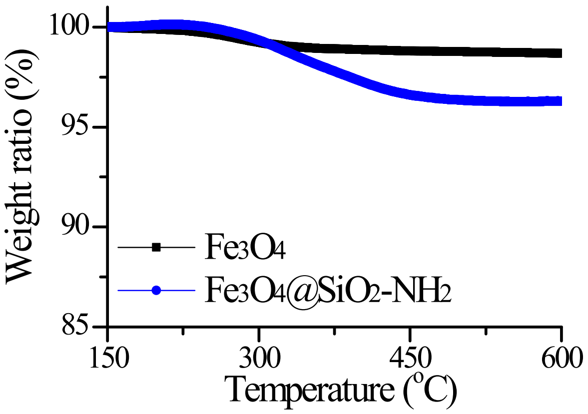


Figure S1 TGA curves of Fe_3O_4 and Fe_3O_4@SiO_2-NH_2 nanoparticles.

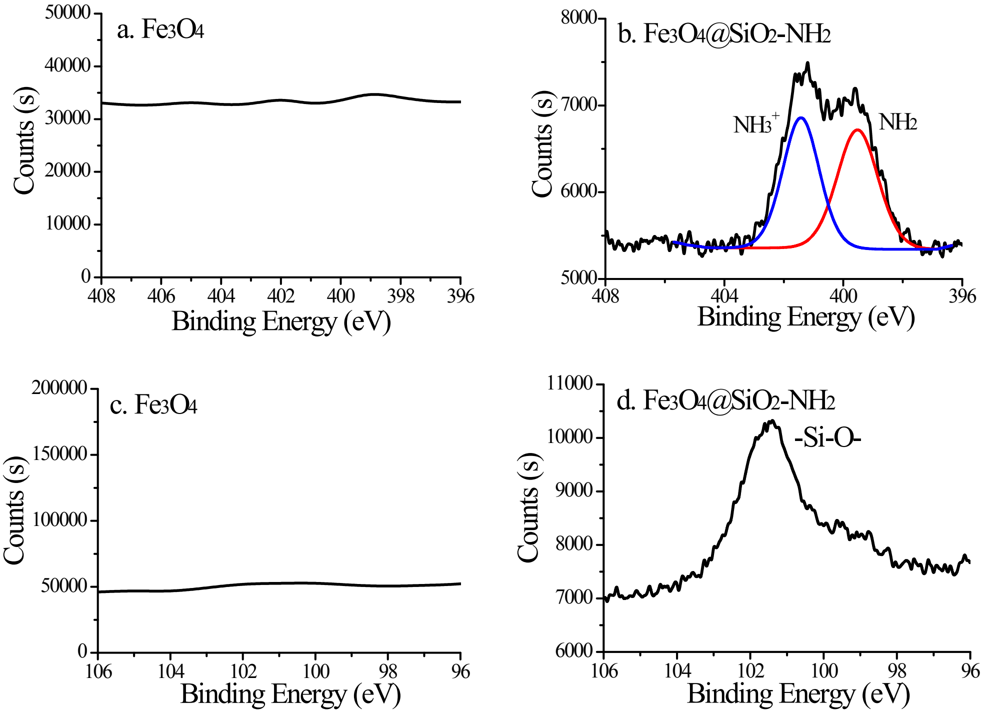


Figure S2 XPS spectra of bare Fe_3O_4 (a, c) and Fe_3O_4@SiO_2-NH_2 (b, d) nanoparticles.

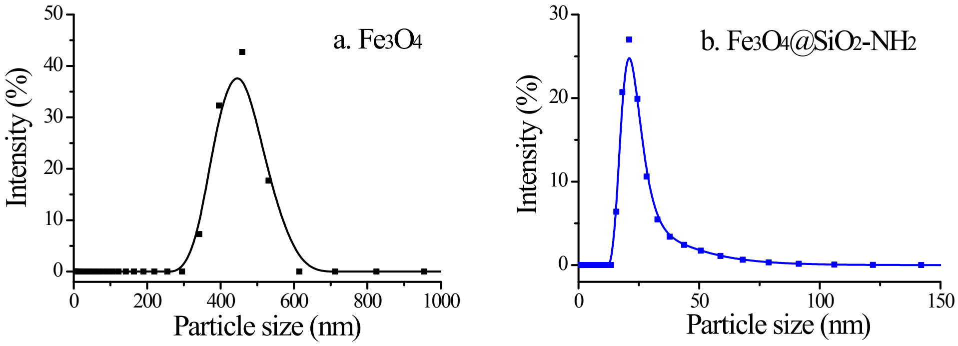


Figure S3 Size distribution of bare Fe_3O_4 and Fe_3O_4@SiO_2-NH_2 nanoparticles.

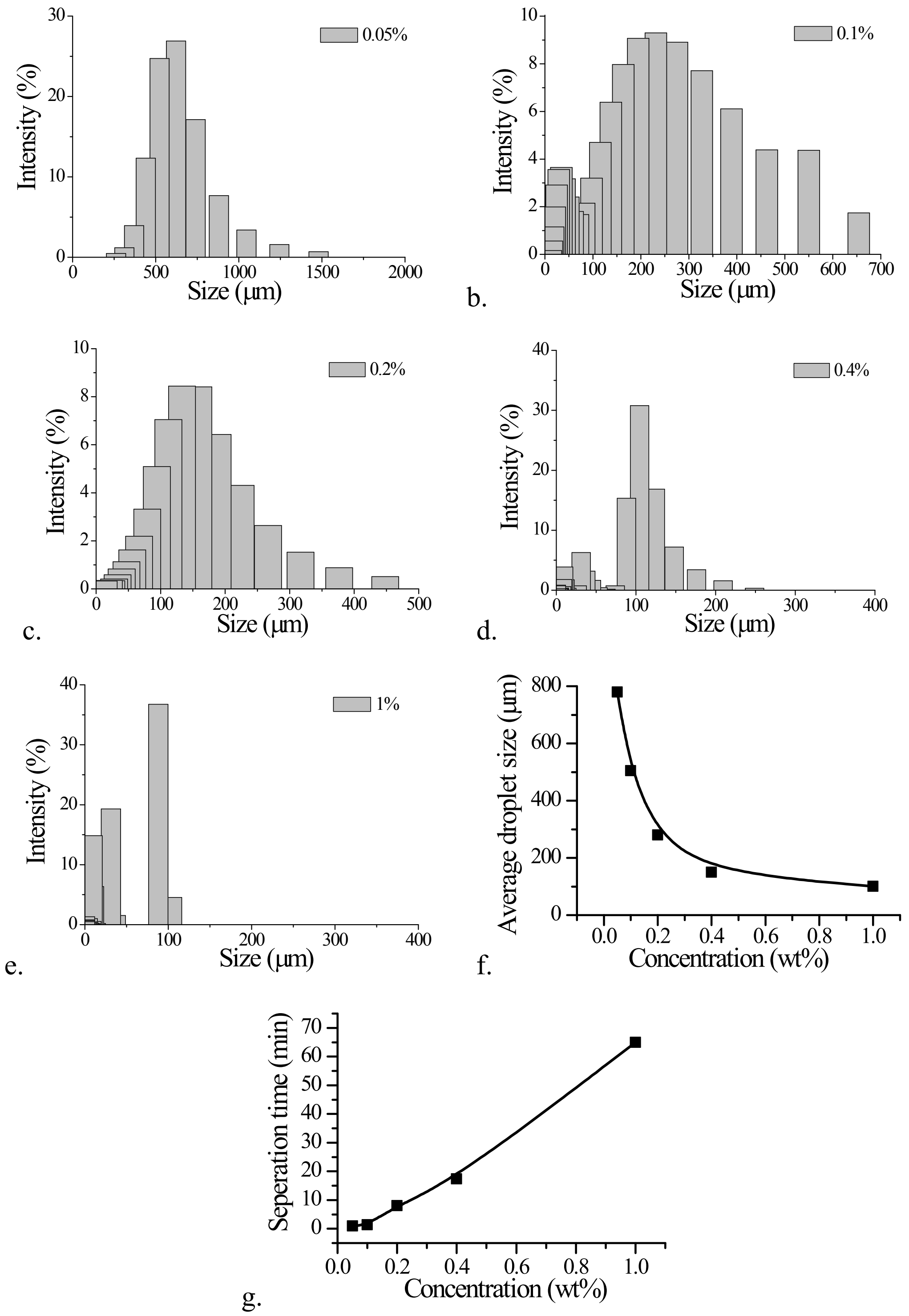


Figure S4 Size distribution of the droplets in the presence of $Fe_3O_4@SiO_2$-NH_2 nanoparticles at different concentrations of (a)~(e) 0.05~1 wt%. (f) variation trend of average droplet size and (g) stability ability of emulsions with the increase of particle concentration.

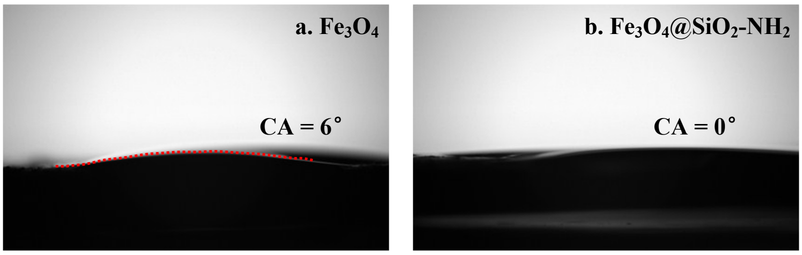
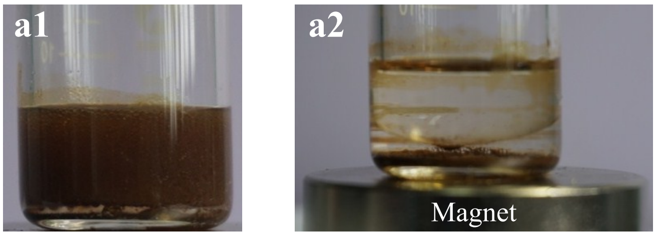
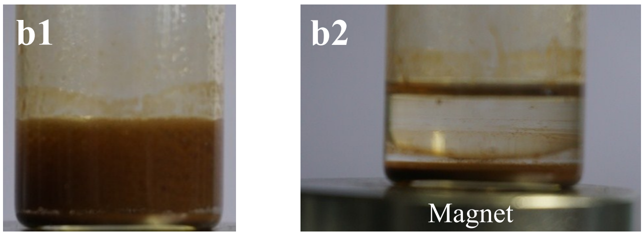


Figure S5 Contact angle (CA) of surfaces pressed by bare (a) Fe_3O_4 and (b) $Fe_3O_4@SiO_2-NH_2$ nanoparticles.

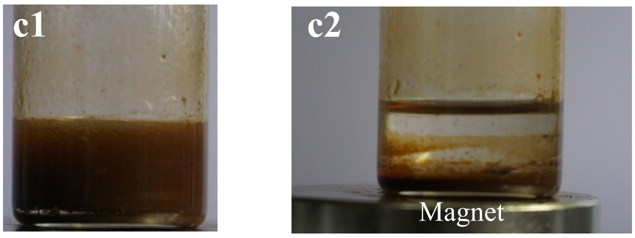
First circulation:



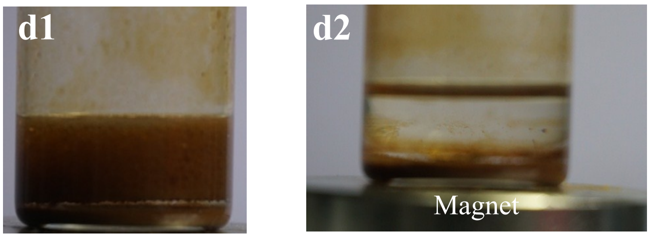
Second circulation:



Third circulation:



Fourth circulation:



Fifth circulation:

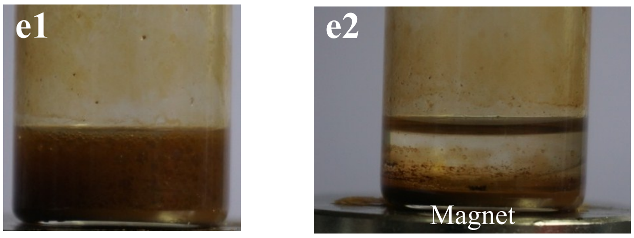
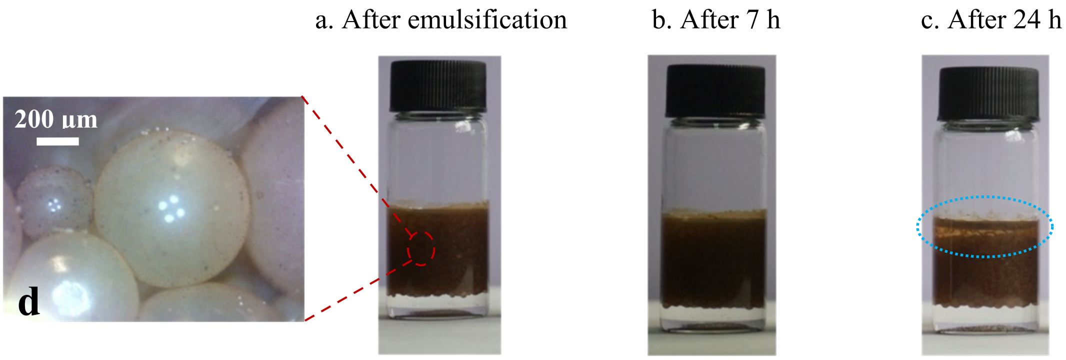


Figure S6 Five circulations of emulsification (a1~e1) and demulsification (a2~e2) of emulsions stabilized $Fe_3O_4@SiO_2$-NH_2 nanoparticles at 0.4 wt%.

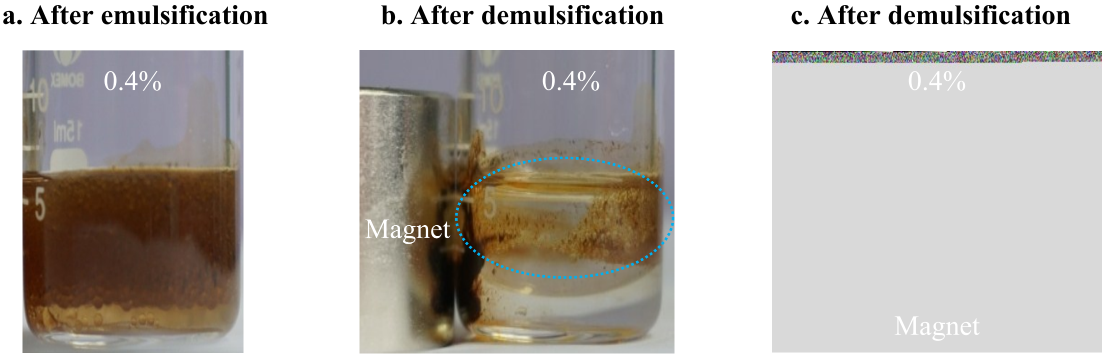


a. After emulsification

b. After 7 h

c. After 24 h

Figure S7 Emulsions stabilized by Fe_3O_4 nanoparticles at 0.2 wt% after preparation (a), placed in 7 h (b) and 24 h (c). (d) Stereo microscopic image of emulsion.



a. After emulsification **b. After demulsification** **c. After demulsification**

Figure S8 Emulsions stabilized by $Fe_3O_4@SiO_2\text{-}NH_2$ nanoparticles at 0.4 wt% after preparation (a), after demulsification with the magnet beside the emulsion vessel (b) and after demulsification with the magnet under the emulsion vessel (c).

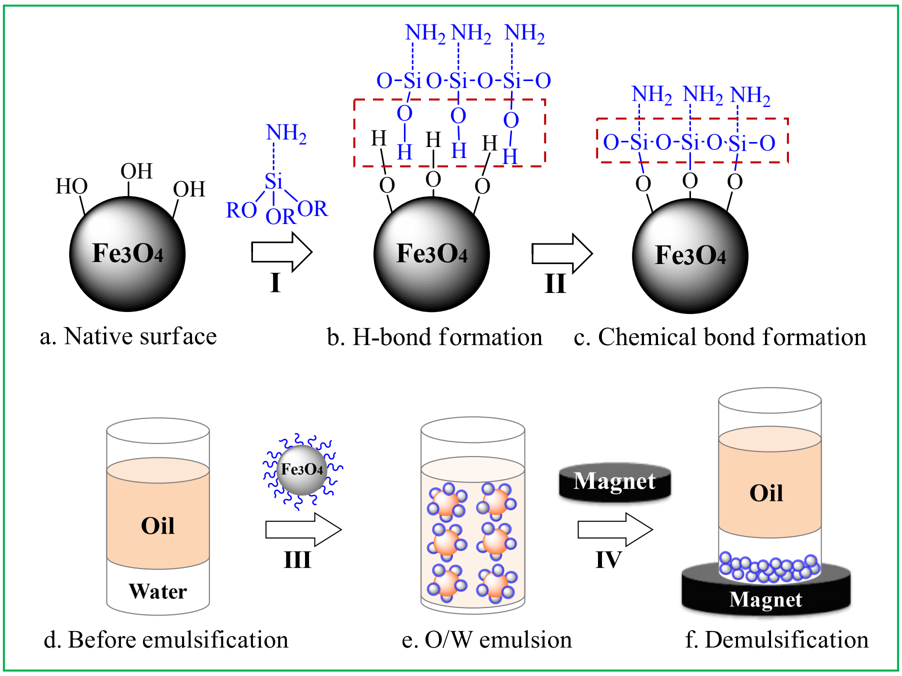
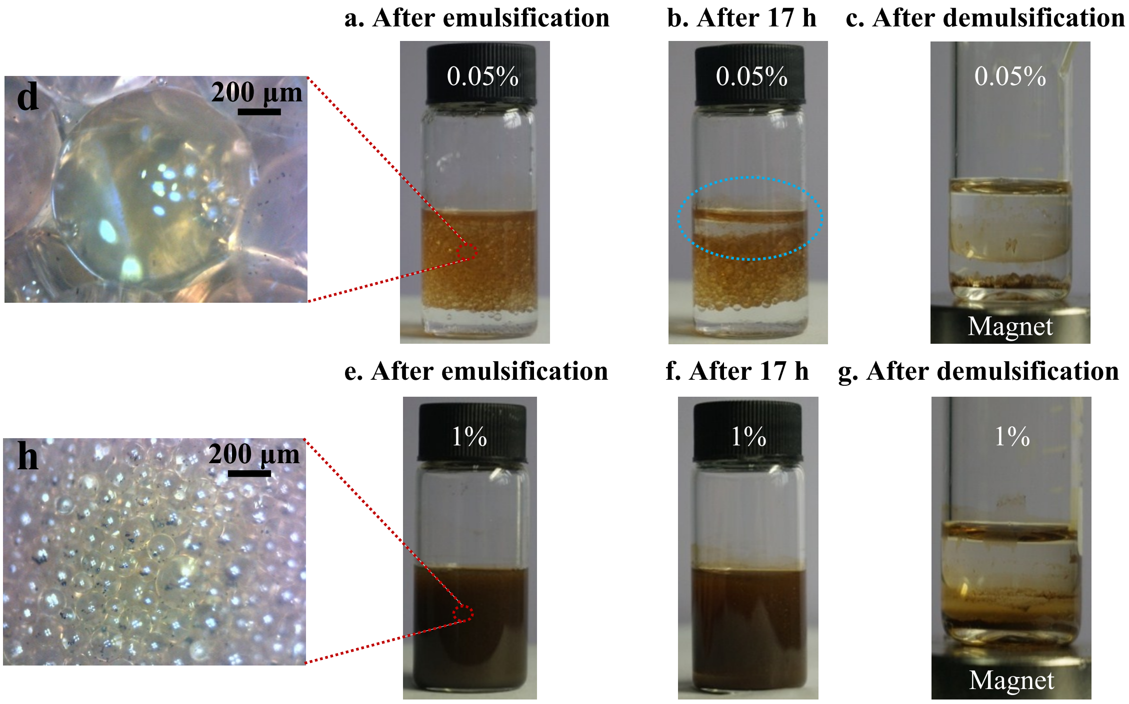


Figure S9 Schematics of preparation of $Fe_3O_4@SiO_2\text{-}NH_2$ nanoparticles: (a) bare Fe_3O_4 nanoparticles; (b) H-bond formation; (c) chemical bond formation. Schematics of the formation of emulsion and demulsion (d)~(f).


a. After emulsification **b. After 17 h** **c. After demulsification**

e. After emulsification **f. After 17 h** **g. After demulsification**

Figure S10 Emulsions stabilized by $Fe_3O_4@SiO_2\text{-}NH_2$ nanoparticles at 0.05 wt% and 1 wt% after preparation (a) and (e), placed in 17 h (b) and (f), after demulsification (c) and (g). Stereo microscopic images of emulsions (d) and (h).

Table S1 Volume of the stable emulsion (V_e), actual volume of the whole system (V_{total} = 6mL), and their ratio (V_e/V_{total}) in the presence of 0.1, 0.2, and 0.4 wt% nanoparticles over time.

	After preparation			**After 25 d**			**After 52 d**		
C (wt%)	0.1	0.2	0.4	0.1	0.2	0.4	0.1	0.2	0.4
V_e (mL)	4.8	5.4	6.0	4.5	5.1	5.4	4.5	5.1	5.4
V_e/V_{total} (%)	80	90	100	75	85	90	75	85	90

Table S2 Conductivity values based on the emulsion phase in the presence of $Fe_3O_4@SiO_2-NH_2$ nanoparticles at different concentrations after preparation.

Concentration (wt%)	**Conductivity (μS/cm)**
0.1	1.32
0.2	4.19
0.4	12.98