

## Electronic Supporting Information

### Facile One-Pot Synthesis of Yolk-shell Superparamagnetic Nanocomposites via Ternary Phase Separations

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## Experimental Section

Materials. All reagents used were analytical grade and available commercially. ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$ ), and oleic acid (90%) were purchased from Shanghai Chemical Reagents Company. Styrene (St), 2,2-azobis(isobutyronitrile) (AIBN), toluene, and ammonium hydroxide ( $\text{NH}_4\text{OH}$ , 28 wt %) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Tetraethoxysilane (TEOS) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich (USA). Hexadecane (HD) was purchased from Acros Organics (USA). The aforementioned chemicals were used as received. Styrene was washed first with 5 wt % sodium hydroxide solution and stored at  $-20^\circ\text{C}$  before use. High-purity nitrogen gas, provided by a local supplier, was used for sparging solutions without further purification. Deionized (DI) water was used throughout the entire experiment.

Methods. *Synthesis of Oleic acid modified iron oxide nanoparticles.* First, preparation of 11 nm OA modified iron oxide nanoparticles (OAIOS) was carried out according to the well-established coprecipitative reaction protocol. (L. Shen, P.E. Laibinis and T.A. Hatton, *Langmuir*, 1999, **15**, 447.) A typical preparation process is described as follows:  $\text{FeCl}_2 \cdot 7\text{H}_2\text{O}$  (9.82 g) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (24 g) were dissolved in DI water (100 mL) with a nitrogen protection. The dispersion was heated to  $80^\circ\text{C}$  and kept for 0.5 h. Then  $\text{NH}_4\text{OH}$  (50 g, 28 wt %) was then added quickly. After adding 3.76 g of oleic acid, the dispersion was further heated at  $80^\circ\text{C}$  for 3 h. Finally, the dispersion was cooled down to room temperature. The obtained OAIOS were collected by using a magnet and washed to neutralize with DI water. OAIOS were

further purified with ethanol and DI water each for three times. The dispersion of OAIOS in octane (65 wt %) was prepared via ultrasound, and the octane was distilled away and the OAIOS powder was kept sealed for further use.

*Synthesis of Yolk-shell magnetic composites (YSMCs).* YSMCs were prepared via a combined process of miniemulsion polymerization and sol-gel reaction. The recipes and main reaction conditions are listed in Table S1. For the preparation of YSMCs, a typical condition and procedure is described in detail as follows: the water phase was prepared by dissolving SDS (0.092 g, 8 mM) in 40 g of DI water. The oil phase was prepared by the following steps: HD (0.4 g) was first dissolved in St monomer (8 g) by 3 min sonication, then OAIOS powder (0.05 g) was dissolved in the monomer phase. Finally, TEOS (2 g) was resolved into the mixture of other hydrophobic components. The water phase and oil phase were then mixed by dropping the oil dispersion dropwise to the water phase under 200 W sonication (KQ-400KDV, Kun Shan Ultrasonic Instruments Co., Ltd.), followed by 250 rpm mechanical stirring for 30 min. Miniemulsion droplets system was developed by sonicating the emulsions for 10 min at 500W with a duty cycle of 50% and a Scientz-IIID sonifier (Ningbo City, China) in an ice bath. Before polymerization, the miniemulsion system was transferred to a three-neck flask and degassed with N<sub>2</sub> for 30 min under 250 rpm mechanical stirring after adding 0.08 g of AIBN. Polymerization of the St monomer was started as the flask was moved into the 70 °C water bath with condenser and under nitrogen atmosphere. In typical process, 0.035 mL of NH<sub>4</sub>OH (28%) was added rapidly into the reaction 60 min after polymerization started. After heating for another

5 h, the reaction system was stirred at room temperature for about 12 h. Then the final products of yolk-shell magnetic composite particles accompanied by some amount of free silica or polystyrene particles were obtained.

Table S1. Main conditions for preparation of the yolk-shell magnetic nanocomposites.

	SDS (mM)	DI water (g)	St (g)	TEOS (g)	OAIOS (mg)	NH <sub>4</sub> OH <sup>a</sup> addition (min)
Latex-1	8	40	8	2	55	60
Latex-2	8	40	9	1	55	60
Latex-3	8	40	8	0	55	60
Latex-4	8	40	8	2	0	60
Latex-5	8	40	8	2	55	24h before Polymerization <sup>b</sup>
Latex-6	8	40	8	2	55	0
Latex-7	8	40	8	2	55	20
Latex-8	8	40	8	2	55	180

Note: <sup>a</sup> Refers to the period of St polymerization before NH<sub>4</sub>OH addition. <sup>b</sup> At this run, the sol-gel reaction take place for 24 h at room temperature by adding NH<sub>4</sub>OH to the miniemulsion droplet system first, followed by the St polymerization at 70°C. 0.08 g of AIBN as initiator, 40 g of DI water and 8 mM SDS (to DI water mass) are used in all runs.

*Selective etching of the polymer core of the YSMCs.* the YSMCs after purification were etched with toluene for 5 h at room temperature. Obtained hollow magnetic composites were washed twice in DI water by using an external magnetic field.

*Characterizations. Dynamic light scattering (DLS).* Hydrodynamic size of the original miniemulsion droplet system and purified yolk-shell magnetic composite nanoparticles (washed twice with DI water under an external magnet) were measured by the DLS instrument (Zetasizer Nano-ZS, Malvern, U.K.).

*Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray Analysis.*

The obtained magnetic composite particles were washed twice in DI water by using

an external magnetic field to get rid of major free silica or polystyrene particles. The washed YSMCs were dispersed in DI water and dried onto carbon-coated copper grids before examination. TEM images and Energy dispersive X-ray (EDX) analysis were obtained with a Philips Tecnai 20 electron microscope.

*Scanning Electron Microscopy (SEM).* The obtained magnetic composite particles were washed twice in deionized water by using an external magnetic field. The sample was sputtered with a very thin gold film. A scanning electron microscope (SM4800, JEOL, Japan) was employed to investigate the morphology of the resulting final product.

*Thermogravimetric Analysis (TGA).* Thermogravimetric analyzer (NETZSCH TG209) was used to analyze surface modification of the iron oxide nanoparticles and YSMCs. The measurement was performed under nitrogen atmosphere from ambient to 1000 °C with the rate of heating at 10 °C/min.

*Magnetization Measurements.* The Vibrating Sample Magnetometer (LakeShore 7407, USA) was used to study the magnetic property of the oleic acid modified iron oxide nanoparticles and YSMCs at room temperature.

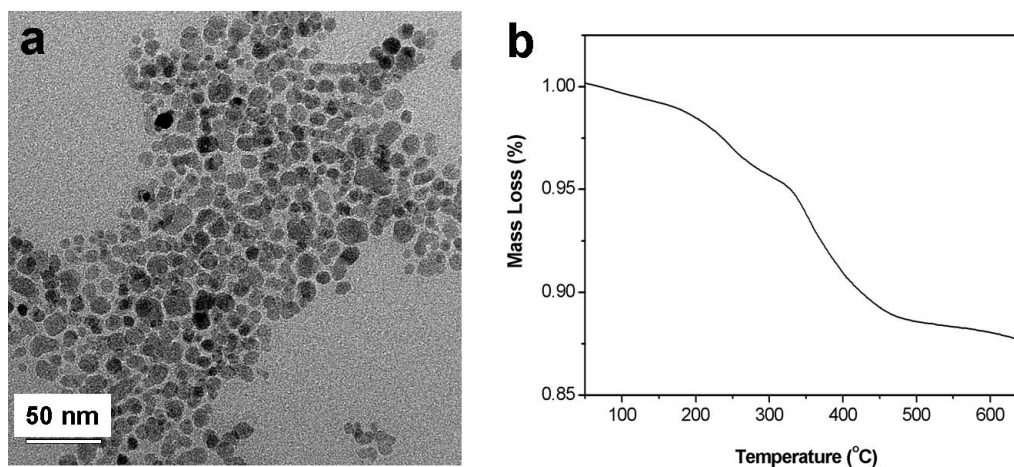


Figure S1. (a) TEM image and (b) TG analysis curve of the oleic acid modified iron oxide nanoparticles.

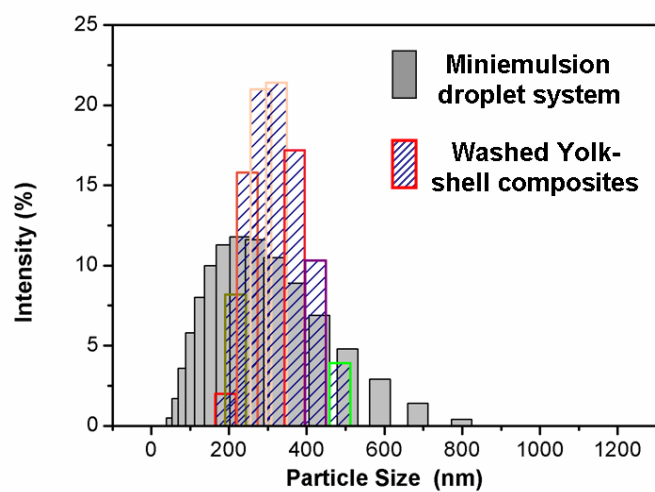


Figure S2. DLS data of the original miniemulsion droplet and aqueous dispersion of purified typical yolk-shell magnetic nanocomposites (Latex-1 of Table S1).

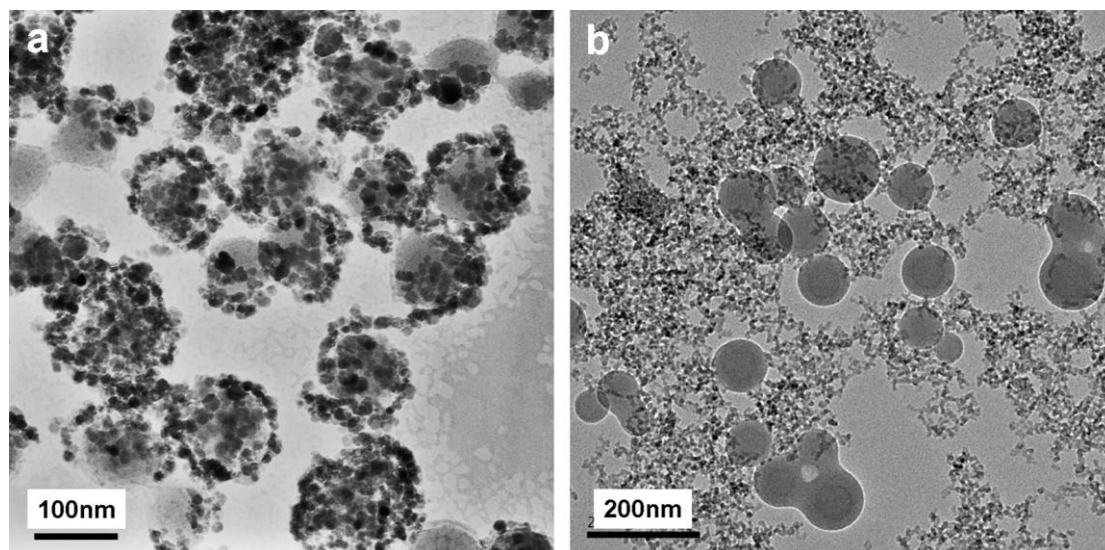
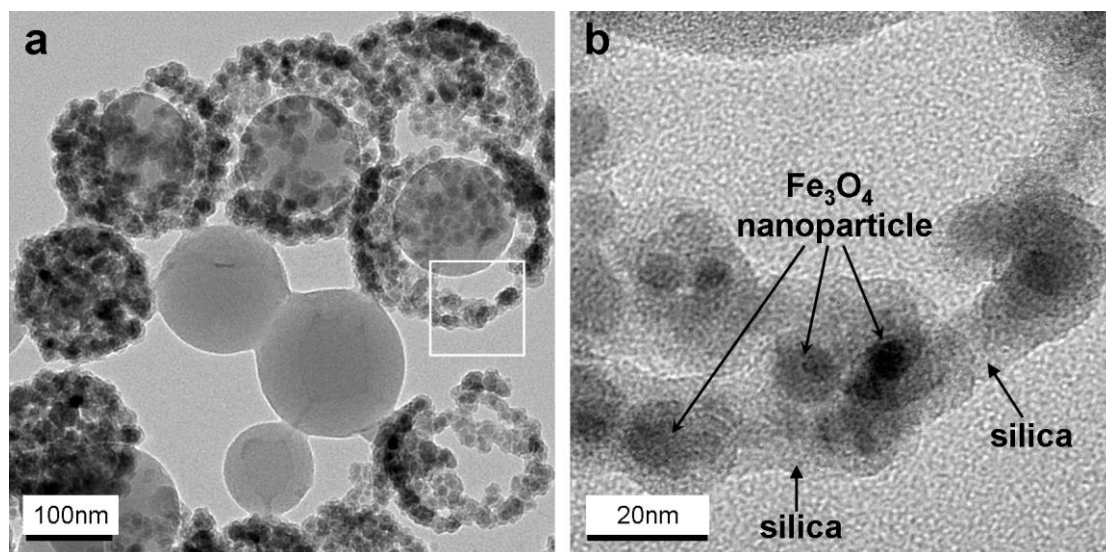


Figure S3. TEM images of the obtained composite particles when the reaction was carried out in absence of (a) TEOS precursor (Latex-3 of Table S1), and (b) oleic acid modified iron oxide nanoparticles (Latex-4 of Table S1), all other conditions are kept the same.





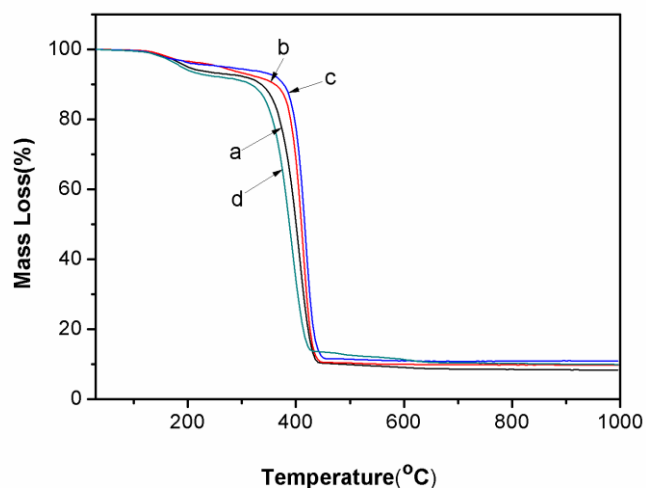


Figure S5. TGA curves of the yolk-shell magnetic composites obtained from the following reactions: (a) as polymerization of St monomer starts after sol-gel reaction ran for 24 h at room temperature (Latex-5 of Table S1), and  $\text{NH}_4\text{OH}$  is added after polymerization of St for: (b) 0 min (Latex-6 of Table S1), (c) 60 min (Latex-1 of Table S1), (d) 180 min (Latex-8 of Table S1).

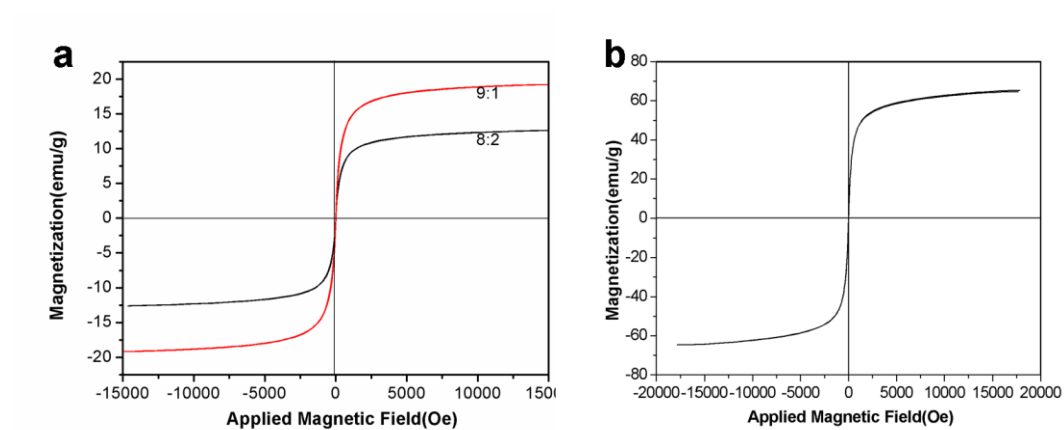


Figure S6. Magnetization curves (at 300 K) of (a) the yolk-shell magnetic nanocomposites (Latex-1,-2 of Table S1), and (b) the oleic acid modified  $\text{Fe}_3\text{O}_4$  nanoparticles.