

## Facile synthesis of uniform yolk-shell structured magnetic mesoporous silica as an advanced photo-Fenton-like catalyst for degrading rhodamine B

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### Experimental section

#### Materials

FeCl<sub>3</sub>·6H<sub>2</sub>O, trisodium citrate, ethylene glycol, sodium acetate, tetraethyl orthosilicate (TEOS), ethanol, concentrated ammonia solution (28 wt%), methanol, hexadecyl trimethyl ammonium bromide and rhodamine B were of analytical grade and purchased from Sigma-Aldrich (USA). All chemicals were used as received without further purification. Millipore water was used for all experiments.

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles

The superparamagnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were prepared *via* a solvothermal method reported previously <sup>1</sup>. Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (3.25 g), trisodium citrate (1.3 g), and sodium acetate (NaAc,

6.0 g) were dissolved in ethylene glycol (80 ml) with agitation. The mixture was stirred vigorously for 1 h at room temperature and then transferred into a Teflon-lined stainless-steel autoclave (100 mL in capacity). The autoclave was heated at 200 °C for 10 h, and then allowed to cool to room temperature. The black products were washed with deionized water and ethanol for 3 times, respectively.

### **Synthesis of core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanospheres**

The core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanospheres were prepared through a versatile Stöber sol-gel method<sup>2</sup>. For a typical synthesis, an ethanol dispersion of the Fe<sub>3</sub>O<sub>4</sub> magnetite particles obtained above (3.0 mL, 50 mg/mL) was added into a three-neck round-bottom flask with a mixture of ethanol (280 mL), deionized water (70 mL) and concentrated ammonia solution (4.0 mL, 28 wt%). The mixed solution was sonicated for 15 min. Then, 2.0 mL of TEOS was added dropwise in 10 min, and the reaction was allowed to proceed for 12 h at room temperature under continuous mechanical stirring (400 rpm). The resultant products (denoted as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>) were separated and collected with a magnet, followed by washing with deionized water and ethanol for 3 times, respectively.

### **Synthesis of core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mesoporous silica (mSiO<sub>2</sub>) nanospheres**

The coating of uniform mSiO<sub>2</sub> shell was prepared *via* a soft template method. Typically, half of the core-shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanospheres obtained above were added into a 250 ml of three-neck flask containing 25 ml of H<sub>2</sub>O, 10 ml of ethanol, 0.25 ml of ammonia and 75 mg of CTAB. The mixture was sonicated for 30 min. Subsequently, 0.12 mL of TEOS was added dropwise in 5 min, and the reaction was allowed to proceed for 6 h at room temperature under continuous mechanical stirring (300 rpm). The product (designated as Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mSiO<sub>2</sub>) was collected by magnets and washed with H<sub>2</sub>O and ethanol for 3 times for further use.

### **Synthesis of yolk-shell $\text{Fe}_3\text{O}_4@\text{void}@m\text{SiO}_2$ nanospheres**

The yolk-shell structured  $\text{Fe}_3\text{O}_4@\text{void}@m\text{SiO}_2$  nanospheres were prepared by using an ultrasound cooperative surfactant-directed selective etching method in a sodium carbonate solution. For a typical procedure, the as-made  $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$  samples were added into a falcon tube with 40 mL water and 212 mg of sodium carbonate, and then placed into an ultrasound bath (2510R-DTH, 42 kHz, 100 W, BRANSON UL TRANSONICS CORPORATION, USA) for 6 h. During the ultrasonic treatment, the temperature in the bath was maintained at 20 °C by refluxing water. The resultant product was collected by magnets and washed with  $\text{H}_2\text{O}$  and ethanol for 3 times. The surfactant CTAB was removed in an ammonium nitrate ethanol solution (6 g L<sup>-1</sup>). The extraction was carried out in a similar method that used in the etching process. The obtained nanospheres were dissolved into a falcon tube with 40 mL water and 240 mg of ammonium nitrate, and then the mixture was subjected to ultrasonic treatment for 3 h. This process was repeated for twice to completely remove the template. Finally, the products (defined as  $\text{Fe}_3\text{O}_4@\text{void}@m\text{SiO}_2$ ) were washed with  $\text{H}_2\text{O}$  and ethanol for three times, and dried in an oven at 60 °C for 6 h.

For comparison, the amorphous silica middle layer in the core-shell structured magnetic mesoporous  $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$  nanospheres was also selectively etched off by using a mechanical stirring assisted approach in a weak alkaline solution reported previously<sup>3</sup>. For a typical synthesis, the as-made  $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$  samples were added into a three-neck round-bottom flask with 40 mL water and 212 mg of sodium carbonate. The mixture was heated at 50 °C under a vigorous stirring (400 rpm) for 12 h, and then the product was collected by centrifugation and washed with  $\text{H}_2\text{O}$  and ethanol for three times. The surfactant CTAB templates were extracted by 6.0 g/ml ammonium nitrate ethanol solution. The extraction was carried out at

60 °C for 24 h for twice to completely remove CTAB templates. The products were washed with H<sub>2</sub>O and ethanol for several times, and dried in an oven at 60 °C for 6 h.

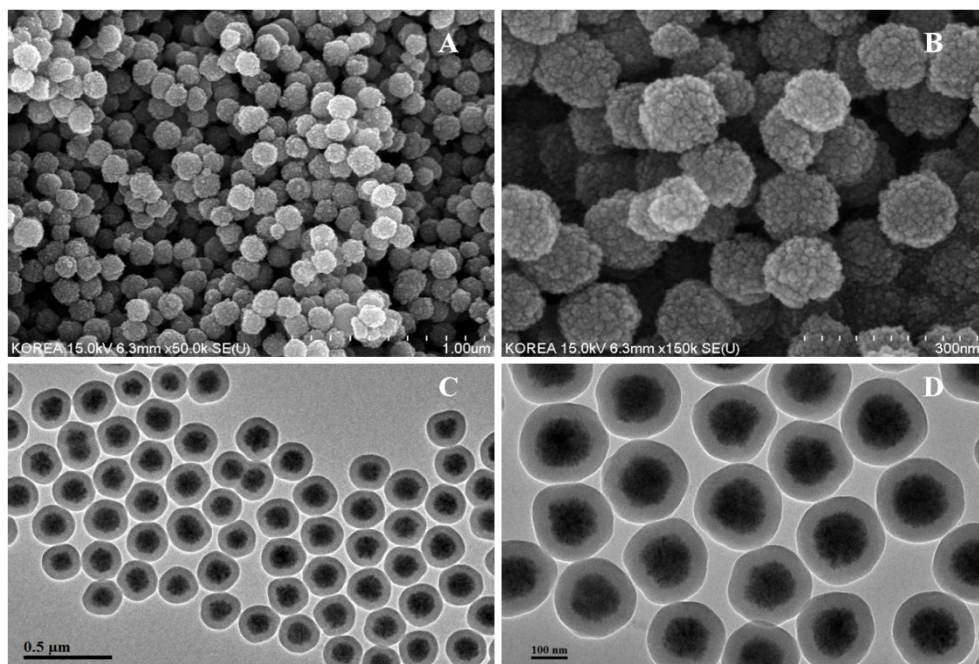
In addition, hollow structured mesoporous silica sphere was synthesized by etching off the inner Fe<sub>3</sub>O<sub>4</sub> core. In typical, the yolk-shell structured magnetic mesoporous silica obtained above was dissolved into 10 ml of HCl (0.1 mol L<sup>-1</sup>) and subjected to ultrasonic treatment for 2 h. The products were washed with H<sub>2</sub>O and ethanol for several times, and dried in an oven at 60 °C for 6 h.

### **Materials characterization**

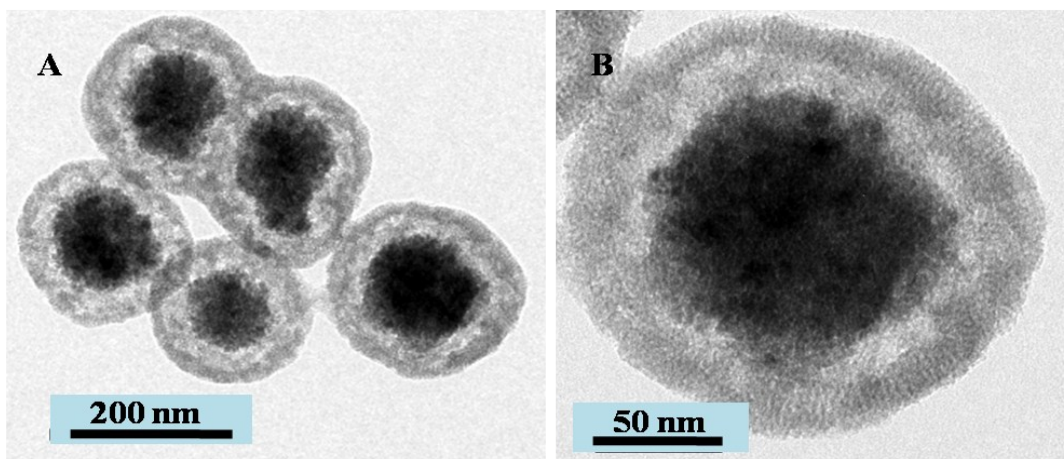
X-ray diffraction (XRD) patterns were recorded on a Bruker D8X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation (40 kV, 40 mA). Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer (USA). Prior to measurements, the samples were degassed in a vacuum at 180 °C for 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas ( $S_{\text{BET}}$ ) using adsorption data in the relative pressure range  $P/P_0 = 0.05 - 0.3$ . Using the Barrett-Joyner-Halenda (BJH) model, the pore size distributions were derived from the adsorption branches of the isotherms, and the total pore volumes were estimated from the adsorbed amount at the relative pressure  $P/P_0 = 0.995$ . Transmission electron microscopy (TEM) was carried out on a JEOL 2011 microscope (Japan) operated at 200 kV. For TEM measurements, the sample was suspended in ethanol and supported on a holey carbon film on a Cu grid. The magnetization was measured using a Vibrating Sample Magnetometer (EV9 including auto-matic sample rotation, Microsense, Japan) under a magnetic field of 10 KOe and a temperature of 24°C.

### **Photo-Fenton-Like Catalytic Experiments**

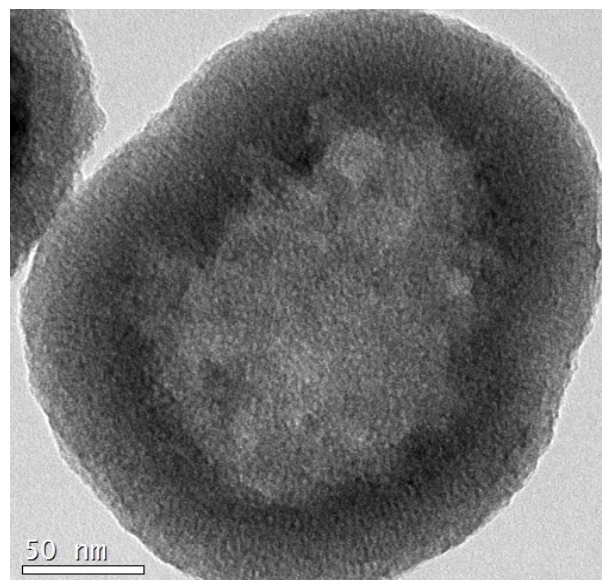
In a typical procedure, aqueous suspensions (100 mL) of RhB ( $10 \text{ mg L}^{-1}$ ) and a given amount of catalyst with equivalent  $\text{Fe}_3\text{O}_4$  (7.5 mg of bare  $\text{Fe}_3\text{O}_4$  or 10 mg of  $\text{Fe}_3\text{O}_4@\text{void}@m\text{SiO}_2$ ) and equivalent of  $\text{SiO}_2$  (2.5 mg of hollow structured mesoporous silica) were added to a reactor consisted of a double-layered cylindrical container with a capacity of 1.0 L ( $\Phi 10.0 \times 14.0 \text{ cm}$ ). The solution temperature was measured using a thermometer (Tecpel DTM-318) and maintained with a water jacket. The pH was adjusted by using  $\text{H}_2\text{SO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) and  $\text{NaOH}$  ( $0.1 \text{ mol L}^{-1}$ ), respectively and detected using a pH meter (Orion 3 Star). Prior to addition of  $\text{H}_2\text{O}_2$  (2 ml, 30%) and irradiation of UV light ( $\lambda = 380 \text{ nm}$ , 16 W), the mixture was mechanically stirred in dark for 30 min to reach the adsorption/desorption equilibrium between the catalyst and pollutants. Afterwards, at given time intervals, 2.0 mL of the suspension was removed using a 5mL syringe and was filtered by a membrane with a pore size of  $0.45 \mu\text{m}$ . Furthermore, 2 mL of methanol was added to the sample above to terminate the reaction. The mixed solution was analyzed by recording the variations of the absorption band maximum (554 nm) using a ThermoSpectronic UV 500 UV-visible spectrometer.



**Fig. S1** SEM images of Fe<sub>3</sub>O<sub>4</sub> particles prepared *via* a facile solvothermal method (A and B) and TEM images of core-shell structured Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanospheres fabricated through modified stöber method (C and D).

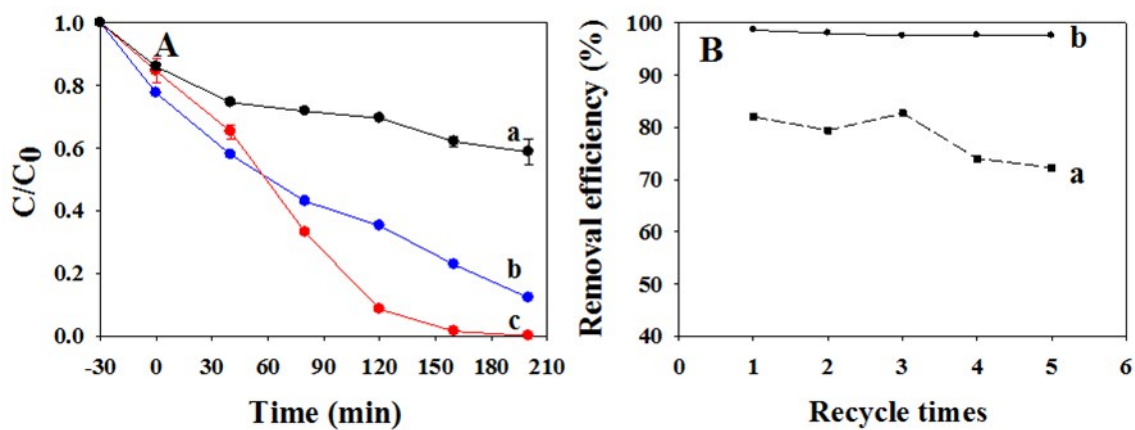


**Fig. S2** TEM images of yolk-shell structured magnetic mesoporous silica fabricated *via* the mechanical stirring assisted etching method.

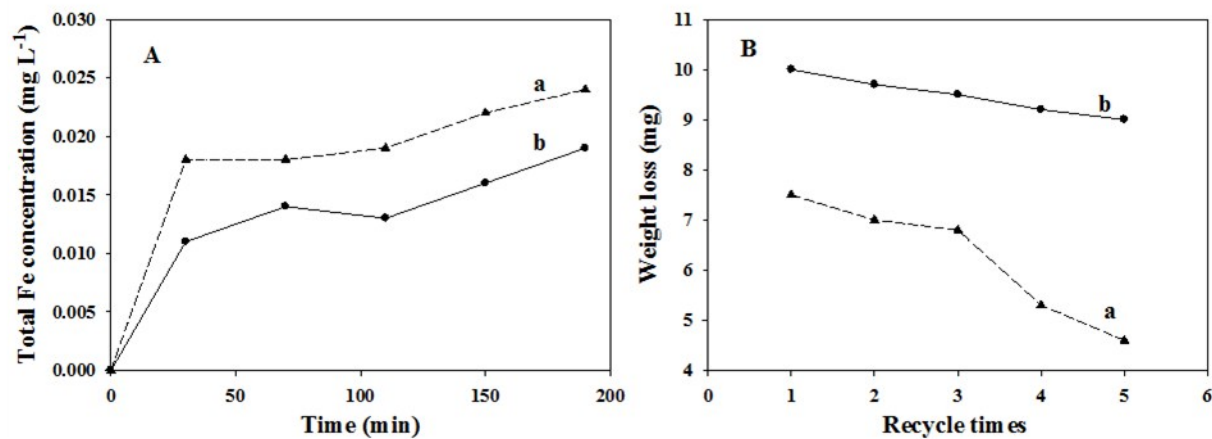


**Fig. S3** TEM images of the hollow mesoporous silica synthesized by etching off the inner magnetite cores.





**Fig. S4** (A) The photo-Fenton catalytic degradation performance of RhB in the presence of  $\text{Fe}_3\text{O}_4@\text{void}@\text{mSiO}_2$  at different pH: (a) pH = 10.0, (b) pH = 6.2, (c) pH = 3.0, and (B) the recycling test of (a) bared  $\text{Fe}_3\text{O}_4$  and (b)  $\text{Fe}_3\text{O}_4@\text{void}@\text{mSiO}_2$  at pH = 3. Before initiation of the reaction, the mixture was mechanically stirred in dark for 30 min to reach the adsorption/desorption equilibrium between the catalyst and pollutants.



**Fig. S5** (A) Total Fe leaching concentration versus reaction time and (B) Catalyst weight loss at each recycle. a) bared Fe<sub>3</sub>O<sub>4</sub> and b) Fe<sub>3</sub>O<sub>4</sub>@void@mSiO<sub>2</sub>.

1. Liu, J.; Sun, Z.; Deng, Y.; Zou, Y.; Li, C.; Guo, X.; Xiong, L.; Gao, Y.; Li, F.; Zhao, D., *Angew. Chem. Int. Ed.* **2009**, *48*, (32), 5875-5879.
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