

Experiment Detail

1 Materials

Polyvinylpyrrolidone (PVP, Mw~40k) and fluorescein isothiocyanate labeled dextran (FITC-dextran, Mw~40 000) were purchased from Sigma Aldrich. Tetraethyl orthosilicate (TEOS) and ammonia hydroxide solution (28 wt%) were purchased from Alfa Aesar. *n*-Pentanol ($\geq 99\%$) was purchased from Acros. Octadecyltrimethoxysilane (OTMS) was purchased from TCI. Hexadecyl trimethyl ammonium bromide and hexamethylenetetramine were obtained from Sinopharm Chemical Reagent Co. Ltd. Other compounds were obtained from Beijing Chemical Reagents Company, China. All of the reagents were of analytical grade and used without further purification. Water used throughout all the experiments was purified with the Millipore system.

2 Preparation of the hematite cubic colloids

The hematite cubic colloids ($\alpha\text{-Fe}_2\text{O}_3$) were synthesized by a process based on a method developed by Sugimoto et al. Briefly, aqueous solutions of sodium hydroxide (100 mL, 5.4 M) and iron(III) chloride (2 M, 100 mL) were mixed and stirred for 10 min to form a gel. The gel in a sealed Pyrex bottle was placed in the oven aged for 8 days at 100 °C. After that, the red products were sedimented before being collected and washed with deionized water several times before drying at 50 °C overnight.

3 Preparation of $\alpha\text{-Fe}_2\text{O}_3$ @meso-SiO₂

The cubic hematite was coated with mesoporous silica according to the method described by Zhao et al. with some modification. The reaction was achieved via a one-pot stratification approach by using cationic surfactant CTAB as the template, TEOS as the silica source, HMAT as the catalyst and cyclohexane as organic solvent. Firstly, CTAB (6 g), HMAT (200 mg) and $\alpha\text{-Fe}_2\text{O}_3$ (100 mg) were added to 60 mL of water and stirred gently at 60 °C for 1 h in a 250 mL round bottom flask. Then 20 mL of TEOS in cyclohexane (v/v, 20 %) was carefully added to the above solution and kept at 60 °C in an oil bath under a magnetic stirring for 12 h. The products were collected by centrifugation and washed with ethanol and water (1:1, v/v) several times. Then the products were extracted with a 0.6 wt % ammonium nitrate (NH_4NO_3) ethanol solution to remove the template at 60 °C for 6 h twice.

4 Etching of the hematite core

The hematite core was etched to modify its surface area based on the top-down method developed by Qi et al. The morphology of the hematite core can be controlled by etching for different time scales. For the etching process, $\alpha\text{-Fe}_2\text{O}_3$ @meso-SiO₂ particles (100 mg) were dispersed in 25 mL of ethanol. Then, hydrochloric acid (25 mL) was added under stirring and the mixture was stirred at 30 °C for different time scales to control the morphology of the core. The products were washed by ethanol and water (1:1, v/v) to diffuse the ions from the dissolved hematite and reach pH ~ 7 .

5 Preparation of the Janus micro-reactors

PVP K30 (6 g) in *n*-Pentanol (60 mL) was dissolved under sonication. Then 30 mg of the products from step 4 were added and sonicated for another 2 h. After that, a mixture of deionized water (640 μL), anhydrous ethanol (6 mL) and sodium citrate solution (400 μL , 180 mM in water) was added to the above solution. The reaction mixture was shaken for 10 min by hand to mix all the components. Ammonium hydroxide solution (1.190 mL, 28 wt %) was added and the flask was shaken again for another 5 min, and then the mixture was left standing for 10 min to release the gas bubble. TEOS (800 μL) was added and the mixture was shaken gently for 1 min. The

reaction was allowed to proceed undisturbed for 12 h at 30 °C. Then the hydrophobic monomer OTMS (400 μ L) was added and the flake was gently shaken again for 1 min. The hydrolysis of OTMS was lasted for another 8 h at 30 °C. The mixture was centrifuged with ethanol several times to collect the amphiphilic micro-reactors.

6 Characterizations

The products were characterized by transmission electron microscopy (TEM, JEOL 1011) and scanning electron microscopy (SEM, JEOL-4800). Nitrogen adsorption-desorption isotherms was obtained on Quantachrome Autosorb AS-1. The power XRD pattern was recorded on Rigaku D/max 2500 (Cu K α radiation). UV-Vis spectrophotometer (HITACHI U-3900).

7 Catalytic properties testing

Typically, a given amount of catalyst (2 mg) was dispersed in *n*-heptane (8 mL). A desired volume of water (2 mL) containing MB (3.33 ppm) was injected to oil phase. The mixture was sonicated for 30 sec and stirred for 15 min in the dark. The Fenton-like reaction was initiated by adding a known concentration of H₂O₂ (60 μ L, 30 wt%) to the mixture. Samples were taken at a given time interval for further UV-Vis detection.

Supplementary Figures

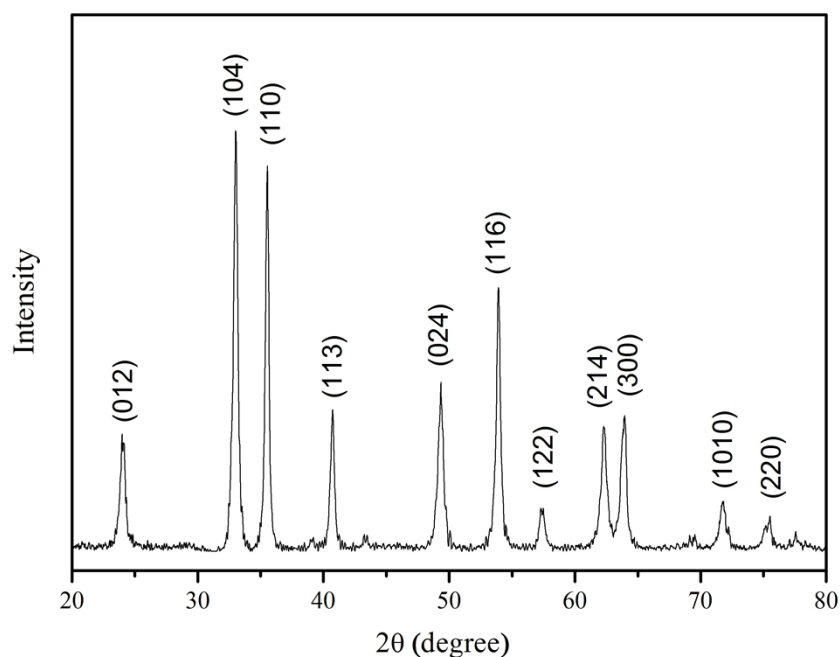


Figure S1. XRD pattern of the microcubes (α -Fe₂O₃). (JCPDS card 89-0597)

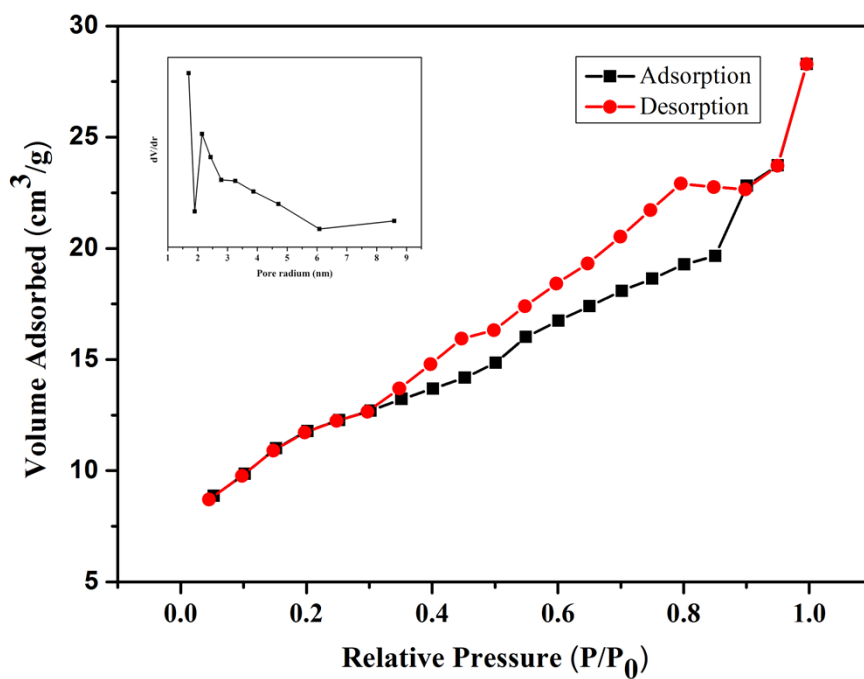


Figure S2. Nitrogen sorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution (inset, left top) of the $\alpha\text{-Fe}_2\text{O}_3$ @mesoporous SiO_2 .

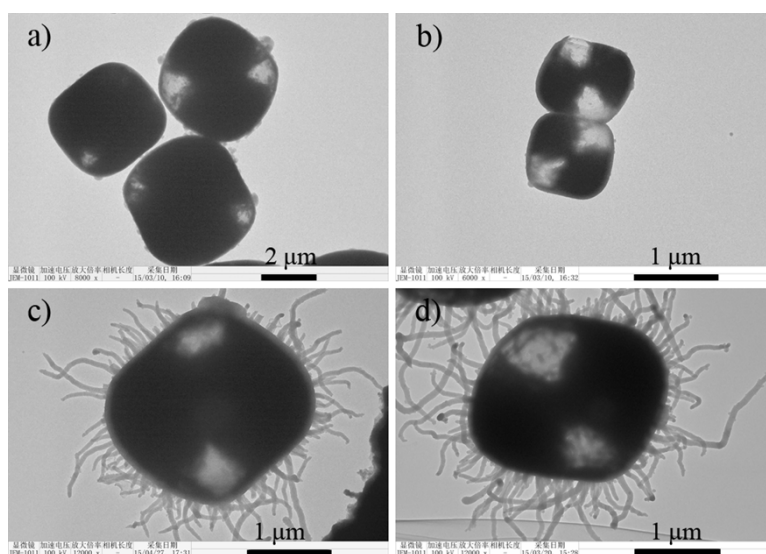


Fig. S3. TEM images of (a) (b) $\alpha\text{-Fe}_2\text{O}_3$ @mesoporous SiO_2 etched for 1 h and 1.5 h, respectively; TEM images of the corresponding amphiphilic rambutan-like micro-reactors with the core etched for 1 h and 1.5 h, respectively.