

Yolk/shell structured Fe₂O₃@mesoporous SiO₂ nanoreactor for enhanced activity as Fenton catalyst in total oxidation of dyes

Zhi-Min Cui, Zhe Chen, Chang-Yan Cao, Lei Jiang and Wei-Guo Song*

Experimental Details:

- 1. Preparation of Spindle Fe₂O₃:** A 75mL mix solution containing 0.02M FeCl₃·6H₂O and 0.45mM NaH₂PO₄ in deionized (DI) water was transferred to a 100mL teflon autoclave, and then heated at 105 °C in an electric oven for 48 h. After the autoclave cooled down, the monodispersed Fe₂O₃ (hematite) particles were centrifuged and washed with DI water.
- 2. Polymeric carbon coated Fe₂O₃:** 200mg Fe₂O₃ particles was dispersed in 5mL DI water by ultrasonication to form a suspension. 1.0 g glucose (C₆H₁₂O₆) was dissolved in another 5mL DI water, and the former suspension and another 5mL of ethanol were added to the solution under gentle stir. The resulting suspension was transferred to a 40mL Teflon autoclave, which was then heated at 190 °C in an electric oven for 12–15 h. The polymeric carbon-coated Fe₂O₃ particles were harvested by centrifugation and washed with DI water, then dried at 110 °C in an oven
- 3. Mesoporous SiO₂ coating:** The polymeric carbon coated Fe₂O₃ particles at last step was dispersed in the solution containing 80mL H₂O, 60mL ethanol, 0.28g CTAB (cetyltrimethylammonium bromide) and 1.14 mL NH₃·H₂O. After ultrasonic for 20min, 400 μL TEOS (tetraethyl orthosilicate) was added, and the mixture was vigorously stirred at room temperature for 6h. The precipitate was harvested after centrifugation and washed with distilled water three times and with ethanol for three times, then dried at 80 °C for 6h .
- 4. Calcination:** There are two different calcination way to get product in different crystalline phase. If the Fe₂O₃@C@SiO₂ product was heat-treated at 400 °C for 2h under N₂ following 6h under air atmosphere to remove the polymeric carbon coating and CTAB, the final product was γ-Fe₂O₃@mesoporous SiO₂ and if the Fe₂O₃@C@SiO₂ product was calcined directly in air at 400 °C, the final product was α-Fe₂O₃@mesoporous SiO₂.
- 5. Characterization:** The products were characterized by scanning electron microscopy (SEM, JEOL-6701), transmission electron microscopy (TEM, JEOL 1010/2010). The powder XRD pattern was recorded on Shimadzu XRD-7000 (Cu Kα radiation). Nitrogen adsorption–desorption isotherms was obtained on Quantachrome Autosorb AS-1. Plasma atom emission spectrometer (ICPE-90000) was employed to reveal the precise chemical composition of the Fe₂O₃@SiO₂ composite. Uv-Vis spectrophotometer (Shimadzu UV-2500)
- 6. Catalytic properties testing:** In a typical run, the reaction suspension was prepared by adding a given amount of catalyst with equivalent Fe₂O₃ (10.0 mg

Fe_2O_3 or 13.0 mg Fe_2O_3 @mesoporous SiO_2) to a 50 mL beaker containing 20ml MB solution (50ppm). Prior to reaction, suspension was sonicated for 5 min and magnetically stirred in the dark for 60 min to establish the adsorption/desorption equilibrium. Fenton-like reaction was initiated by adding a known concentration of H_2O_2 (1.2 mL, 30 wt %) to the solution. Samplings were taken at a given time intervals during the reaction. The sample was separated quickly by centrifugation and 150 μL of them was diluted to 3 mL for the further Uv-Vis detection.

Supporting Figures

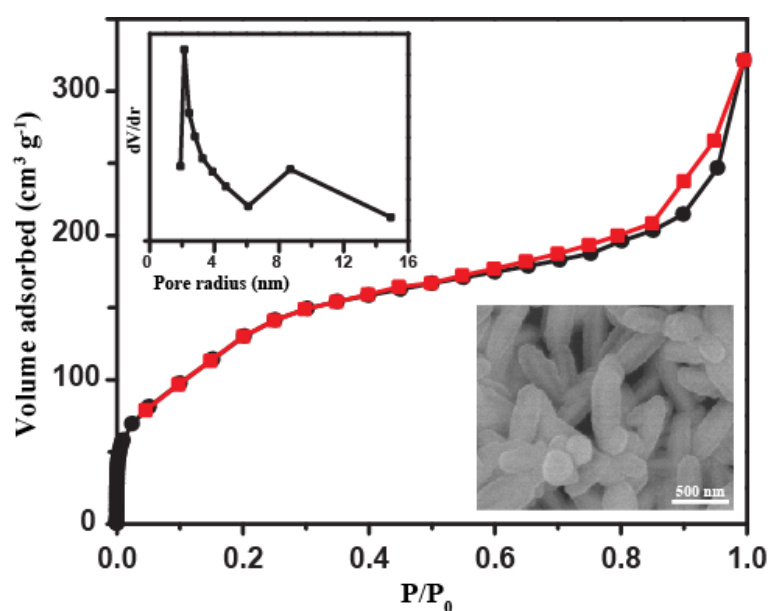


Figure S1. Nitrogen sorption isotherm and Barrett-Joyner-Halenda (BJH) pore size distribution (insert, top) of the yolk/shell structured Fe_2O_3 @mesoporous SiO_2 nanoreactor. Two evident peaks at 2.1 nm and 8.7 nm were due to the pore size of the mesoporous shell at about 2 nm and the void space between the yolk and shell, respectively. Insert (bottom) is their corresponding SEM image.

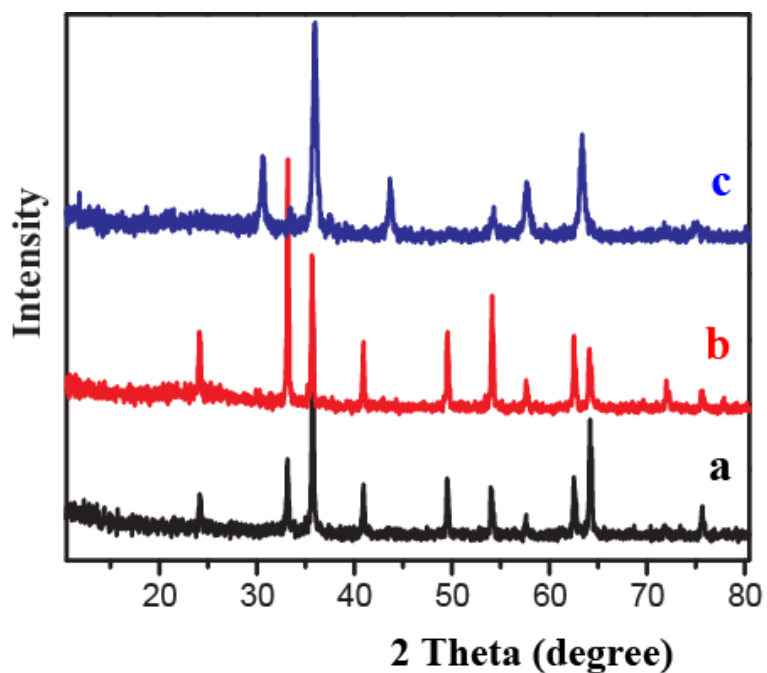


Figure S2 XRD pattern of a) as-synthesized spindle Fe₂O₃, b) α-Fe₂O₃@mesoporous SiO₂ obtained by calcination at 400 °C in air, and c) γ-Fe₂O₃@mesoporous SiO₂ obtained by calcination at 400 °C first in N₂ then in air

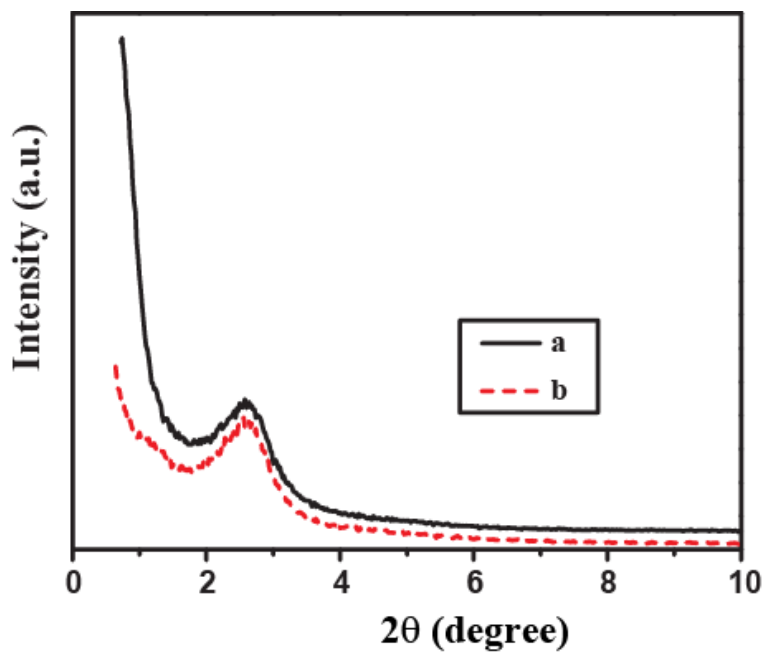


Figure S3 Low angle XRD pattern of a) fresh Fe₂O₃@mesoporous SiO₂ nanoreactor and b) the used Fe₂O₃@mesoporous SiO₂ nanoreactor

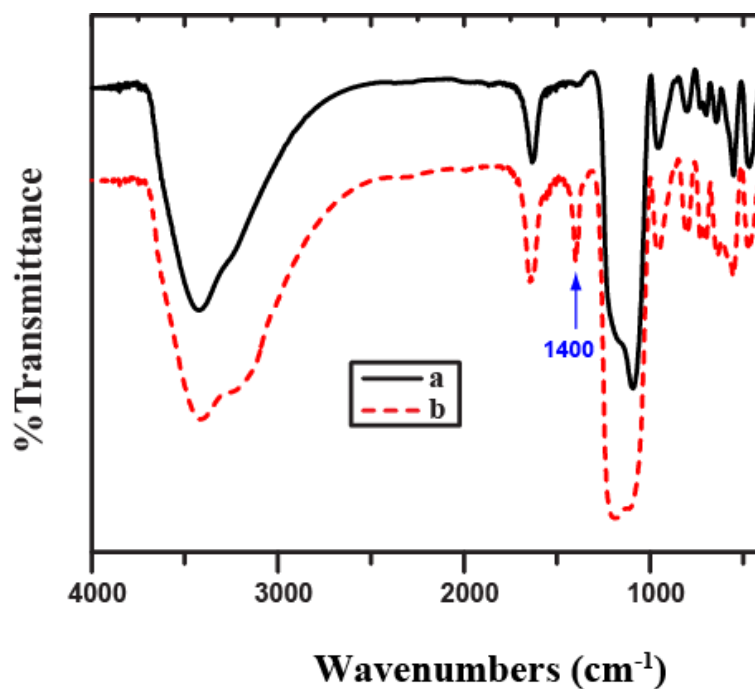


Figure S4 FTIR spectra of a) fresh and b) used Fe₂O₃@mesoporous SiO₂ nanoreactor. The fresh and the used Fe₂O₃@SiO₂ have almost the same adsorption, indicating that there is no organic residue on the shell of the catalysts. A new peak at 1400 cm⁻¹ was attributed to carboxylate that was produced by the oxidation of MB.

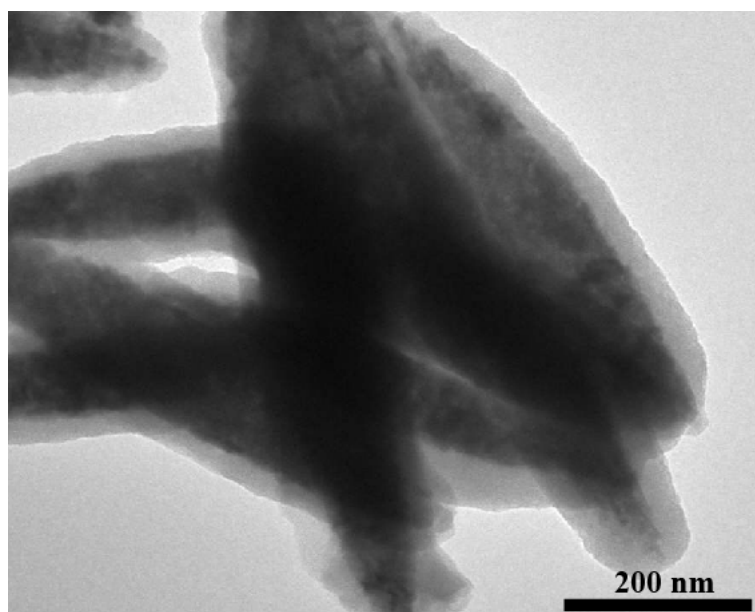


Figure S5 TEM image of Fe₂O₃@mesoporous SiO₂ composite with no void space between the spindle Fe₂O₃ core and the mesoporous SiO₂ shell.

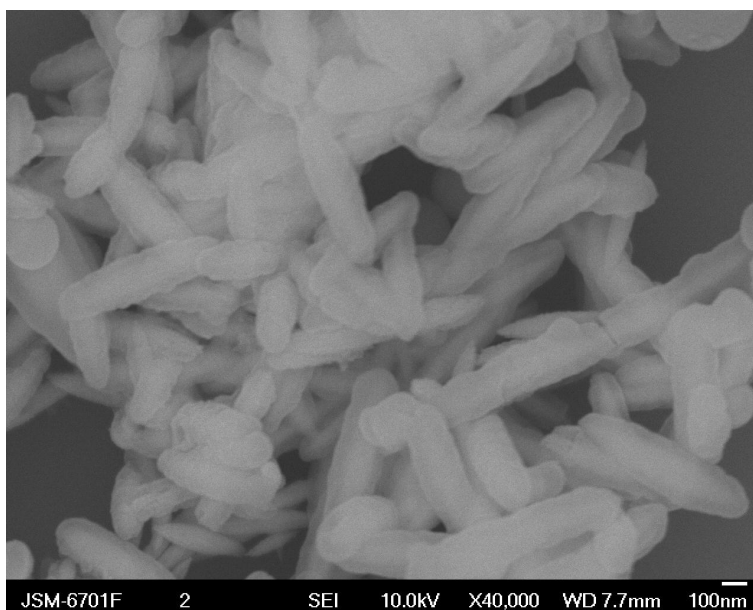


Figure S6 SEM image of Fe_2O_3 @mesoporous SiO_2 composite with void space of 40 nm.