Electronic supplementary Information

Formation of Fe_xO_y hollow nanospheres inside cage type highly ordered mesoporous material: a nanocasting pathway

Hongxiao Jin,[a] Chiya Wang,[a] Bo Hong,*[a] Langsheng Ling,[b] Xiaojian Gu, Dingfeng Jin,[a] Xiaoling Peng,[a] Xinqing Wang[a] and Hongliang Ge[a]

[a] *Zhejiang Province Key Laboratory of Magnetism, College of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, People's Republic of China. Fax: +86-571-8687-5600; Tel: +86-571-8687-5600; E-mail: Bohong@cjlu.edu.cn or hongbo@mail.ustc.edu.cn.*

[b] *High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, People's Republic of China.*

1. Experimental Section

1.1 Materials. Tetraethyl orthosilicate (TEOS) (99%), 1,3,5-trimethylbenzene (TMB), potassium chloride (KCl), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and Iron (III) nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] were purchased from Shanghai Chemical Reagent Factory of China without further treatment. Triblock copolymer poly (ethylene oxide)-b-poly (propylene oxide)-b-poly(ethylene oxide) Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, MW = 12600) was purchased from Aldrich. Distilled water was used in all experiments.

1.2 Synthesis of LP-FDU-12 Silica. The synthesis of mesoporous silica LP-FDU-12 has been reported previously by Fan and co-workers (*J. Am. Chem. Soc.* 2005, **127**, 10794). The synthesis was as follows: 4.0 g of F127, 4.8 g of TMB, and 20 g of KCl were dissolved in 240 mL of H_2O and 50 mL of HCl at 15 °C. After 6 h of stirring, 20 mL of TEOS was added to this solution. After further stirring for 20 h, the mixture was transferred into an autoclave and heated at 100 °C for 24 h. As-made products were obtained by filtration and dried at room temperature in air. To achieve less shrinkage pore structure, the sample was refluxed in 4 M H_2SO_4 for 20 h to remove the template (*Chem. Mater.* 2004, **16**, 2918).

1.3 Preparation of the hollow nanospheres. In a typical synthesis of Fe_xO_y hollow nanospheres, 6.73 g of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 30 mL of ethanol followed by the addition of 2 g of mesoporous silica template. The mixture was stirred at room temperature until a nearly dry powder had been obtained; the sample was then heated slowly to 200 °C and calcined at the same temperature for 3 h to pyrolyze the nitrate, followed by calcination at 450 °C for 6 h with a ramp 1 °C min^{-1} for metal oxide to crystallize. The resulting sample was twice treated with a hot 2 M NaOH solution to remove the silica template, followed by washing with water and ethanol several times, and then drying at 60 °C. This procedure leads to Fe_xO_y hollow nanospheres with a poor-crystaline structure. Reduction for Fe_3O_4 hollow nanospheres was achieved by heating at 350 °C for 1 h under a 50 mL/min H_2/Ar (5:95) atmosphere. For the preparation of γ-Fe_2O_3 hollow nanospheres, the as-prepared Fe_3O_4 hollow nanospheres were heated at 250 °C for 2 h in air. Both the oxidation and reduction reaction were monitored by TG showing almost stoichiometric ratio of the reactants were transform to products in the reactions.

1.4 Characterization. The Iron oxides hollow nanospheres phase were monitored by low-angle X-ray diffraction (XRD) and recorded on a Siemens D8 Advance diffractmeter with Ni-filtered Cu Kα radiation. Transmission electron microscopy (TEM) experiments were conducted on a JEOL-JEM-2010 microscope operated at 200 kV. Nitrogen physisorption experiments were measured at 77 K on a nitrogen adsorption apparatus (ASAP 2020) after degassing samples at 180 °C for 5 h. The Brunauer−Emmett−Teller (BET) surface area (S_{BET}) was estimated using adsorption data in a relative pressure range from 0.04 to 0.2. The mesopore size distributions (PSD) were calculated by analyzing the adsorption data of the N_2 isotherm using the Barrett−Joyner−Halenda (BJH) method. TG and DTA analyses were carried out using SDT-Q600 (TA instuments).The magnetic properties were measured by using a Superconducting Quantum Interference Device (SQUID) MPMS system under a 0.005 T magnetic field. The samples were first cooled down to 4 K without any external magnetic field. Then, the M−T measurements were performed with warming to 300 K at a 0.005 T field. The FC curve was obtained after the temperature was reduced to 4 K at 0.005 T field and then measured with heating up to 300 K at the same magnetic field. The M−H hysteresis loops were measured with a field sweep from 6 to −6 T at different temperatures.

2. Table and Figures

Table S1. Structural properties of the template and iron oxides hollow nanospheres.

Sample	S_{BET} (m^2 g^{-1})	V_T (cm^3 g^{-1})	d_0 (nm)	D_w (nm)
LP-FDU-12	1007.5	0.790	14.8	19.8
Fe_xO_y	107.9	0.248	13.5	16.3
Fe_3O_4	91.5	0.248	14.7	16.1
γ-Fe_2O_3	88.0	0.222	13.4	15.8

S_{BET} is the specific surface area deduced from the isotherm analysis in the relative pressure range of 0.05-0.2; V_T is the total pore volume at relative pressures 0.95; d_0 is the pore diameter calculated from the adsorption branch of the isotherm using the BJH method; D_w is the average sphere diameter measured from TEM.

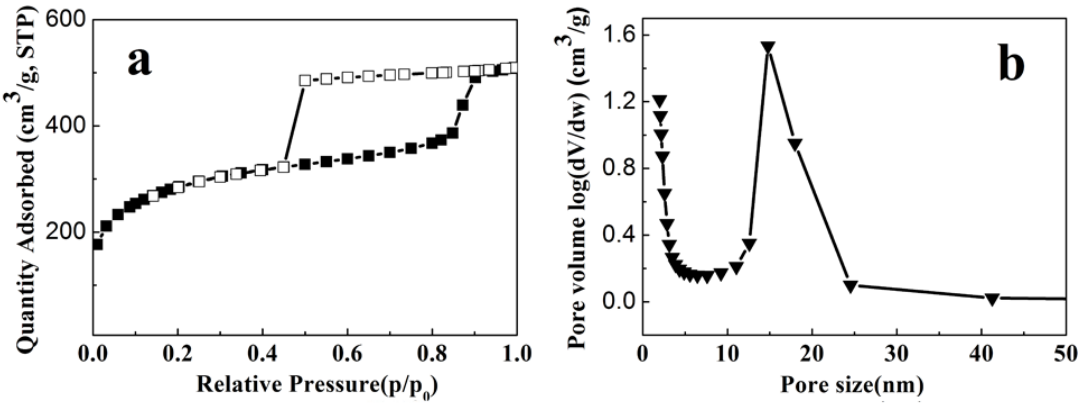

Figure S1 Nitrogen physisorption and pore size distributions for the LP-FDU-12

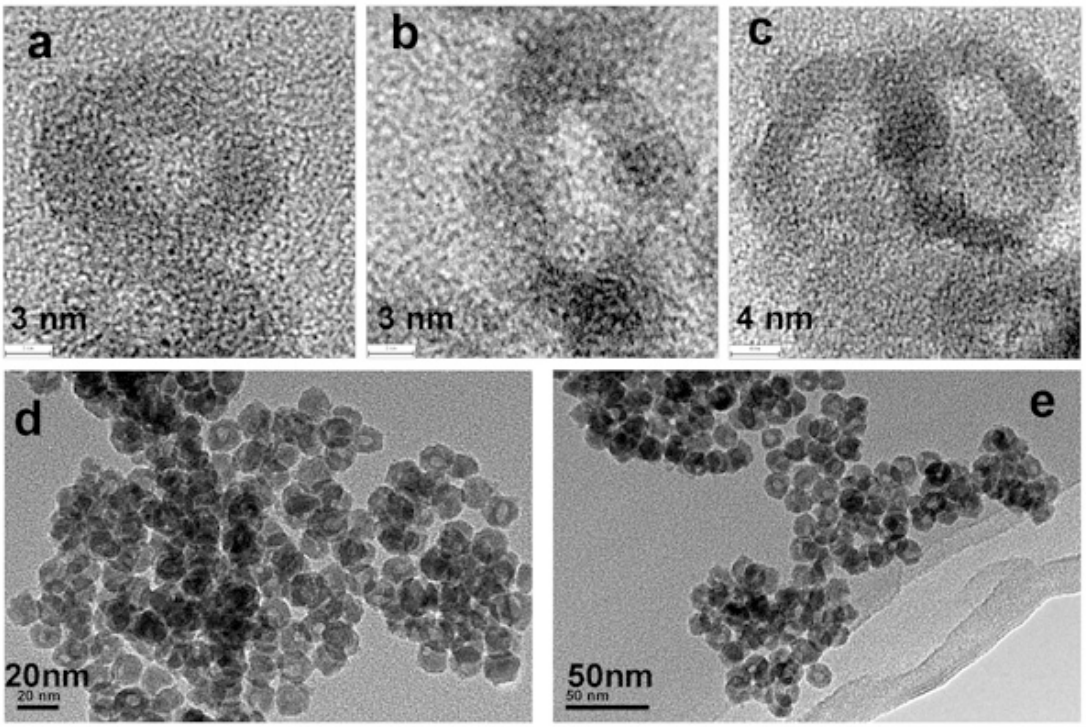

Figure S2 TEM images of Fe_xO_y hollow nanospheres: (a-c) HRTEM images, (d, e) TEM images.

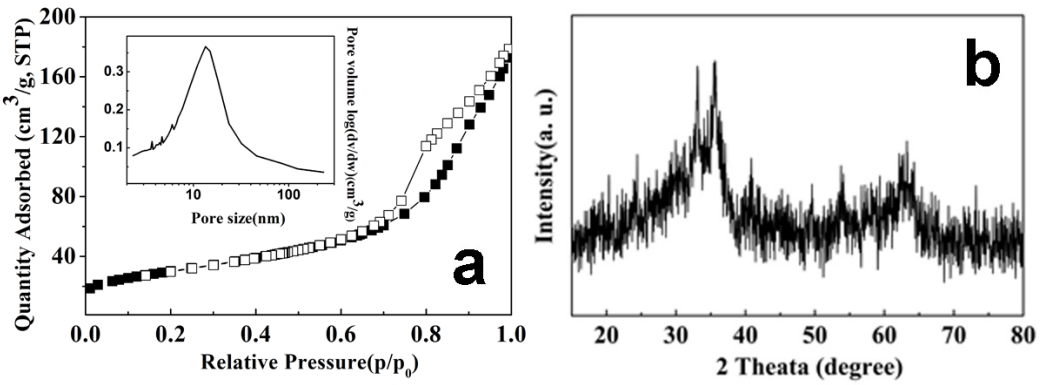

Figure S3 Nitrogen physisorption and pore size distributions (Left) and Wide-angle powder XRD pattern (Right) for the Fe_xO_y hollow nanospheres.

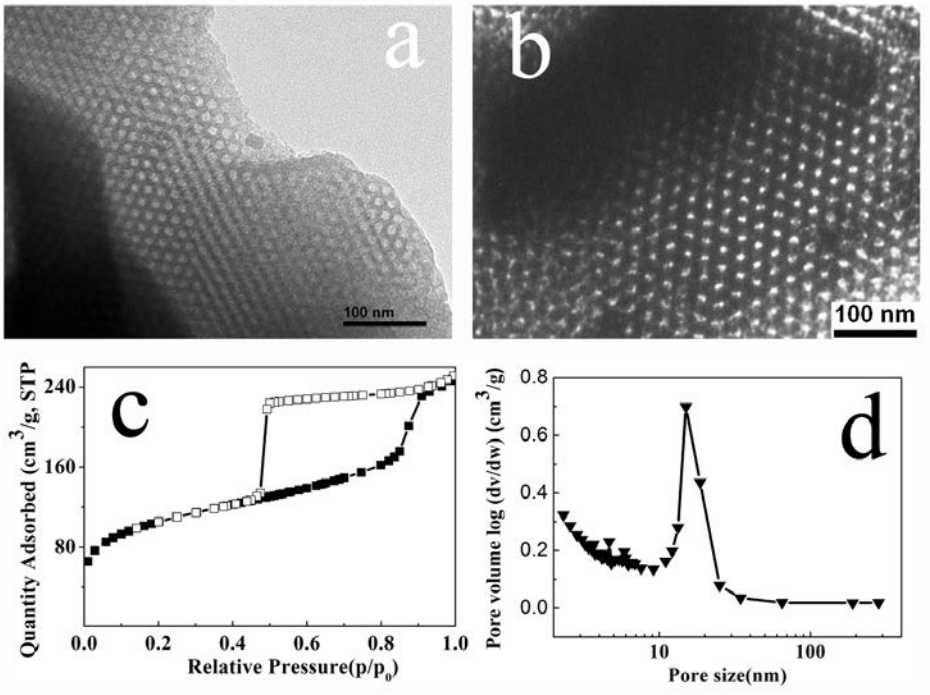

Figure S4 TEM images of (a) LP-FDU-12 and (b) hybrid of LP- FDU-12 and Fe_xO_y, and (c) nitrogen physisorption and (d) pore size distributions for the hybrid.

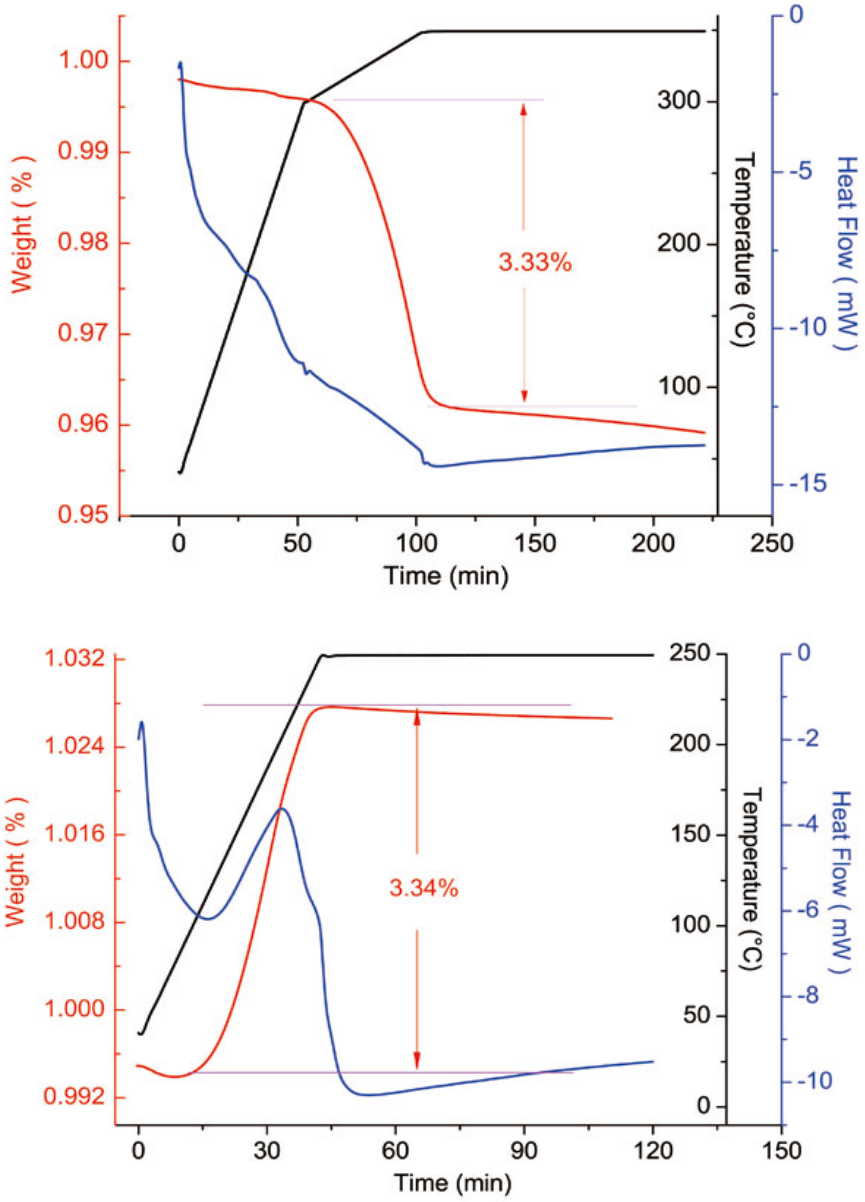

Figure S5 TG-DSC analyses as a function of time for reduction syntheses of Fe_3O_4 hollow nanospheres (up, heating rate: ramp 5 ℃/min to 300 ℃, then 1 ℃/min to 350 ℃ and isotherm at 350 ℃ for 1h) and oxidation syntheses of γ-Fe_2O_3 hollow nanospheres (down, heating rate: ramp 5 ℃/min to 250 ℃ and isotherm at 250 ℃ for 2h). Curves in red: percent of weight loss or gain; curves in blue: heat flow; curves in black: temperature. The results show theoretical percent weight lost or gained in the syntheses.

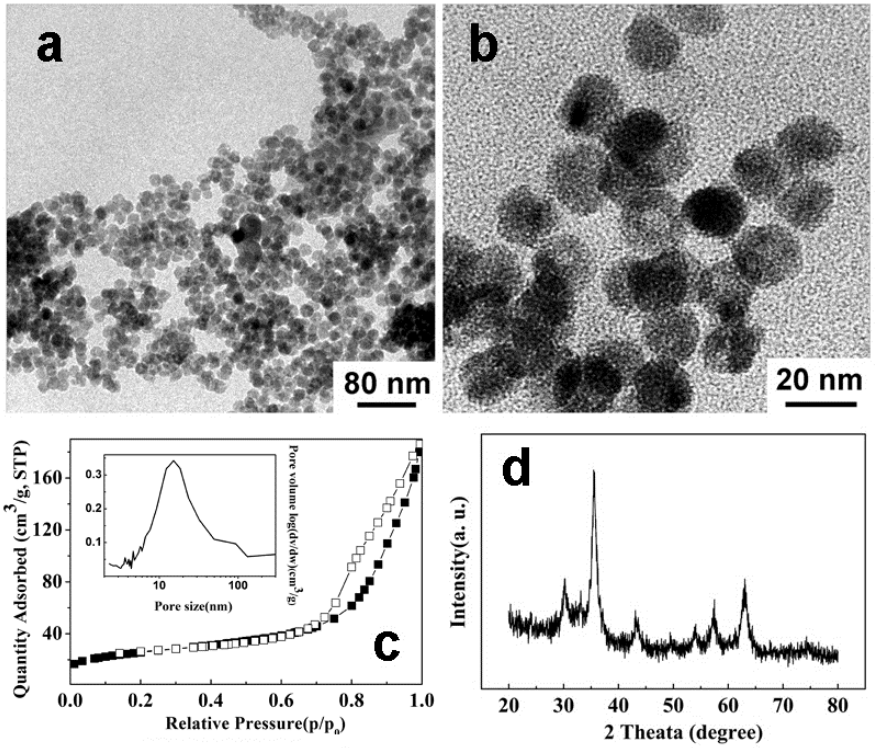

Figure S6 Structural characterization of Fe_3O_4 hollow nanospheres: (a, b) TEM images, (c) Nitrogen physisorption and pore size distributions, (d) XRD pattern.

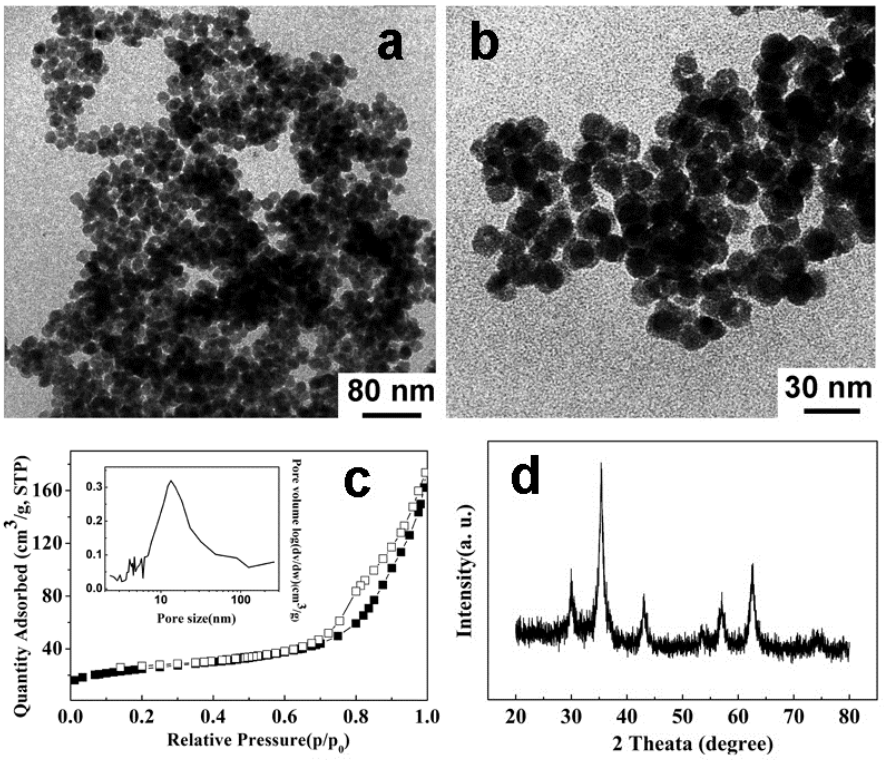

Figure S7 Structural characterization of γ-Fe_2O_3 hollow nanospheres: (a, b) TEM images, (c) Nitrogen physisorption and pore size distributions, (d) XRD pattern.