Supplementary Information for
Facile Preparation and Characterization of Glass/Fe_3O_4 Core/Shell Composite Hollow Spheres

Experimental details

Preparation

The hollow glass spheres All reagents were of analytical grade and used without further purification. The hollow glass spheres used as the core particles were synthesized by a two-step spraying-drying and subsequent fire torching method. A slurry was made by adding SiO_2, CaO, Na_2CO_3 with a certain proportion (determined by the final proportion of Si, O, Ca and Na in the HGS) into deionized water and stirred vigorously for 2.0h. Then the slurry was spry dried and quasi spherical precursor with hollow cores was obtained, caused by evaporation of the solvent and surface tension. The precursor particles were then immediately introduced into a propane/air torch to get spherical glass particles with hollow cores and smooth surface. In the high temperature smelting process, the precursor particles encountered the flame and were further sphericized due to the high flame temperature and surface tension of the glass melt. The SEM image and the EDX spectrum of the as-obtained HGS are shown in the Supplementary Information (Figure S1).

Glass/Fe_3O_4 core/shell composite hollow spheres In a typical experiment, 6mmol of ferrous chloride ($FeCl_2$•$4H_2O$) was added into 30ml of a mixture of ethanol and deionized water (the volume ratio of ethanol and deionized water varies depending on different solvent system required, see TABLE S1) and stirred until totally dissolved. After adding 0.3g of hollow glass spheres (HGS), the mixture was stirred vigorously for 5min and then was transferred into a 50mL Teflon-lined stainless steel autoclave. The autoclave was heated at a rate of 15℃/min to 180℃ and kept for 12h. Solvothermal reactions with different time intervals (1, 5, 10 h) were carried out at 180 ℃ to investigate the morphology evolution of the shell layer. Afterwards, the autoclave was cooled to room temperature naturally and the red floater in the reaction solution was isolated and rinsed twice with distilled water. The dried powder obtained in the solvothermal process were then annealed in a tube furnace at 360℃ under a continuous hydrogen/argon [$H_2/(H_2+Ar)$ = 8/100] gas flow for 5 h and then cooled to room temperature naturally. The obtained black products were glass/Fe_3O_4 core/shell composite spheres.

Characterization

X-ray diffraction (XRD) analysis was carried out on a Regaku D/max2200PC diffractometer with Cu-Kα radiation (λ=1.5406 Å). The scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were obtained using a Hitachi S-4300 microscope and EMAX Horiba, respectively. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were performed with a Philips TECNAI-20 transmission electron microscope at an acceleration voltage of 200 kV. The particle density of the composite hollow spheres was measured by Archimedes method with water as the immersion fluid. The temperature dependence magnetization measurements were performed on a physical property measurement system (PPMS-9T), zero-field cooling (ZFC) and field cooling (FC) curves were recorded at an applied magnetic field of 100Oe between 5K and 300K. Room temperature magnetic measurements were carried out using a vibrating sample magnetometer (VSM, Lakeshore 7307, USA) with a maximum magnetic field of 1T.

Figure S1. SEM image and EDX spectrum (inset) of the pristine hollow glass spheres used as the core.

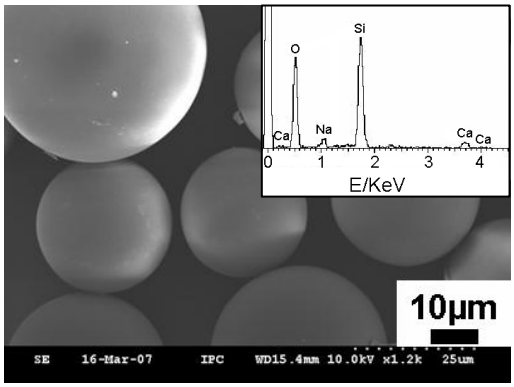

Figure S2. XRD patterns of: (a) the pristine HGS, (b) the as-obtained glass/Fe_3O_4 core/shell composite hollow spheres.

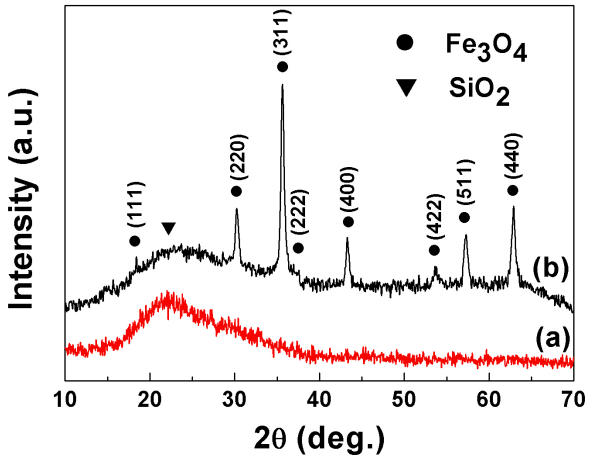

Figure S3. SEM image of the glass/α-Fe_2O_3 composite spheres as the precursors prepared after solvothermal treatment with an ethanol/water ratio of 4:1 (v/v, Sample A). The scale bar in the inset presents 500nm.

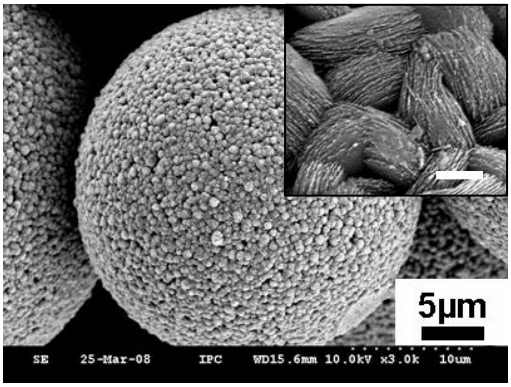

Figure S4. (a) TEM image of a single multilayered wafer from the composite spheres, and (b) HRTEM image taken near the tip of the wafer.

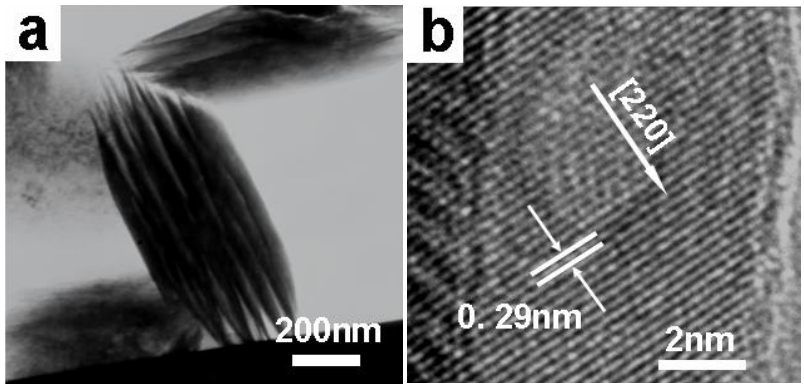

Figure S5. SEM images of: (a) the glass/Fe_3O_4 core/shell composite hollow spheres obtained with a $FeCl_2$ concentration of 0.05M, (b) isolated Fe_3O_4 particles obtained in the absence of HGS. The scale bar in the inset of panel (a) presents 5μm.

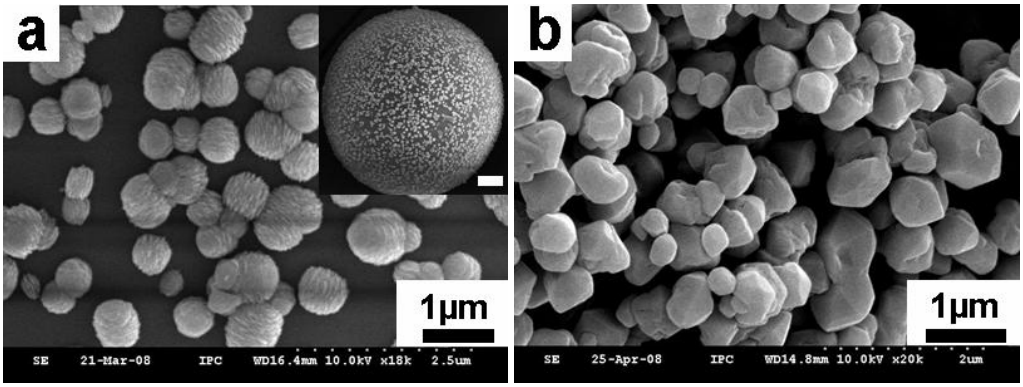

TABLE S1: Typical Solvent Compositions for the Preparation of Different Samples.

Sample no.	Composition of the solvent: Ethanol/water (v/v)	Building units of the magnetite shell
A	4: 1	Multilayered wafers (~10 layers)
B	0: 1 (pure water)	Single-layered wafers
C	1: 0 (pure ethanol)	Multilayered wafers (10~15 layers)
D	2: 1	Multilayered wafers (5~10 layers)
E	1: 1	Multilayered wafers (1~5 layers)