SUPPORTING INFORMATION

Preparation of Hollow Spheres with Controllable Interior Structures by Heterogeneous Contraction

Jianguo Guan,* Fangzhi Mou, Zhigang Sun and Weidong Shi

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P. R.China.

Experimental Section

An aqueous solution containing 22 wt.% iron citrate and 18 wt.% polyvinylpyrrolidone (PVP, k-30) was transferred into a syringe connected to a metallic nozzle, and fed at a constant rate of 0.1 $mL \cdot h^{-1}$ through a syringe pump (TJ-1A, Longer Pump, China). The metallic nozzle was connected to a high voltage supply (HB-Z303-20AC, Heng Bo High Voltage Power Supply Plant, China), and the collector was placed 15 cm below the metallic nozzle. Upon applying a high voltage of 25 kV, a fluid jet was ejected from the metallic nozzle and broken up into tiny droplets owning to electrostatic repulsion. These charged tiny droplets then underwent a violently and rapidly solution evaporation, and the gel microspheres were collected on an Al substrate. To obtain γ-Fe_2O_3 microspheres with various structures, the electrospray gel microspheres were calcined at 500 ^oC for 2h in air with various heating rate (R) of 1, 10, 20, 50 and 250 $^oC \cdot min^{-1}$, respectively. To verify the proposed heterogeneous contraction mechanism, the electrospun iron citrate (80 wt.%)/polyvinylpyrrolidone (PVP) (20 wt.%) gel fibers were also calcined at 500 ^oC for 2 h in air with R of 100 and 250 $^oC \cdot min^{-1}$ to fabricate the γ-Fe_2O_3 fiber-in-tube and tube-in-tube structures, respectively.

Scanning Electron Microscopy (SEM) images were obtained using a Hitachi S-4800 (Japan) Field-emission SEM. Transmission Electron Microscopy (TEM) images were captured on a JEM-2100F instrument at 200.0 kV. Thermogravity-differentiate scanning calorimeter (TG-DSC) analysis was carried out on a NETZSEC STA-449C (Germany) thermal analyzer. The phase purity of the products was examined by an X-ray diffraction (XRD) pattern obtained using a Rigaku D/max-IIIA (Japan) diffractometer at a voltage of 40 kV and a current of 200 mA with Cu-Kα radiation (λ=1.5406 Å), in the 2θ range from 10 to 90° at a scanning step of 0.02 °. A micro-Raman study was

performed on the Renishaw inVia (Britain) laser confocal Raman microscope at room temperature under the excitation of 514.5 nm wavelength of an Ar^+ laser. The laser power was limited to 0.5 mW to avoid possible phase transition during the laser irradiation.

Supplementary Figures:

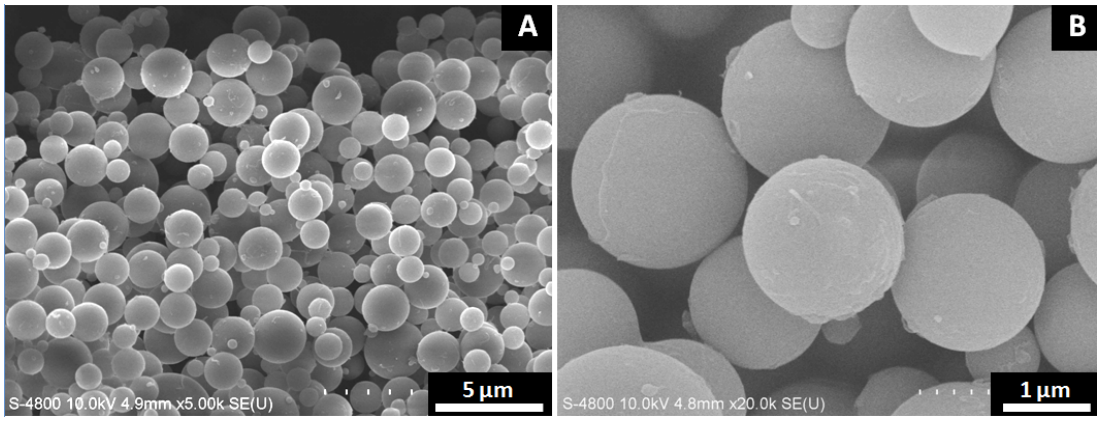

Fig. S1 SEM images of iron citrate (55 wt%)/PVP (45 wt%) composite microspheres obtained by electrospraying the 40 wt% aqueous solution.

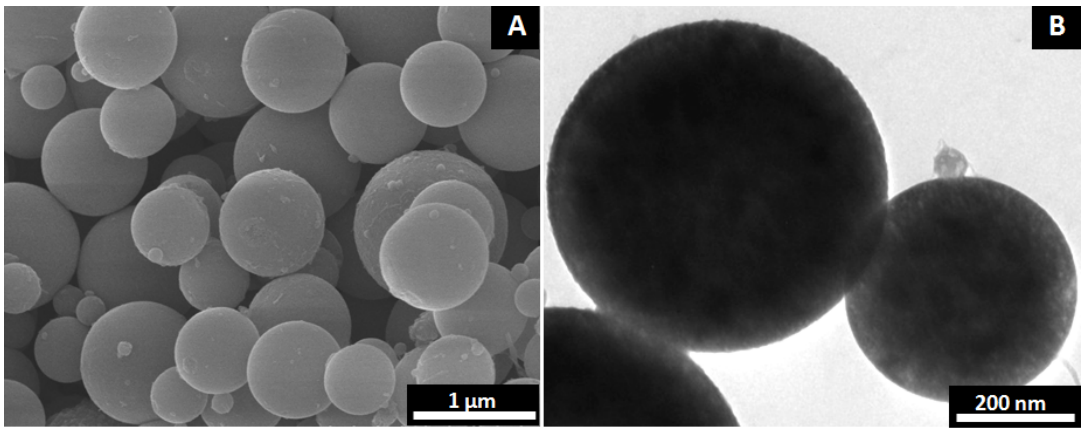

Fig. S2. SEM (A) and TEM (B) images of the solid γ-Fe_2O_3 spheres obtained by calcinating the electrosprayed gel microspheres at 500 ^oC for 2h with the heating rate of 1 $^oC \cdot min^{-1}$.

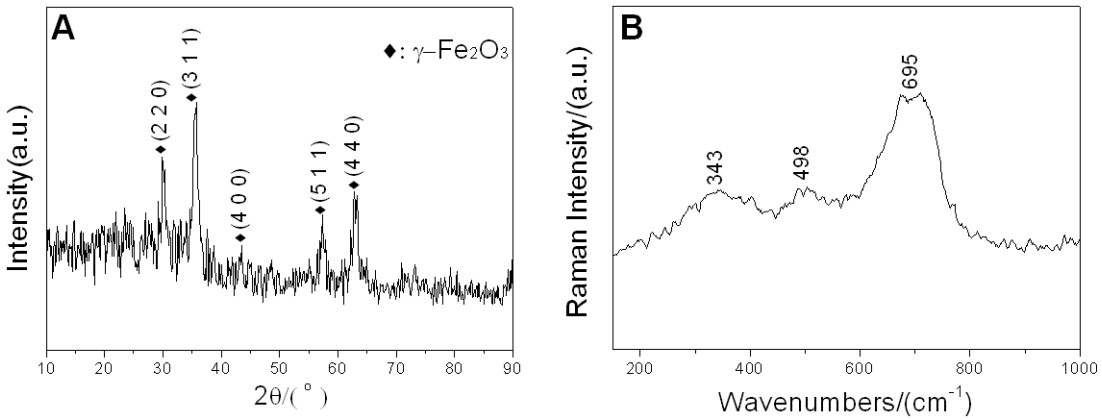

Fig. S3. The XRD Pattern (A) and Raman spectrum (B) of the as-obtained core-in-double-wall hollow spheres; the XRD Pattern is matched well with the standard XRD pattern of maghemite (JCPSD Card NO. 19-0629), and the Raman peaks at 343, 498 and 695 cm^{-1} are consistent with the E_g, T_{2g} and A_{1g} modes of inverse spinel structure of γ-Fe_2O_3.

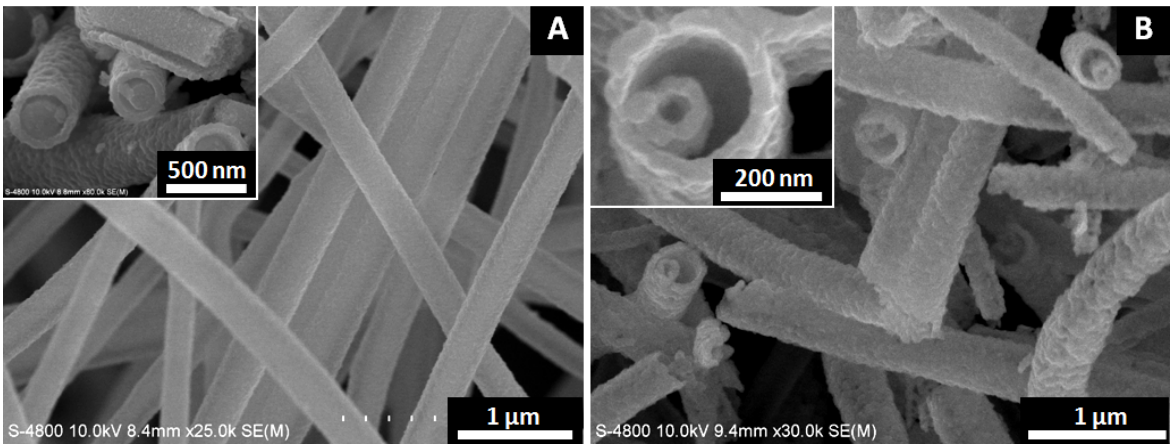

Fig. S4. SEM images of maghemite fibers with fiber-in-tube (A), and tube-in-tube (B) structures obtained by sintering the electrospun iron citrate (80 wt%)/ PVP (20 wt%) gel fibers at 500 ^oC for 2 h with the heating rate of 100 and 250 $^oC \cdot min^{-1}$, respectively.