SUPPORTING INFORMATION

Preparation of Hollow Spheres with Controllable Interior Structures by Heterogeneous Contraction

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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·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-Fe₂O₃ microspheres with various structures, the electrospray gel microspheres were calcined at 500 °C for 2 h in air with various heating rate (R) of 1, 10, 20, 50 and 250 °C·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 °C for 2 h in air with R of 100 and 250 °C·min⁻¹ to fabricate the γ-Fe₂O₃ 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 25 (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-Fe₂O₃ spheres obtained by calcinating the electrosprayed gel 10 microspheres at 500 °C for 2h with the heating rate of 1 °C·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 $E_g$, 5 $T_{2g}$ and $A_{1g}$ modes of inverse spinel structure of $\gamma$-Fe$_2$O$_3$.

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 °C for 2 h with the heating rate of 100 and 250 °C·min$^{-1}$, respectively.