Fabrication and growth mechanism of hierarchical porous Fe_3O_4 hollow sub-microspheres and their magnetic properties

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S1. **XRD patterns of the products with different reaction times**

The formation process of hierarchical porous Fe_3O_4 hollow sub-microspheres is indicated in the following series of experiments (2.0 mmol of $Fe(acac)_3$ was dissolved in 20 mL of diphenyl ether to form a solution, then 10.0 mmol of 1,6-hexanediol was added into the solution. The resulting mixture was then sealed into a 50 mL Teflon-lined autoclave. After that, the autoclave was transferred to an electric oven at 220 °C and kept for 1h, 3h, 4h and 10h respectively). Fig. S1 displays the X-ray diffraction (XRD) patterns of hierarchical porous Fe_3O_4 hollow sub-microspheres prepared at 220°C with reaction time of 1h, 3h, 4h and 10h respectively. The XRD patterns clearly show the phase transformation from Fe_2O_3 to Fe_3O_4 (Fig. S1, ESI). All four systems give the same transformation trend, which means that the pure Fe_2O_3 is the only template in forming Fe_3O_4 hollow sub-microspheres. In Fig. S1a, the sample prepared at 220°C with reaction time of 1h is identified as single phase Fe_2O_3 with rhombohedral structure (a =5.038 Å, c=13.772 Å, JCPDS file No. 24–0072). No peaks from other phases are found, indicating that the as-obtained solid sub-microspheres are single phase α-Fe_2O_3. In Fig. S1b, XRD analyses indicate that the as-obtained sample is a mixture with two phases, Fe_2O_3 with rhombohedral structure (a =5.038 Å, c=13.772 Å, JCPDS file No. 24–0072, signal +) and Fe_3O_4 with cubic structure (a=8.393 Å, JCPDS file No. 85-1436, signal #). The result confirms that the reductive reaction of hematite to magnetite occurs and an incompact layer of Fe_3O_4 is formed on the surface of the initial α-Fe_2O_3 particles. As shown in Fig. S1b-d, moreover, the crystallinity of the Fe_3O_4 in the samples gradually increases

with the reaction time, which indicates that Ostwald ripening (crystallites grow at the expense of the smaller ones) is one of the underlying mechanisms in this hollowing process.

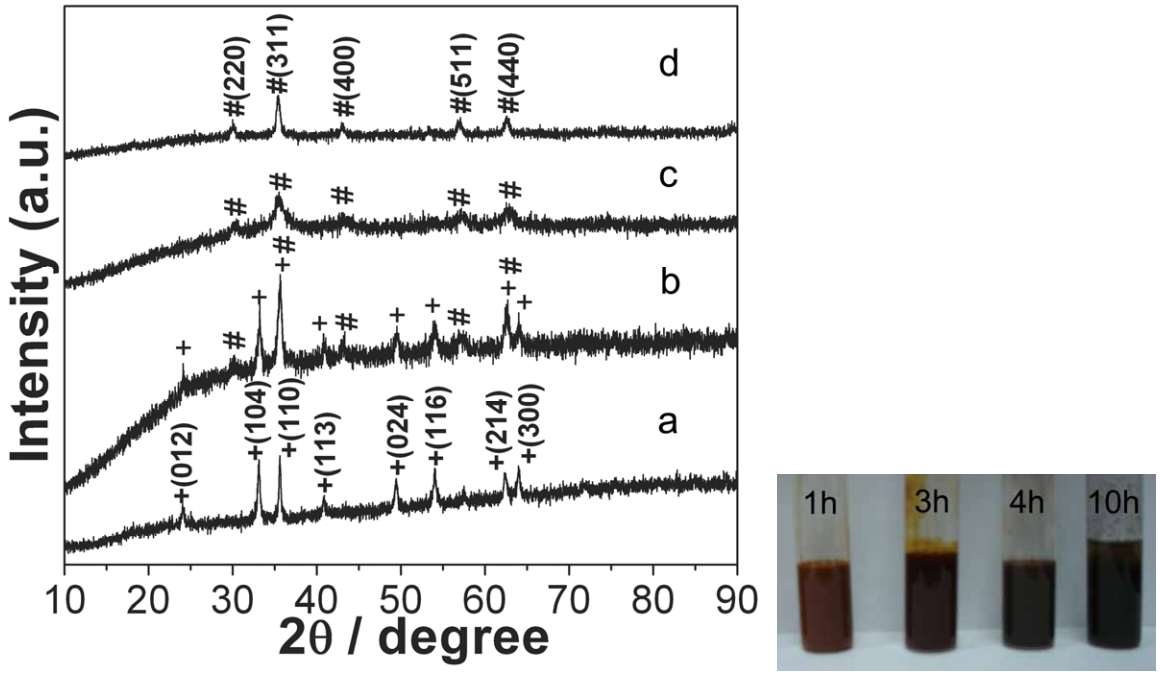

Fig. S1 X-ray diffraction patterns of Fe_3O_4 hierarchical hollow sub-microspheres prepared at 220°C with different experimental time: (a)1h; (b)3 h; (c) 4 h; (d) 10 h. Fe_2O_3 (+) and Fe_3O_4 (#).

S2. Good dispersion of hierarchical Fe_3O_4 hollow sub-microspheres

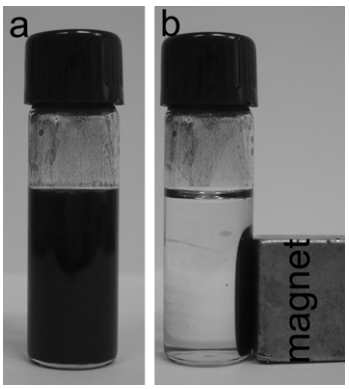

Fig. S2 Photographs of sample (a) before and (b) after using an applied magnetic field for 30 s.