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Supporting Information

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Synthesis and Characterization of Monodisperse Hollow Fe_3O_4 Nanoparticles

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Experimental Section

The synthesis was carried out using commercially available reagents, and all chemicals were used as received. Iron pentacarbonyl (Fe(CO)5), oleylamine (70%), 1-octadecene (90%), and trimethylamine N-oxide, Me_3NO (98%) were purchased from Sigma Aldrich. The experiments were carried out using standard airless setup.

Synthesis of 13 nm Fe/Fe_3O_4 nanoparticle seeds. A mixture of 1-octadecene (20 mL) and oleylamine (0.3 mL, 0.9 mmol) was degassed under Ar at 120°C for 30 min. The temperature was raised to 180°C, and under a blanket of Ar, $Fe(CO)_5$ (0.7 mL, 5.2 mmol) was added. The mixture was kept at 180°C for 20 minutes before it was cooled down to room temperature. The supernatant was decanted and the magnetic bar coated with the product was washed with hexane under N_2 protection and the product was transferred into hexanes via three washing cycles (3 x 15 mL hexane). The combined hexane dispersion was concentrated under N_2 to 15 mL and the product was precipitated out by adding absolute ethanol (25 mL). The product was once again dispersed into hexane and precipitated out by adding absolute ethanol. The purified product was then redispersed in hexane (15 mL) in the presence of oleylamine (0.01 mL) for hollow Fe_3O_4 nanoparticle synthesis.

Controlling the ratio of oleylamine/$Fe(CO)_5$ in the synthesis could tune the size of Fe/Fe_3O_4 nanoparticles. For example, 11 nm Fe/Fe_3O_4 nanoparticles were synthesized by using 0.5 mL oleylamine/0.14 mL $Fe(CO)_5$, while 15 nm Fe/Fe_3O_4 nanoparticles were prepared from 0.15 mL oleylamine/0.7 mL $Fe(CO)_5$.

Synthesis of 16 nm hollow Fe_3O_4 nanoparticles using 13 nm Fe/Fe_3O_4 nanoparticle seeds. A mixture of 1-octadecene (20mL) and Me_3NO (30mg) was magnetically stirred and flushed with Ar for 10 min at room temperature, followed by heating at 130°C for 1 h. 80 mg of Fe/Fe_3O_4 seeds in hexane dispersion was added via a syringe at 130°C and heated for 2 h to remove hexane completely. Finally the solution was heated up to 210°C for 2 h. The black-brown colored solution was cooled down to room temperature by removing the heating source. Isopropanol (30 mL) was added and the mixture was centrifuged (8500 rpm, 10 minutes). The precipitate was then dispersed into hexane and precipitated out by adding ethanol. The purified product was dispersed in hexane and stored for further use.

The procedures for controlled oxidation process at different temperatures were similar to those described above, except that for the low temperature synthesis, the reaction mixture was kept at 130°C for 10 h while for the high temperature synthesis, the reaction mixture was heated at 250°C for 10 min after hexane was evaporated from the reaction system.

The hollow Fe_3O_4 nanoparticles with variable size from 10-20 nm were readily synthesized using smaller or bigger Fe/Fe_3O_4 seeds. For example, the hollow Fe_3O_4 nanoparticles with overall diameter of 12 nm and 18 nm had been prepared by using the 11 nm and 15 nm nanoparticle seeds.

Thermal annealing of the as-synthesized 16 nm hollow Fe_3O_4 nanoparticles. The hexane dispersion of the nanoparticles was dropped into a quartz boat and hexane was allowed to evaporate at room temperature. The nanoparticles were annealed in a tube furnace. Three different annealing conditions were applied to the nanoparticle assemblies: (1) 500°C, 2 h under Ar; (2) 300°C, 8 h under air; (3) 500°C, 2 h under air.

Nanoparticle characterizations. Samples for TEM analyses were prepared by drying the dispersion of the particles on amorphous carbon coated copper grids, while HRTEM samples were prepared using carbon coated gold grids. Particles were imaged using a Philips EM 420 (120 kV) for TEM and a JEOL 2010 for HRTEM. X-ray powder diffraction patterns of the particle assemblies were collected on a Bruker AXS D8-Advanced diffractometer with Cu K*a* radiation (λ = 1.5418 Å). Magnetic studies were carried out using a Lakeshore 7404 high sensitivity vibrating sample magnetometer (VSM) with fields up to 1.5 tesla at room temperature.

Supporting Data:

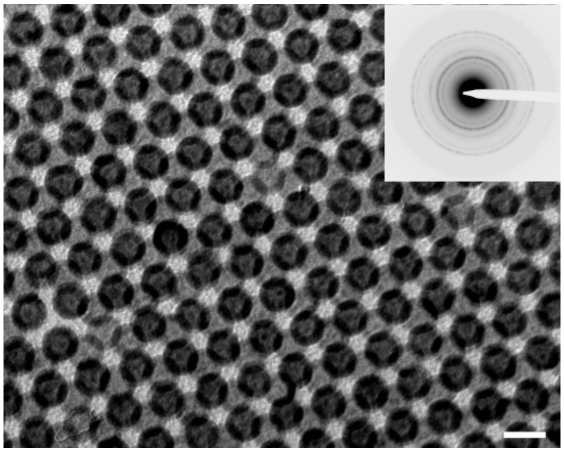

Figure S1: TEM image of a superlattice array of 16 nm hollow Fe_3O_4 nanoparticles (scale bar is 20nm). The inset shows the selected area electron diffraction (SAED) of the superlattice.

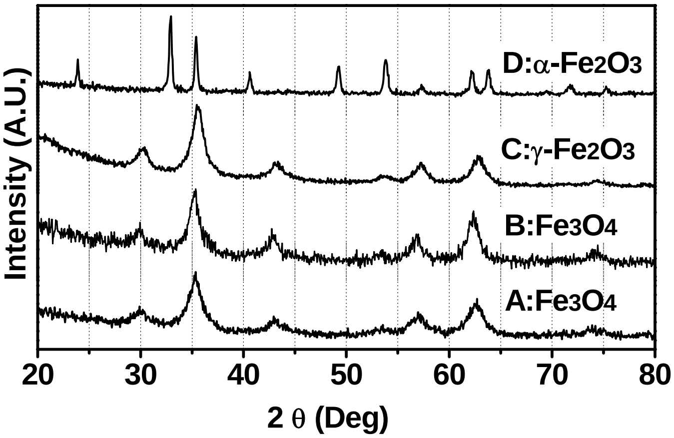

Figure S2: XRD patterns of (A) the as-synthesized 16 nm hollow Fe_3O_4 nanoparticles; (B) the nanoparticles in (A) annealed in Ar at 500°C for 2 h; (C) the nanoparticles in (A) annealed in air at 300°C for 8 h; (D) the nanoparticles in (A) annealed in air at 500°C for 2 h.

The diffraction peaks of the as-synthesized 16 nm hollow Fe_3O_4 nanoparticles (Figure S2A) match well with the standard magnetite pattern. The presence of Fe_3O_4 is further confirmed by annealing the assembly in Ar at 500°C for 2 h (Figure S2B). Under this annealing condition, the diffraction peaks overlap with those in Figure S2A. If γ-Fe_2O_3 exists in the nanoparticles, 500°C annealing would convert it to α-Fe_2O_3. In fact, we obtained γ-Fe_2O_3 by annealing the hollow Fe_3O_4 nanoparticles in air at 300°C for 8 h, as shown in Figure S2C with peaks shifting slightly to higher angles. The resulted γ-Fe_2O_3 nanoparticles show no sintering or morphology change according to both XRD and TEM study. Direct annealing of the hollow Fe_3O_4 nanoparticles in air at 500°C for 2 h resulted in α-Fe_2O_3 with a completely different pattern (Figure S2D). The sharp peaks indicate the sintering of the hollow nanoparticles under this annealing condition. These phase transformation observations agree well with the previous work. [Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. *J. Am. Chem. Soc.* **2004**, *126*, 273-279.]

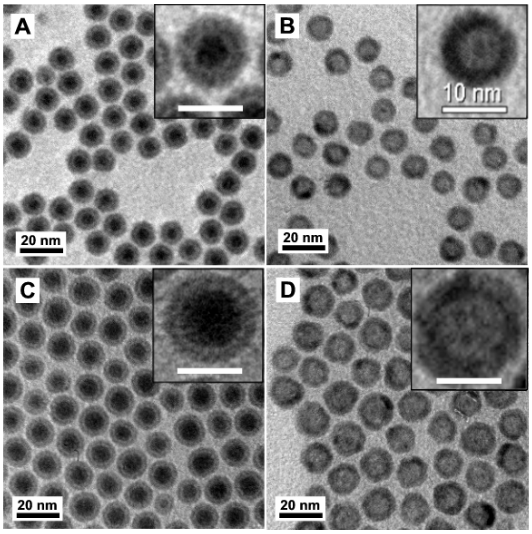

Figure S3: TEM images of (A) 11 nm Fe/Fe_3O_4 nanoparticles, (B) 12 nm hollow Fe_3O_4 nanoparticles from the 11 nm Fe/Fe_3O_4 seeds, (C) 15 nm Fe/Fe_3O_4 nanoparticles and (D) 18 nm hollow Fe_3O_4 nanoparticles from the nanoparticles in (C). Inset scale bars are 10nm.

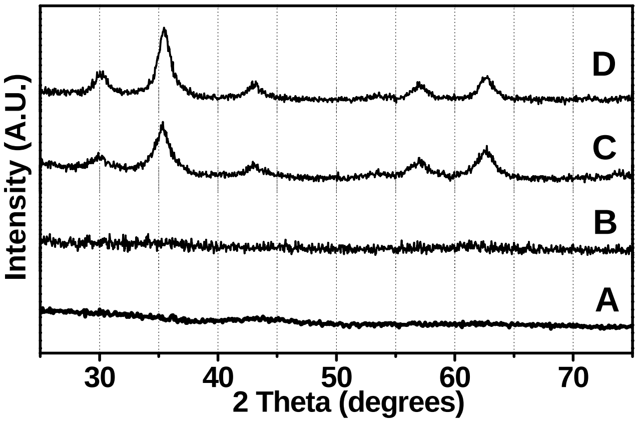

Figure S4: XRD patterns of: (A) the 13 nm Fe/Fe_3O_4 nanoparticle seeds; and the hollow Fe_3O_4 nanoparticles synthesized using the nanoparticles in (A) at (B) 130°C; (C) 210°C; (D) 250°C.