

Supporting Information

Synthesis and Stabilization of Monodisperse Fe Nanoparticles

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The synthesis was carried out using commercially available reagents. Iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), oleylamine (70%), 1-octadecene (ODE, 90%), trimethylamine N-oxide ($(\text{CH}_3)_3\text{NO}$, 98%), α,ω -bis(2-carboxyethyl)polyethylene glycol ($M_w = 3000$), dopamine hydrochloride, and sodium carbonate were purchased from Sigma Aldrich. *N*-hydroxysuccinimide (NHS) and *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC) hydrochloride were from Pierce. Nanosep 100k OMEGA was from Fisher.

Synthesis of 13 nm Fe nanoparticles. ODE (20 mL) and oleylamine (0.3 mL, 0.9 mmol) were mixed and degassed under Ar (99.999% purity) at 120 °C for 30 min. The temperature was raised to 180 °C, and under a blanket of Ar, $\text{Fe}(\text{CO})_5$ (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 hexanes and precipitated out by adding absolute ethanol. The purified product was dispersed in hexane (15 mL) and kept under N_2 for long-term storage.

Controlled oxidation of the as-synthesized Fe nanoparticles to form 2.5-nm/5-nm $\text{Fe}/\text{Fe}_3\text{O}_4$ nanoparticles. The mixture of ODE (15 mL) and $(\text{CH}_3)_3\text{NO}$ (6 mg) was magnetically stirred and flushed with Ar for 10 min at room temperature. The mixture was heated up to 130 °C for 30 min, and then Fe nanoparticles (80 mg in 2 mL hexane dispersion without exposure to air) was added via a syringe at that temperature and heated for another 2 hours. Then the solution was heated up to 250 °C for 30 min under Ar blanket. The black-brown colored ODE solution was cooled down to room temperature by removing the heating source. Isopropanol (25 mL) was added and the mixture was centrifuged (8000 rpm, 10 minutes). The precipitate was then dispersed into hexane and precipitated out by adding ethanol. The purified product was dispersed in hexane (15 mL), giving a black-brown hexane dispersion of 2.5-nm/5-nm $\text{Fe}/\text{Fe}_3\text{O}_4$ nanoparticles.

Ligand replacement reaction using the dopamine-based surfactant. α,ω -bis(2-carboxyethyl)polyethylene glycol (20 mg), NHS (3 mg), and dopamine hydrochloride (1.27 mg) were dissolved in pyridine (2 mL) that contained anhydrous

sodium carbonate (1 mg). EDC (3 mg) was dissolved in CHCl_3 (100 μL) and added to the pyridine solution. At room temperature, the mixed solution was stirred for 3 hours before $\text{Fe}/\text{Fe}_3\text{O}_4$ nanoparticles (3 mg) was added, and the solution was shaken for overnight. The modified $\text{Fe}/\text{Fe}_3\text{O}_4$ nanoparticles were precipitated by adding hexane, collected by applying bar magnet and dried under N_2 for 1 hour. The product was then dissolved in PBS (3 mL, 137 mM NaCl, 2.7 mM KCl, 10 mM $\text{Na}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$, pH = 7.4). After a brief sonication, the dispersion was purified by filtering off the free surfactant though the Nanosep 100k OMEGA. The final product was dispersed in PBS with the concentration reaching about 1 mg/mL.

Nanoparticle characterization. Samples for transmission electron microscopy (TEM) analyses were prepared by drying the dispersion of the particles on amorphous carbon coated copper grids. Particles were imaged using a Philips EM 420 (120 kV). X-ray powder diffraction patterns of the particle assemblies were collected on a Bruker AXS D8-Advanced diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). 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. The size of the nanoparticles in dispersion was evaluated using a Malvern Zeta Sizer Nano S-90 Dynamic light scattering (DLS) instrument.

Figure S1: DLS analysis of the as-synthesized 4-nm/2.5-nm $\text{Fe}/\text{Fe}_3\text{O}_4$ nanoparticles in hexane dispersion.

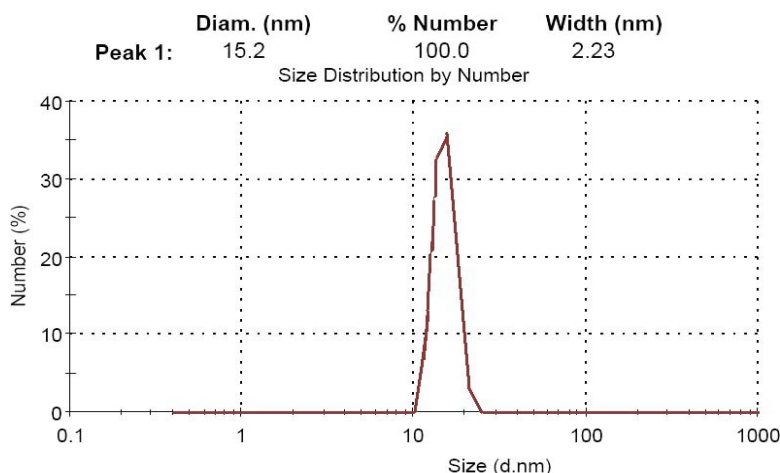


Figure S2: XRD patterns of (A) the as-synthesized 4-nm/2.5-nm Fe/Fe₃O₄ nanoparticles powders, (B) sample (A) after aged in air at 70°C for 12 h, (C) sample (A) annealed under Ar at 300°C for 2 h, (D) sample (A) annealed under Ar at 400°C for 1h.

The as-synthesized nanoparticles (Figure S2A) shows no diffraction peaks, indicating that both the Fe core and the Fe₃O₄ shell are amorphous. After annealing the as-synthesized nanoparticles in air at 70°C for 12 h, Fe₃O₄ peaks show up but the crystallinity is still poor (Figure S2B). XRD pattern of the assembly annealed at 300°C under Ar shows typical Fe₃O₄ diffraction peaks, but metallic core is still amorphous (Figure S2C). XRD of the assembly annealed at 400°C shows well crystallized fcc-Fe₃O₄ and bcc-Fe (Figure S2D). The sharp peak related to bcc-Fe also indicates that 400°C annealed assembly experiences dramatic change in nanoparticle morphology. The presence of Fe₃O₄ in the core/shell structure is further confirmed by annealing the assembly at 500°C. Under this annealing condition, the diffraction peaks from the Fe₃O₄ stayed the same. If γ -Fe₂O₃ was formed in the structure, 500°C annealing would convert it to α -Fe₂O₃. [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.]

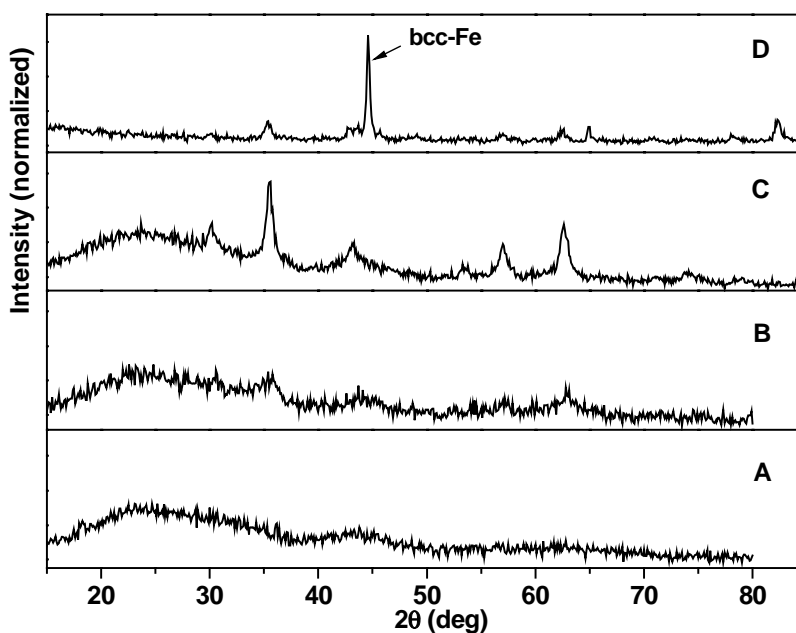


Figure S3. XRD patterns of (A) the as-synthesized 4-nm/2.5-nm Fe/Fe₃O₄ nanoparticles, (B) the 2.5-nm/5-nm Fe/Fe₃O₄ nanoparticles from controlled oxidation of the as-synthesized Fe nanoparticles, (C) oxidation of the as-synthesized Fe nanoparticles with excess of (CH₃)₃NO, and (D) the 2.5-nm/5nm Fe/Fe₃O₄ nanoparticles annealed under Ar at 400°C for 1 h.

These patterns show that after controlled oxidation, crystalline Fe₃O₄ evolves from the nanoparticles, but metallic Fe is still amorphous (Figure S3B&C). Figure S3D shows two groups of diffraction peaks from Fe₃O₄ and bcc-Fe, indicating that the core in the nanoparticles contains metallic Fe.

