Supporting information

Controlled Growth of Monodisperse Self-Supported Superparamagnetic Nanostructures of Spherical and Rod-Like $CoFe_2O_4$ Nanocrystals

Ningzhong Bao, Liming Shen, Yuhsiang Wang, Jianxing Ma, Dipanjan Mazumdar, and Arunava Gupta

Center for Materials for Information Technology, University of Alabama, Tuscaloosa, AL 35487

Experimental Details:

Materials: The synthesis of the $CoFe_2O_4$ ferrite nanostructures was carried out using commercially available reagents. All the chemicals, including absolute ethanol, hexane, oleic acid, 1-octadecene (90 %), diethylene glycol (maximum limits of impurities), sodium oleate ($CH_3(CH_2)_7CH=CH(CH_2)_7COONa$, 95+ %), $FeCl_3$ (99+ %), and $CoCl_2$ (97+ %) were purchased from Fisher Scientific. Poly(acrylic acid) (PAA, Mw ≈ 1800) was purchased from Aldrich. All the chemicals were used as-received without any further purification. As per the information from the Material Safety Data Sheets (MSDS): ***1-octadecene*** may cause eye and skin irritation, and cause respiratory and digestive tract irritation. The toxicological properties of this material have yet to be fully investigated. ***Oleic acid*** causes eye, skin, and respiratory tract irritation. ***Sodium oleate*** has little or no health hazards. All the reported experimental procedures were carried out in a fume hood with appropriate handling of the chemicals.

Synthesis of Metal Oleate Complexes: The mixed metal ($Co^{2+}Fe_2^{3+}$)-oleate complex was prepared by reaction of sodium oleate and a mixture of Fe^{3+} and Co^{2+} chlorides. In a typical synthesis, 4 mmol $FeCl_3$, 2 mmol $CoCl_2$, 16 mmol sodium oleate ($C_{18}H_{33}NaO_2$), 10 ml H_2O, 10 ml ethanol and 20 ml hexane were mixed and refluxed at 60°C for 4 h. The mixed $Co^{2+}Fe_2^{3+}$-oleate complex ($CoFe_2(C_{18}H_{33}O_2)_8$) was obtained by separation of the water phase and subsequent evaporation of the residual ethanol and hexane at 70°C, and water at 110°C.

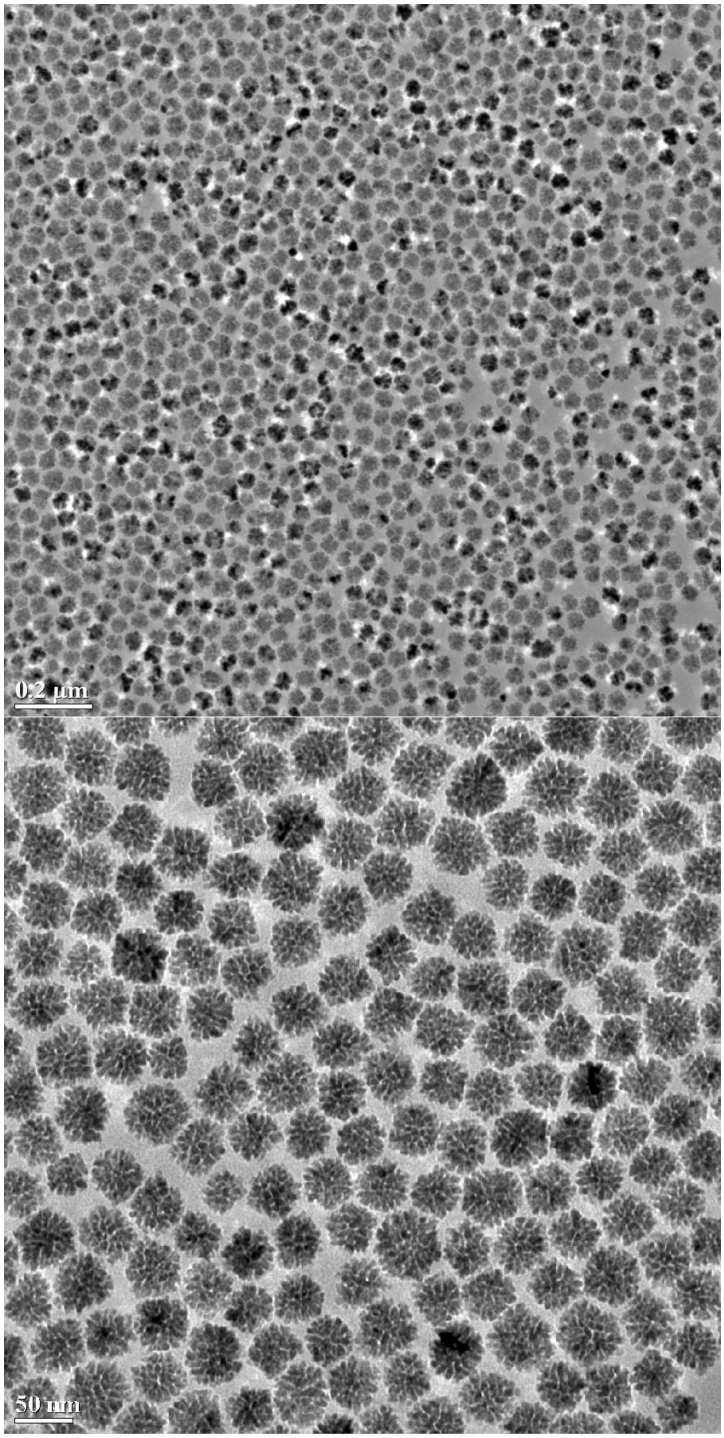
Synthesis of Self-Supported Spherical Nnanostructures of Inter-Grown Spherical $CoFe_2O_4$ Nanocrystals.

For the synthesis of spherical nanostructures, 5 g of the mixed metal ($Co^{2+}Fe_2^{3+}$)-oleate complex, 20 ml 1-octadecene, and 0.5 g oleic acid were mixed and magnetically stirred for 1 hour under flowing N_2. The mixture was then heated to 320 °C at a heating rate of 10 °C/min and maintained at this temperature for up to 3h under N_2 flow with continuous stirring. A small amount (0.05 ml) of hexane was injected into the reaction system at 300, 305, 310, 314, 316, 318, 320 ºC, during heating, and also at 320 ºC after aging for 0, 2, 5, 10, 17, 25, 30, 70, 85, and 95 minutes. A burst of boiling accompanied by a temperature drop (maximum of about 10 ºC) due to the evaporation of hexane was observed following each injection. The final product, in the form of a black powder, prepared after aging at 320 ºC for 3h minutes was obtained by centrifugation at 8000 rpm for 15 minutes, which was then washed with hexane several times and then dried.

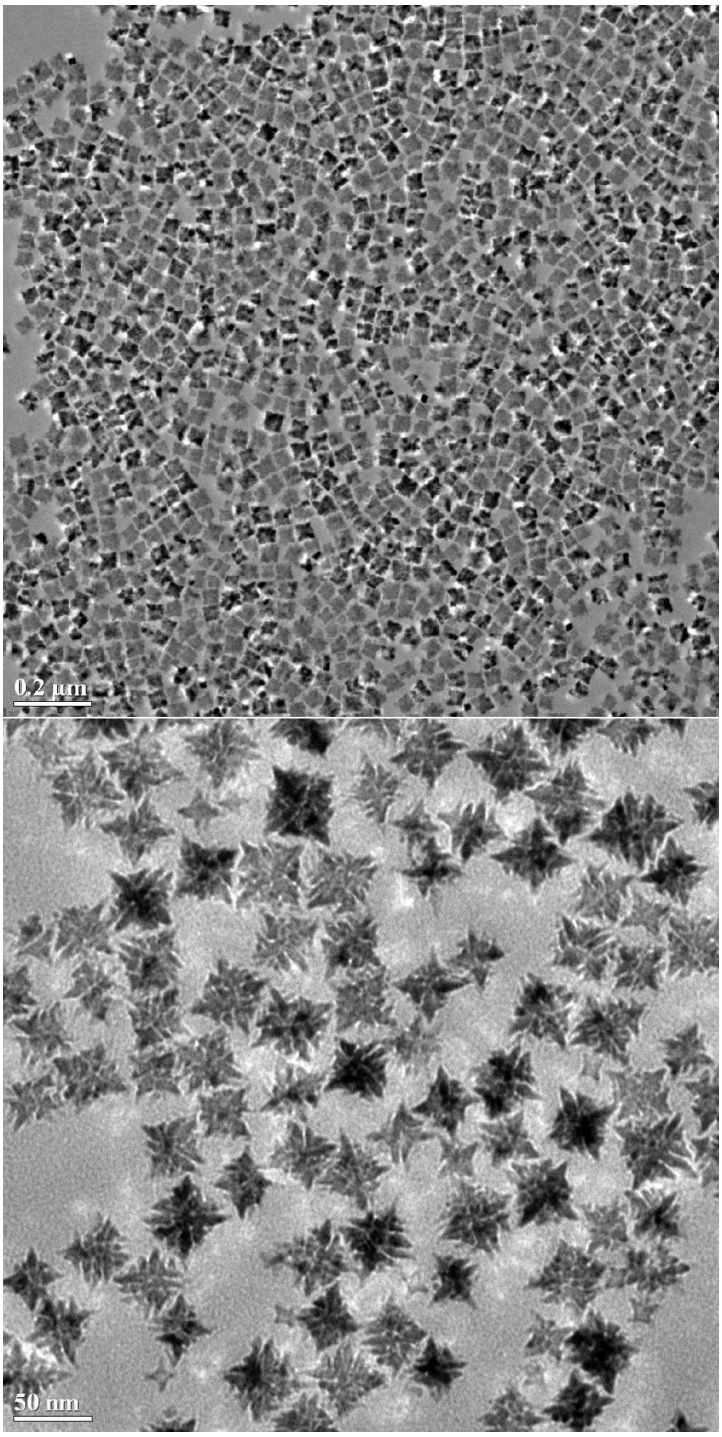
Synthesis of Self-Supported Cubic Nanostructures of Inter-Grown Rod-like $CoFe_2O_4$ Nanocrystals.

For the synthesis of cubic nanostructures, 5 g of the mixed metal ($Co^{2+}Fe_2^{3+}$)-oleate complex, 20 ml 1-octadecene, and 0.5 g oleic acid were mixed and magnetically stirred for 1 hour under flowing N_2. The mixture was then heated to 320 °C at a heating rate of 5 °C/min and maintained at this temperature for up to 3h under N_2 flow with continuous stirring. A small amount (0.05 ml) of hexane was injected into the reaction system at 300, 310, 314, 318, 320 ºC, during heating, and also at 320 ºC after aging for 0, 2, 4, 6, 8, 10, 12, 20, 30, 45, 75, and 95 minutes. A burst of boiling accompanied by a temperature drop (maximum of about 10 ºC) due to the evaporation of hexane was observed following each injection. The final product, in the form of a black powder, prepared after aging at 320 ºC for 3h minutes was obtained by centrifugation at 8000 rpm for 15 minutes, which was then washed with hexane for several times and then dried.

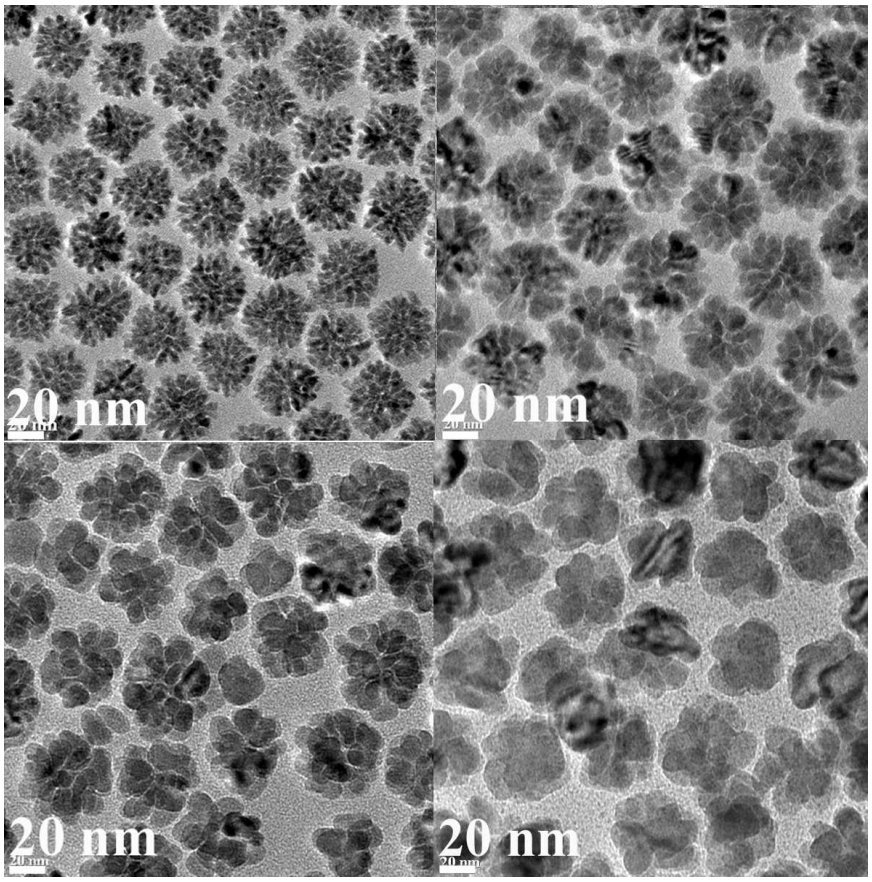
Characterization of materials: The morphology and structure of the products was observed using transmission electron microscopy (TEM) coupled with high resolution (HR) (Tecnai F-20). Alternating gradient magnetometry (AGM) was used to measure the magnetic properties of the samples drawn from the reaction mixture at 320 ºC after aging for 0, 2, 5, 7, 10, 18, 28, 44, and 95 minutes. A 0.1 ml of the hexane (0.5 ml)-diluted reaction solution (0.1 ml) was dried on a 1.5×1.5 mm^2 Si wafer for magnetic measurements at room temperature using an AGM.



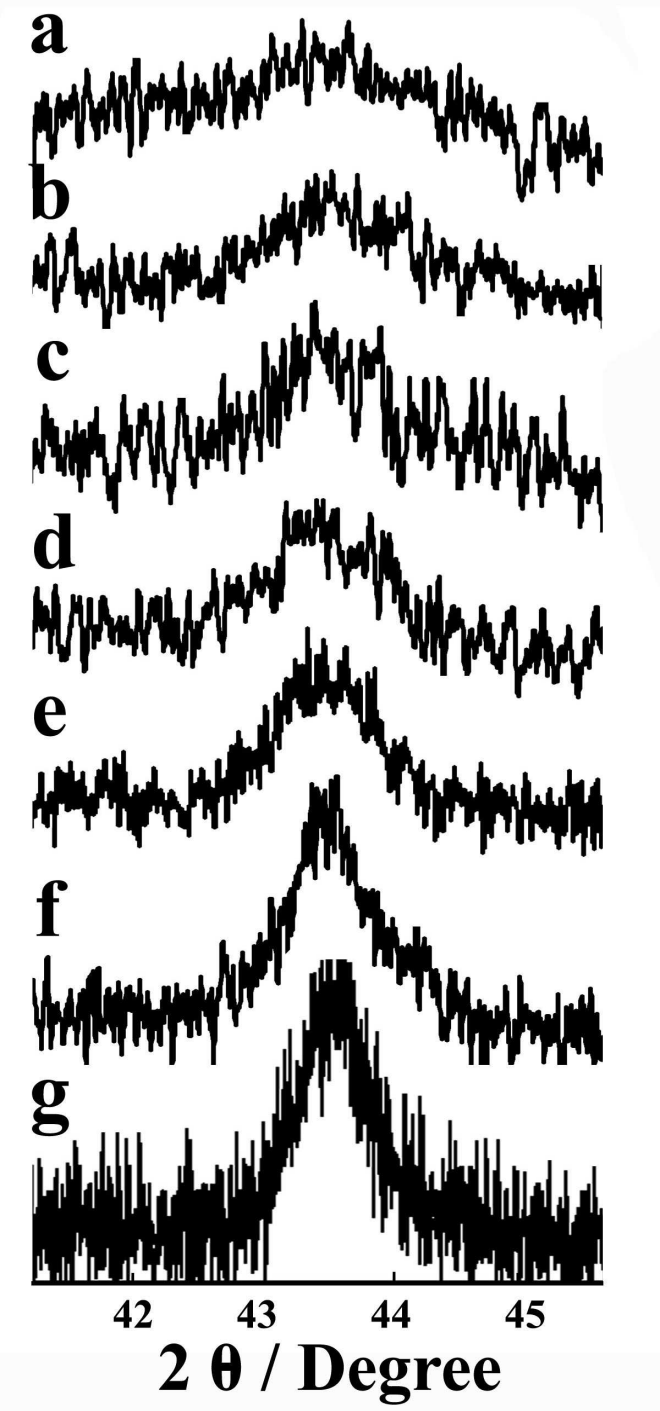
SI 1: Large area TEM image of monodisperse self-supported spherical nanostructures composed of inter-grown spherical $CoFe_2O_4$ nanocrystals synthesized using a heating rate of 10 °C/min to 320 ºC and then aged for 2 minutes.



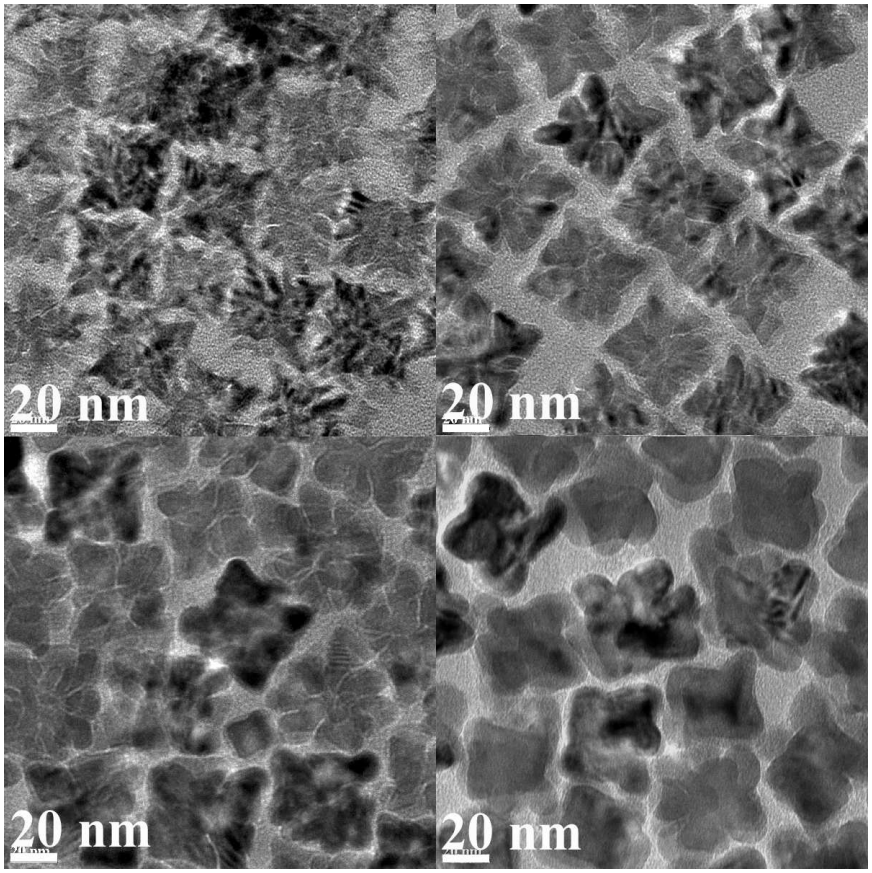
SI 2: Large area TEM image of monodisperse self-supported cubic nanostructures composed of inter-grown rod-like $CoFe_2O_4$ nanocrystals synthesized using a heating rate of 5 °C/min to 320 ºC and then aged for 2 minutes.



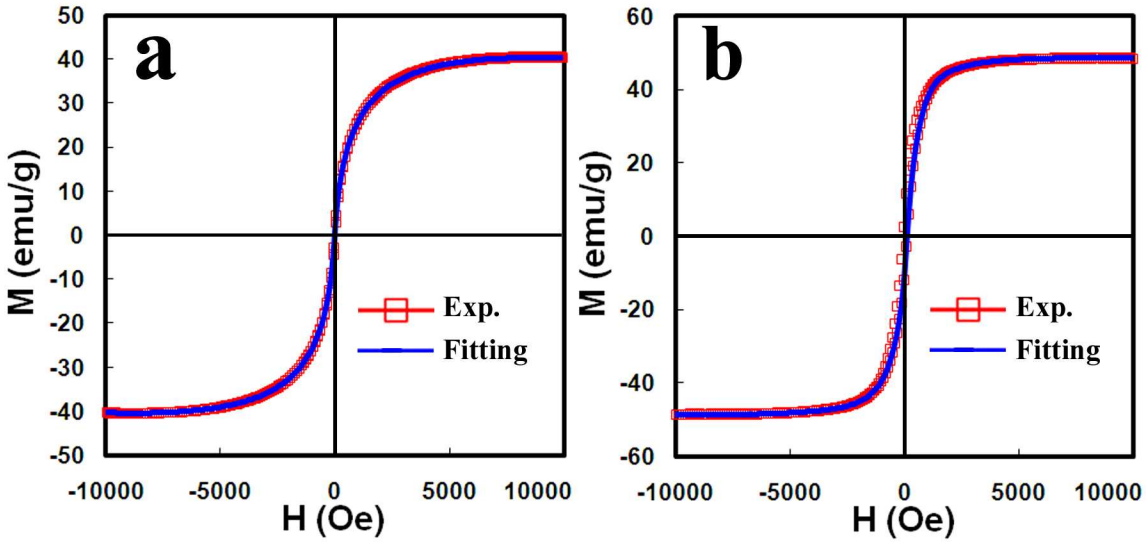
SI 3: TEM images of monodisperse self-supported spherical nanostructures composed of inter-grown spherical $CoFe_2O_4$ nanocrystals formed after aging at 320 °C for (a) 5 min, (b) 30 min, (c) 95 min, and (d) 3h.



SI 4: XRD patterns of products formed at 320 °C after aging for (a) 2, (b) 5, (c) 10, (d) 30, (e) 45, (f) 95, and (g) 180 minutes. The systematic narrowing of the (400) peak with aging time indicates an increase in the grain size of the synthesized $CoFe_2O_4$ nanostructures.



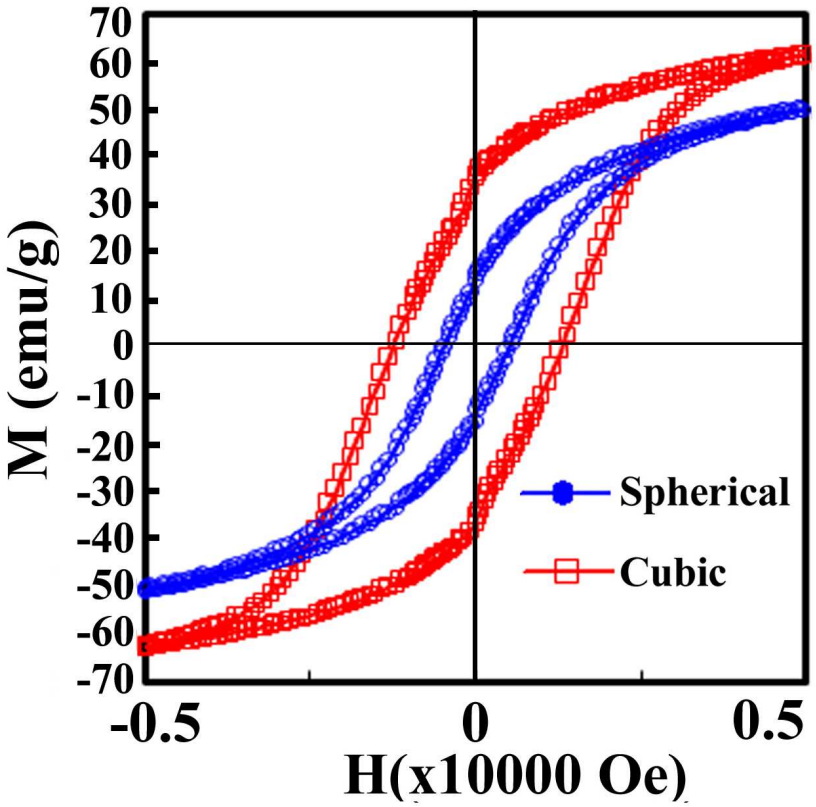
SI 5: TEM images of monodisperse self-supported cubic nanostructures composed of inter-grown rod-like $CoFe_2O_4$ nanocrystals formed after aging at 320 °C for (a) 5 min. (b) 30 min, (c) 95 min, and (d) 3h.



SI 6: *M* versus *H* data measured at 300K along with the fitted Langevin functions for (a) the spherical (40.5±4.5 nm, Fig. 1a-f) $CoFe_2O_4$ nanostructures composed of individual spherical nanocrystals of < 5 nm in size, and (b) the cubic (36.5±2.5 nm, Fig. 1c-d) $CoFe_2O_4$ nanostructures composed of nanorods with dimensions of ~ 3.6 nm in length and 25 nm in diameter. *M* versus *H* data for $CoFe_2O_4$ nanostructures measured at 300 K along with the fits to the *Langevin* function:

$$M = C_1[\coth(C_2H) - (1/C_2H)] + C_3H,$$

where C_1 is the saturation magnetization, in emu/gm, C_2 = (μ/k_BT), and C_3 is a constant accounting for the paramagnetic background contribution from the holder. From the fittings, we obtain C_1 = 41.9 and 50.5 emu/g, C_2 = 0.00235 and 0.00445 and C_3 = 1.2 E-12 and 4.8E-7, respectively, for the spherical and cubic $CoFe_2O_4$ nanostructures. From the value of μ (emu) and the calculated volumes, assuming spherical and rod-like shapes for the spherical and cubic nanostructures, respectively, the average size of the nanostructures is determined to be 3.9 in diameter for the spherical nanostructures and 8.2 nm in length (assuming a 3.6 nm rod diameter) for the cubic nanostructures, respectively.



SI7: Room-temperature hysteresis loops of spherical and cubic nanostructures after aging at 320 °C for 3 hr.