Supporting Information

Oxidation-induced constitute separation of magnetic exchange biased Fe/CoO nanocrystals

Experimental Section

Preparation: All chemicals and solvents are used as obtained. Typically, cobalt (II) and iron (II)-oleate precursors mixture was prepared at 70 ºC from the reactions of 4-mmol sodium oleate with 1.75-mmol $CoCl_2$•$6H_2O$ and 0.25-mmol $FeCl_2$•$6H_2O$ in a mixture of hexane, ethanol, and water (hexane/ethanol/water=10-mL/6-mL/4-mL) for 6 hours. The obtained upper hexane layer was washed with DI water for four times followed by solvent removal via evaporation under vacuum. Then 25-mL octyl ether was added in the flask, and the obtained mixture was heated at 150 ºC under vacuum for 2 hours, followed by rapid heating (~ 14 ºC /min) to boiling (287 ºC) within 10 min. A violent reaction lasted for 30 min to form a black particle solution which was further annealed for 3 hours. The product was purified by a commercial magnet using hexane/ethanol for 3-cycle. The diffusion-limited growth is the plausible mechanism for the formation of star-shaped nanocrystals.

Characterization: Low-magnification and high-resolution TEM images were obtained with a Zeiss 912 Omega transmission electron microscope (TEM) operating at accelerate voltage of 120 kV and a FEI Tecnai F20 transmission electron microscope (HRTEM) operating at accelerate voltage of 200 kV, respectively. Electron energy loss (EEL) spectra and element mappings images were recorded on a Zeiss 912 microscope operated with an in-column Omega energy filler. Energy loss was calibrated before measurement using a standard NiO_x sample to the peak of Ni-L_3 edge at 854 eV. All spectra were recorded using a parallel-mode with a spectral magnification of 163X. The energy resolution was about 1.8 eV with an energy dispersion of 0.12 eV $pixel^{-1}$. Magnetic studies were carried out using a Quantum design MPMS-5S SQUID magnetometer with temperatures from 1.8 to 390 K. X-ray diffraction (XRD) was run on a MPD multi-purpose diffractometer with Co K_α (λ = 0.178897 nm) radiation and X'Celerator detector (Philips). Iron and cobalt contents were measured by using a Perkin-Elmer Optima 3000 Spectrometer.

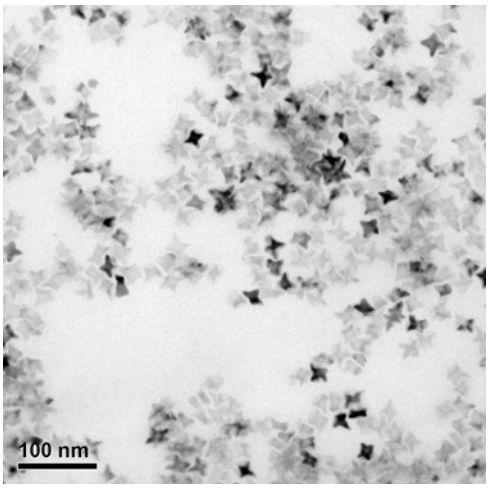

Figure S1. Additional TEM image of Fe/CoO nanocrystals.

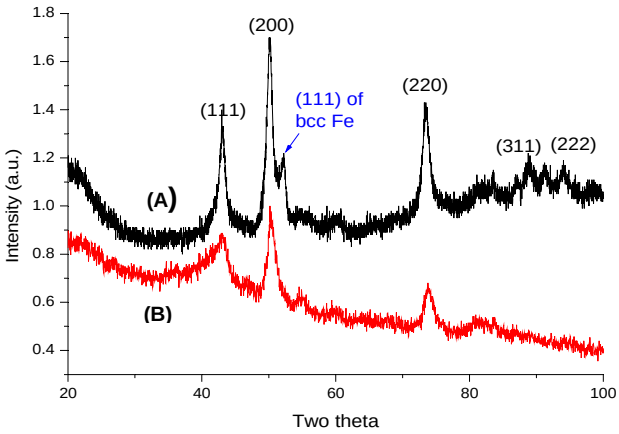

Figure S2. XRD patterns of (**A**) as-synthesized Fe/CoO nanocrystals and (**B**) Fe/CoO nanocrystals after oxidative dissociation under ambient conditions over a time of period of 2-month. However, the corresponding XRD patterns didn't give out the peaks of cubic magnetite, which may result from their amorphous nature (low crystallinity).

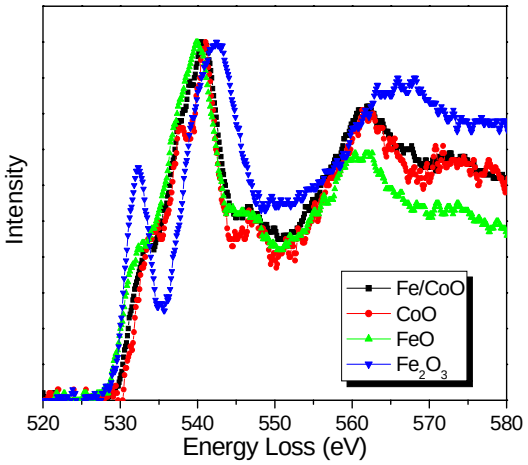

Figure S3. EELS oxygen valence analysis spectrum of the Fe/CoO nanocrystals.

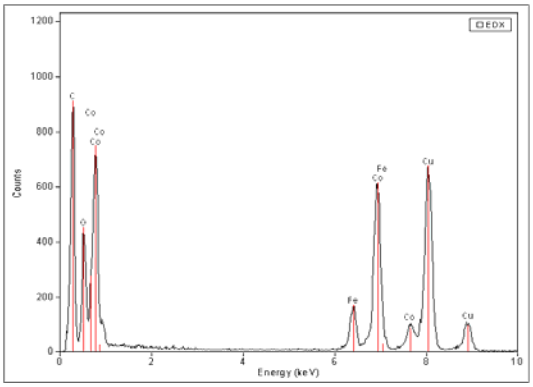

Figure S4. EDS analysis results for the as-synthesized Fe/CoO nanocrystals.

Quantification Results

Element	Weight %	Atomic %	Uncertainty %	Correction	k-Factor
C(K)	52.719	79.260	0.415	0.173	6.279
O(K)	8.079	9.119	0.097	0.514	1.980
Fe(K)	3.291	1.064	0.054	0.994	1.480
Co(K)	15.844	4.854	0.109	0.995	1.576
Cu(K)	20.065	5.701	0.127	0.997	1.757

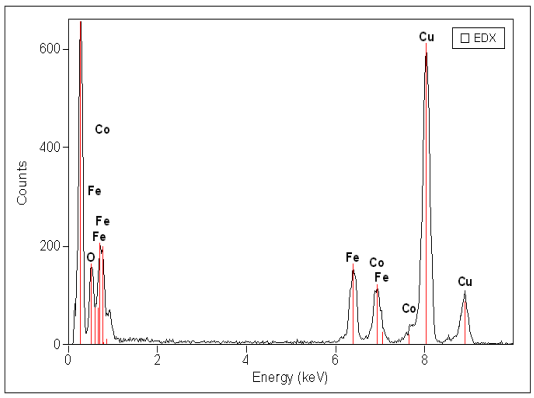

Figure S5. EDS analysis results for the etched-out small nanocrystals of 5 ~ 10 nm in sizes.

Quantification Results

Element	Weight %	Atomic %	Uncertainty %	Correction	k-Factor
C(K)	59.813	85.916	0.575	0.173	6.279
O(K)	3.592	3.873	0.091	0.514	1.980
Fe(K)	4.926	1.521	0.080	0.994	1.480
Co(K)	4.227	1.237	0.069	0.995	1.576
Cu(K)	27.439	7.449	0.186	0.997	1.757

In comparison, the composition of the Fe/CoO nanocrystals was analyzed by ICP-AES. The molar ratio of iron and cobalt in Fe/CoO nanocrystals before and after oxidation-induced phase separation are 0.19:1 and 1.23:1, respectively.