

Supporting Information

Synthesis and Stabilization of FeCo Nanoparticles

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All the reagents used in this synthesis are commercially available. Iron (III) acetylacetonate ($\text{Fe}(\text{acac})_3$), cobalt (II) acetylacetonate ($\text{Co}(\text{acac})_2$), 1,2-hexadecanediol, oleylamine, oleic acid, trioctylphosphine (TOP) were purchased from Sigma Aldrich. All reactions were carried out using standard schlenk line technique.

Synthesis of 20 nm FeCo nanoparticles. $\text{Fe}(\text{acac})_3$ (0.75 mmol, 0.265g) and $\text{Co}(\text{acac})_2$ (0.5 mmol, 129g) were weighed out accurately and charged into a reaction flask. 1,2-hexadecanediol (1.5 mmol, 0.387g), oleylamine (5 mmol, 1.7ml), oleic acid (5 mmol, 1.6ml) were added to the reaction mixture. The reaction mixture was degassed for 20 minutes at room temperature using a gas mixture of Ar 93% + H_2 7%. The reaction was heated to 100°C and kept at this temperature for 10 minutes. Thereafter, the reaction temperature was again raised to 300°C and the mixture was refluxed for 120 minutes before cooling down to room temperature by removing the heat source. Hereafter, the product was handled in air. The product was collected from the surface of a magnetic bar and dissolved in hexane (10ml) and precipitated using absolute ethanol (40 ml). The product was washed three times using mixture of hexane and absolute ethanol (10 ml hexane and 40 ml ethanol) and finally dispersed in hexane. A gas mixture (Ar 93% + H_2 7%) was flowed (1000ml/minute) through out the reaction time. FeCo nanoparticles of atomic percentage 60 to 40 for Fe to Co were obtained with above mentioned metal precursors. Similarly, by varying the molar ratio of $\text{Fe}(\text{acac})_3$ to $\text{Co}(\text{acac})_2$ precursors, FeCo nanoparticle having atomic ratio similar to their metal precursors ratio were obtained.

Synthesis of 10 nm FeCo nanoparticles. $\text{Fe}(\text{acac})_3$ (0.75 mmol, 0.265g) $\text{Co}(\text{acac})_2$ (0.5 mmol, 129g), 1,2-hexadecanediol (1.5mmol, 0.387g) and oleic acid (5 mmol, 1.6ml) were mixed and degassed for 20 minutes using a gas mixture of Ar 93% + H_2 7%. Under the blanket of the gas mixture, TOP (5 mmol, 2.28ml) was injected to the reaction mixture and temperature was raised to 100° C and kept at this temperature for 10 minutes. The reaction mixture was heated to 300°C and refluxed at this temperature to 120 minutes. Reaction mixture was cooled down to room temperature by removing the heat source. The product was isolated and purified using similar method as described above for 20 nm FeCo particles. With above mentioned metal precursor molar ratio, FeCo nanoparticles of atomic percentage 60 to 40 for Fe to Co was obtained. Fe/Co composition was controlled by varying the initial molar ratio of $\text{Fe}(\text{acac})_3$ to $\text{Co}(\text{acac})_2$, which is similar as 20 nm particle described above.

Annealing procedure. As-synthesized FeCo nanoparticles was washed three times with a mixture of absolute ethanol and hexane (10 ml hexane and 40 ml ethanol) and transferred to an alumina boat. The boat was then placed in a heating furnace and purged with a mixture gas (Ar 93% + H_2 7%) for 20 minutes. Under continuous flow of the mixture gas, furnace was heated to 300° C at 10° C/minute and then to 500° C at 5° C/minute. The furnace temperature was kept at 500° C for 30 minutes before cooling down to room temperature. The FeCo powder obtained after annealing was used for magnetic studies and a hexane dispersion of this powder was used for TEM images. Annealing was performed on FeCo sample having Fe/Co atomic ratio of 1.5.

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Atomic absorption experiment procedure. Around 2ml of hexane dispersion of FeCo nanoparticles were taken in a vial. Particles were washed at least 3-4 time with hexane/ethanol mixture and finally three times with water vortexing each time. A magnet was placed next to the vial and the solvent was poured off. The particles remained inside the vial.

The FeCo particles were freeze-dried overnight. 1.25 mg of FeCo nanoparticles recovered after ensured that they were completely dry. Next, 2 ml of aqua regia was added to the vial to digest the FeCo. The resulting solution was heated to $\sim 50\text{-}60^\circ\text{C}$ for 3 hours. The solution turned color from a light yellow to a bright neon green. After 3 hours of digestion, the solution was allowed to cool down and diluted down with deionized water to the appropriate concentration for atomic absorption experiment. The results show that FeCo particles contain (by weight) 47.2% of Fe and 30.7% of Co.

Nanoparticle Characterization. Samples for transmission electron microscopy (TEM) analyses were prepared by drying the hexane dispersion of the particles on amorphous carbon coated copper grids. X-ray diffraction patterns of the particle assemblies were collected on a diffractometer with Cu K α radiation ($\lambda = 1.5418\text{ \AA}$). Magnetic measurements were carried out using Superconducting Quantum Interference Device (SQUID) magnetometer. Raman spectra were recorded on Horiba Jobin Yvon instrument.

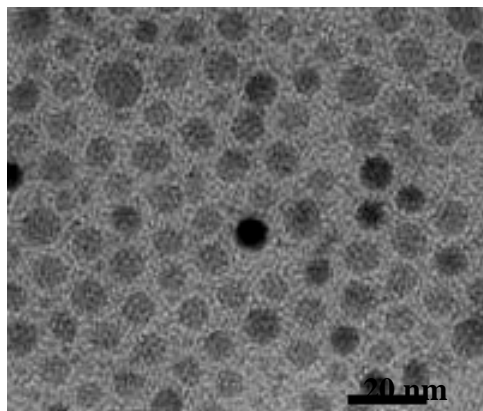


Figure S1. TEM image of FeCo particles of average diameter 10 nm.

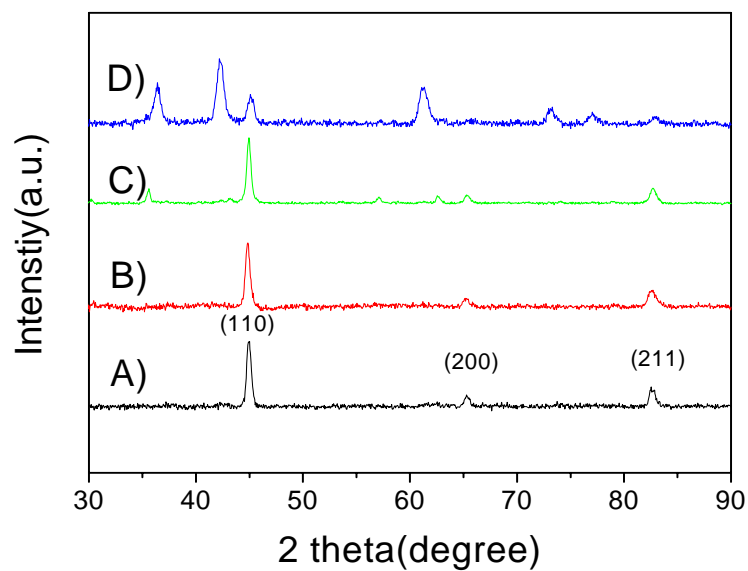


Figure S2. XRD patterns of 20 nm FeCo nanoparticles with different Fe/Co molar ratio of metal precursors (A) 1 (B) 1.5 (C) 2 and (D) 2.5. The final composition (atomic ratio) of Fe/Co is the same as their molar ratio of precursors.

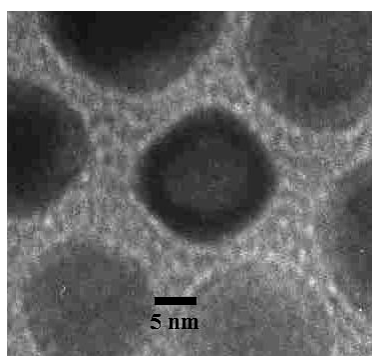


Figure S3. Magnified view of TEM image of FeCo nanoparticles with oxide shell when particles were exposed to air.

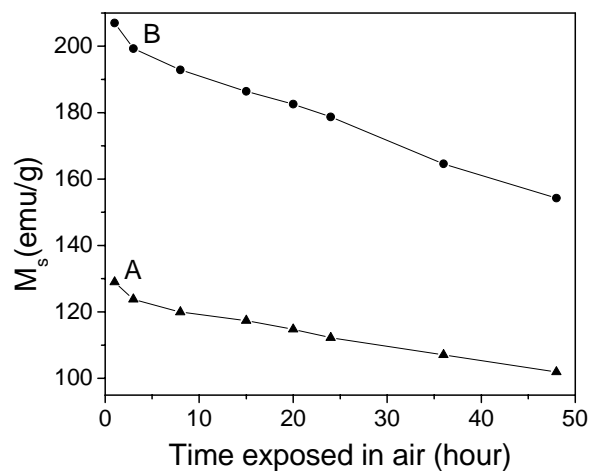
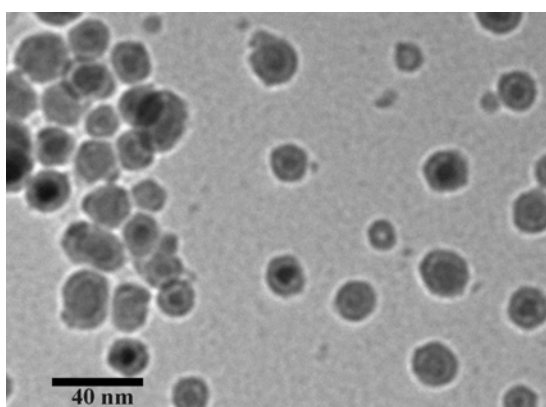
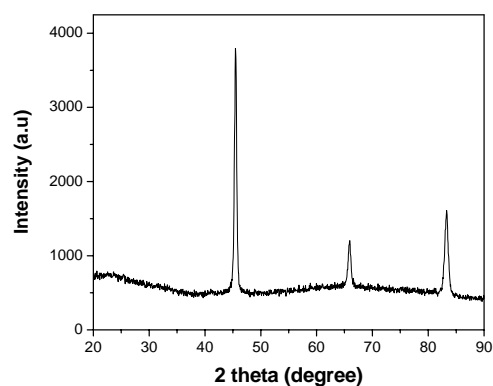


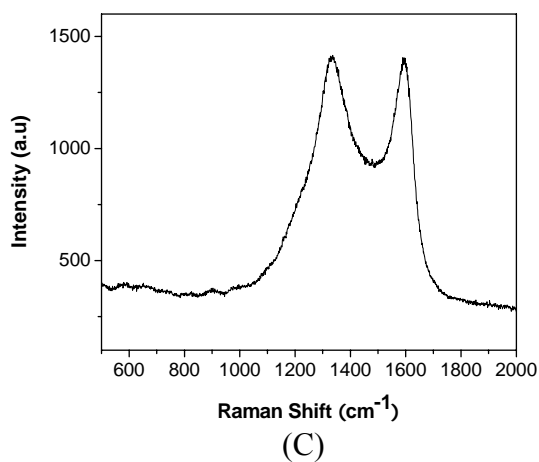
Figure S4. Variation of magnetization with air-exposure time for (A) 10 nm and (B) 20 nm as-synthesized FeCo nanoparticles.



(A)



(B)



(C)

Figure S5. (A) TEM image of 20 nm FeCo nanoparticles after annealing at 500°C for 30 minutes; (B) XRD patterns of 20 nm FeCo nanoparticles after annealing at 500 °C for 30 minutes and (C) Raman spectra of the annealed FeCo particles showing Raman Shift (cm^{-1}) at 1328 and 1594, which are the characteristic peaks for carbon¹.

Reference:

- (1) Ferrari, A. C.; Robertson, J. *Physical Review B*, **2001**, 64, 075414-13