Supporting Information

Monolayer Assembly of Ferrimagnetic $Co_xFe_{3-x}O_4$ Nanocubes for Magnetic Recording

Liheng Wu,[†] Pierre-Olivier Jubert,[‡] David Berman, [‡] Wayne Imaino, [‡] Alshakim Nelson, [‡] Huiyuan Zhu, [†] Sen Zhang, [†] and Shouheng Sun[†]*

[†] Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

[‡] IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, USA

Experimental Section

Chemicals and Materials. The following chemicals were used as received. Iron (III) acetylacetonate (99%) was purchased from Strem Chemicals. Sodium oleate (90%) was purchased from Spectrum Chemicals. Cobalt(II) acetylacetonate hydrate, oleic acid (90%) and benzyl ether (98%) were all purchased from Sigma Aldrich.

Synthesis of 20 nm $Co_{0.6}Fe_{2.4}O_4$ NCs: Under a gentle flow of Ar, iron(III) acetylacetonate (1.0 mmol, 350 mg), cobalt(II) acetylacetonate hydrate (0.48 mmol, 140 mg), sodium oleate (1 mmol, 300 mg) and oleic acid (2 mL) were mixed with benzyl ether (10 mL). The mixture was magnetically stirred under a flow of Ar and then heated to 120 ^oC for 1 h. Under Ar blanket, the solution was heated up to 290 ^oC at a heating rate of 15 ^oC/min and kept at this temperature for 1 h. Then the mixture was cooled down to room temperature by removing the heating mantle. Under ambient conditions, 10 mL of hexane and 30 mL of ethanol were added to the mixture to precipitate the product. Centrifugation (8500 rpm for 8 min) was applied to collect the product. The product was redispersed in hexane and precipitated out by addition of ethanol for further purification. Then the final product was dispersed in hexane for further characterizations.

For the synthesis of 15 nm $Co_{0.6}Fe_{2.4}O_4$ NCs, the synthetic procedure was the same except the amounts of metal precursors were decreased to 280 mg (0.8 mmol) of iron(III) acetylacetonate and 134 mg (0.46 mmol) of cobalt(II) acetylacetonate hydrate. By further decreasing the amount of cobalt(II) acetylacetonate hydrate to 122 mg (0.42 mmol), 10 nm $Co_{0.6}Fe_{2.4}O_4$ NCs were synthesized.

Monolayer Assembly of the NCs: Large-area monolayer assemblies of the 20 nm NCs were fabricated using the self-assembly approach at the water-air interface. Briefly, the NCs were diluted and dispersed in the mixture of toluene and hexane (volume ratio of 1:1) with the concentration of 0.5 mg/mL. 120 μL of the dispersion was drop-cast and spread onto the surface of deionized water in a Telfon column (diameter: 3.8 cm), which was then slowly dried at room temperature. After complete evaporation of toluene and hexane, the monolayer assemblies of the NCs floating on the water surface were transferred onto Cu TEM grids or Si substrates for further characterizations.

Characterization: TEM and HRTEM images were obtained on a Philips CM 20 microscope and a JEOL 2010 microscopy with an accelerating voltage of 200 kV, respectively. SEM images were acquired on a LEO 1530 microscope at an accelerating voltage of 10 kV. Elemental analysis was done on a JY2000 Ultrace ICP Atomic Emission Spectrometer equipped with a JY AS 421 autosampler and 2400g/mm holographic grating. X-ray diffraction was performed on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ=1.5418 Å). Magnetic measurements were carried out using a Lakeshore 7404 high-sensitivity vibrating sample magnetometer (VSM). The magnetic recording performance was obtained using a contact magnetic tester. A Physik Instrumente piezoelectric nanopositioning stage was used to control the sample position during magnetic recording measurements. A hard disk drive (HDD) head

with a Giant Magneto-Resistive (GMR) read sensor that is 115 nm wide and a longitudinal write element that is 160 nm wide was used to write and read magnetic signals on the sample.

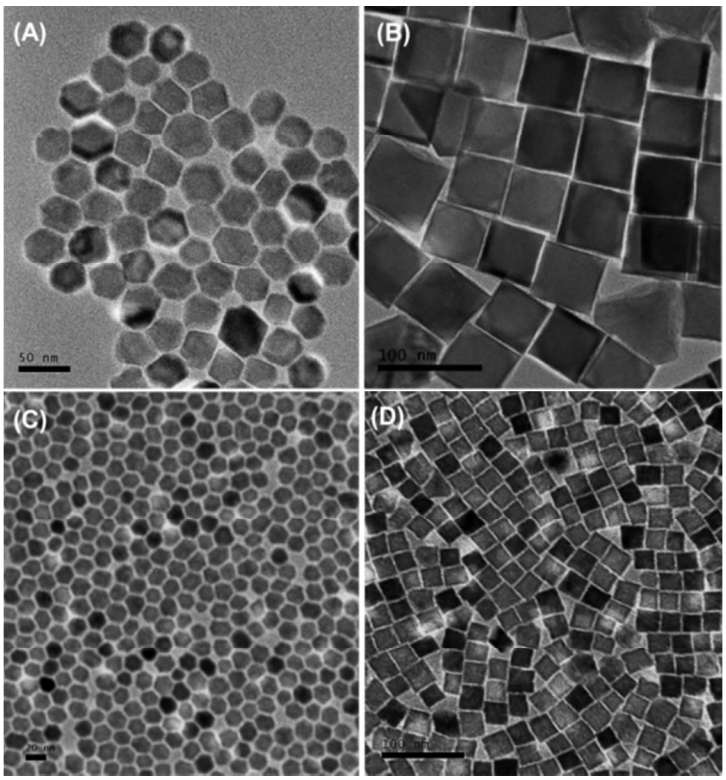

Figure S1. TEM images of Co-ferrite NPs (A) polyhedral NPs synthesized without using sodium oleate, (B) 60 nm cubic NPs, (C) 15 nm polyhedral NPs and (D) 25 nm cubic NPs.

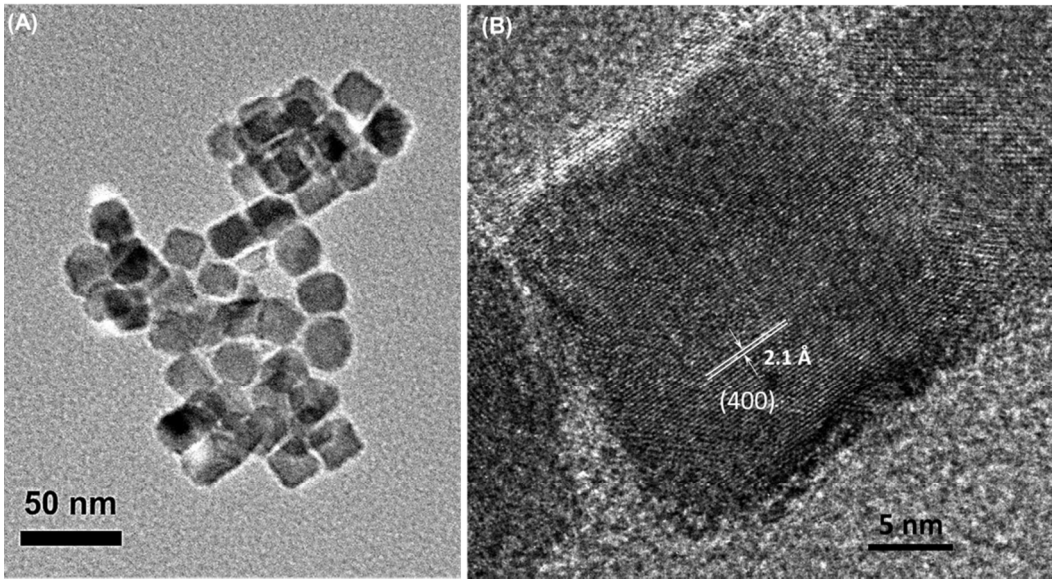

Figure S2. (A) TEM image of the 20 nm NCs and (B) HR-TEM image of a single 20 nm NC after annealing in oxygen at 300 ^{o}C for 1 h

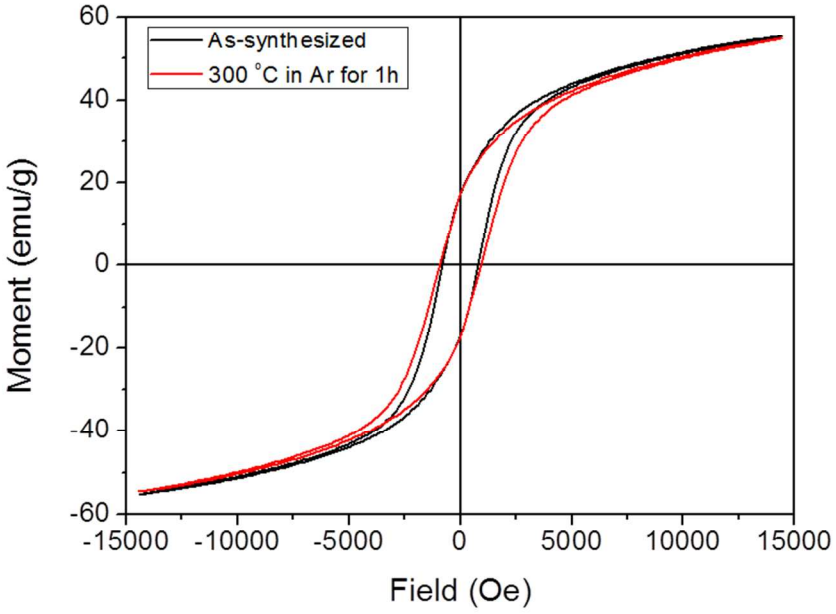

Figure S3. Hysteresis loops of the 20 nm NCs before and after annealing in Ar gas at 300 ^{o}C for 1 h.

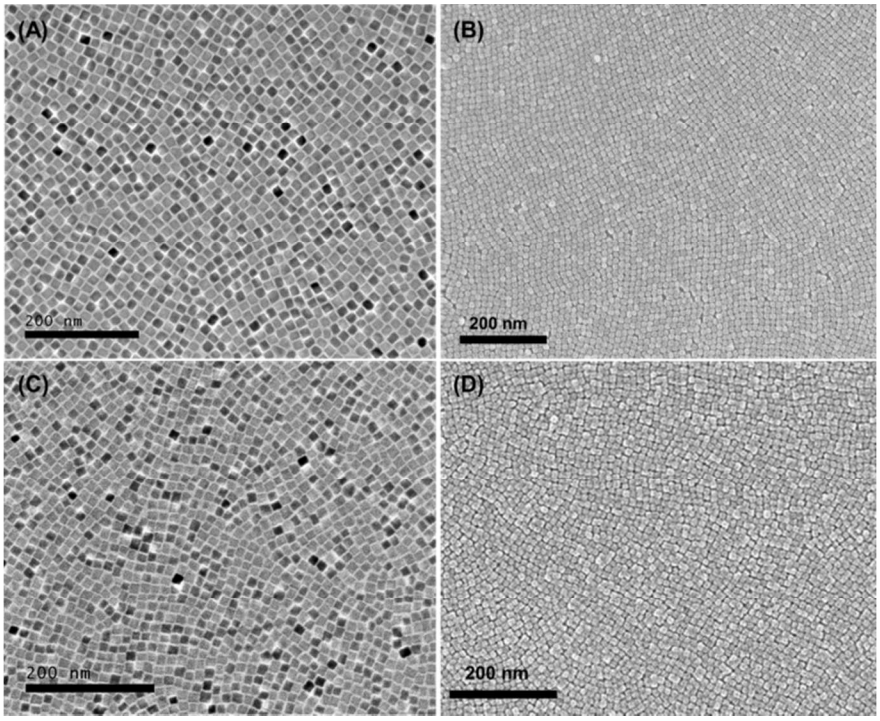

Figure S4. (A)TEM image and (B) SEM image of the self-assembled monolayer of 15 nm NCs; (C) TEM image and (D) SEM image of the self-assembled monolayer of 10 nm NCs.

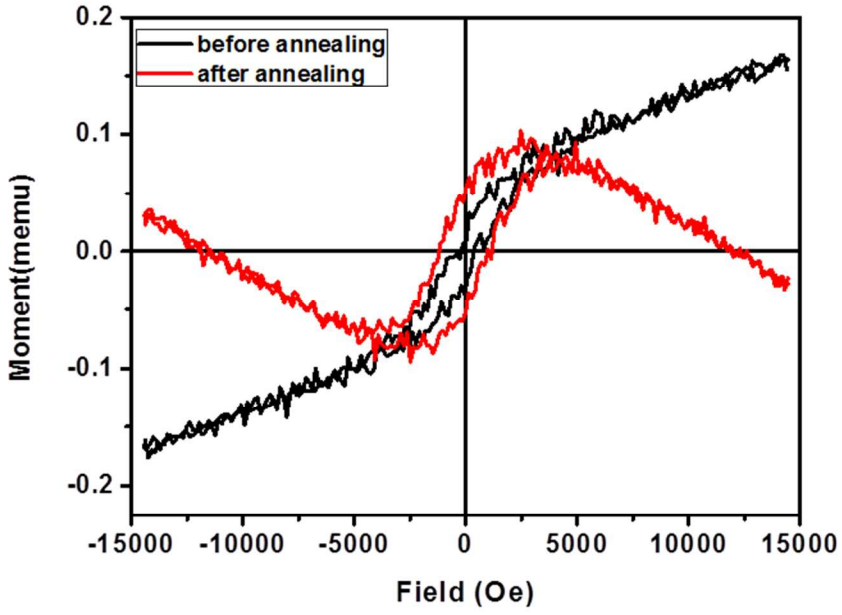

Figure S5. Out-of-plane hysteresis loops of the monolayer assembly on a Si before and after annealing in O_2 at 300 ^{o}C for 1h.

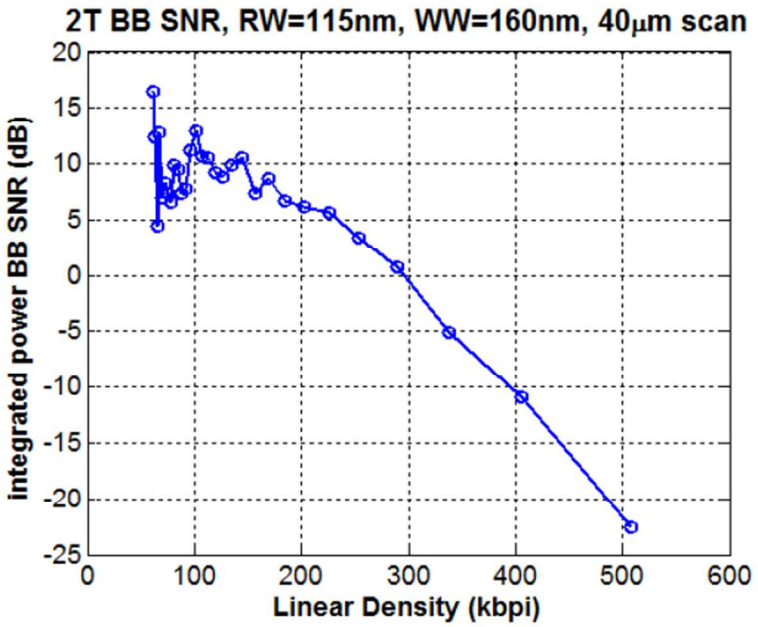

Figure S6. The dependence of SNR (signal-to-noise ratio) on the writing signal at different linear densities.