Supporting Information

Synthesis and Assembly of Barium-doped Iron Oxide Nanoparticles and Nanomagnets

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Experimental Section

Chemicals: Iron(III) acetylacetonate (99%), barium stearate (technical grade) were purchased from Strem Chemicals. Strontium stearate (98.5%) was purchased from VWR International. Oleic acid (90%), oleylamine (70%) and 1-octadecene (90%) were all purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Synthesis of Ba-Fe-O NPs: In a typical synthesis of $Ba_{0.082}$-Fe-O NPs, barium stearate (60 mg, 0.085 mmol), iron(III) acetylacetonate (300 mg, 0.85 mmol), oleic acid (1 mL), oleylamine (8 mL) and 1-octadecene (3 mL) were mixed and magnetically stirred at room temperature under a gentle flow of Ar gas for 20 min. Then the mixture was heated directly to 320 ^{o}C at 10 ^{o}C/min. The reaction was kept at this temperature for 1.5 h. Then the mixture was cooled to room temperature by removing the heating mantle. The NPs were precipitated by 2-propanol (30 mL) and collected by centrifugation (8500 rpm, 8 min). The product was re-dispersed in hexane and

separated again by adding ethanol followed by centrifugation (8500 rpm, 8 min). The final product was dispersed in hexane for further characterization.

Assembly of Ba-Fe-O NPs: Monolayer assembly of the $Ba_{0.082}$-Fe-O NPs was prepared using the water-air interfacial self-assembly approach reported previously.[13] Briefly, the NPs were dispersed in the mixture of hexane and toluene (v:v = 1:1) at the concentration of 0.5 mg/mL. 160 μL of the dispersion was drop-cast on the water surface in the Teflon column (diameter: 3.8 cm). Upon complete evaporation of the organic solvent, the formed monolayer assembly floating on the water surface was transferred to TEM Cu grids or Si substrates for further characterization. Multilayer assembly of the NPs was prepared by drop-casting 16 μL of the dispersion on a Si substrate (0.7 cm × 0.7 cm).

Characterization: Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were collected using a Philips CM20 and JEOL 2010 with an accelerating voltage of 200 kV, respectively. Scanning electron microscopy (SEM) images of the assemblies were acquired on a LEO 1530 microscope at an operating voltage of 10 kV. Energy dispersive X-ray (EDX) spectrum was obtained by Oxford energy-disperse X-ray spectroscopy equipped in the SEM at an operating voltage of 20 kV. X-ray diffraction (XRD) patterns of the samples were collected on a Bruker AXS D8-Advanced diffractometer with Cu Kα radiation (λ = 1.5418 Å). The Ba/Fe composition was determined by elemental analysis using a JY2000 Ultrace ICP Atomic Emission Spectrometer. Magnetic properties were measured on a Lakeshore 7404 high-sensitivity vibrating sample magnetometer (VSM) with fields up to 14.5 kOe at room temperature (~298K).

Supplementary Figures:

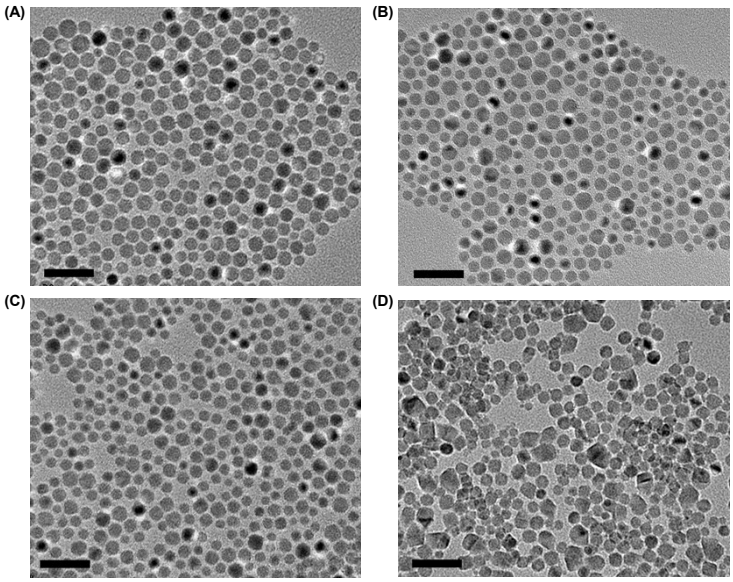

Fig. S1 TEM images of the as-synthesized Ba-Fe-O NPs with different Ba compositions. (A) $Ba_{0.055}$-Fe-O NPs. (B) $Ba_{0.065}$-Fe-O NPs. (C) $Ba_{0.075}$-Fe-O NPs. (D) $Ba_{0.095}$-Fe-O NPs. All scale bars represent 50 nm.

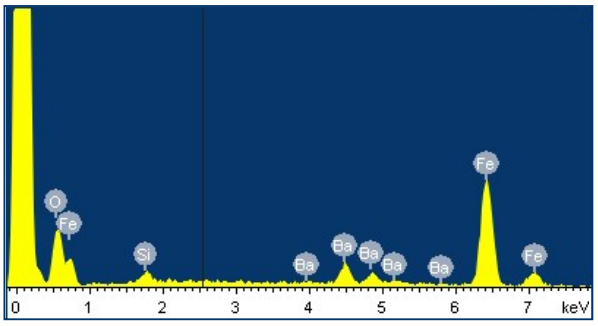

Fig. S2 EDX spectrum of the $Ba_{0.082}$-Fe-O NPs deposited on a Si substrate.

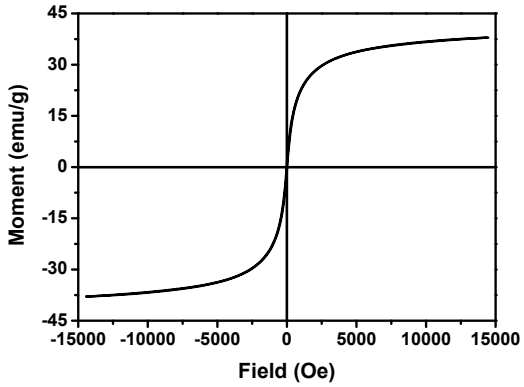

Fig. S3 Hysteresis loop of $Ba_{0.082}$-Fe-O NPs after annealing in O_2 at 600 ^oC for 1h.

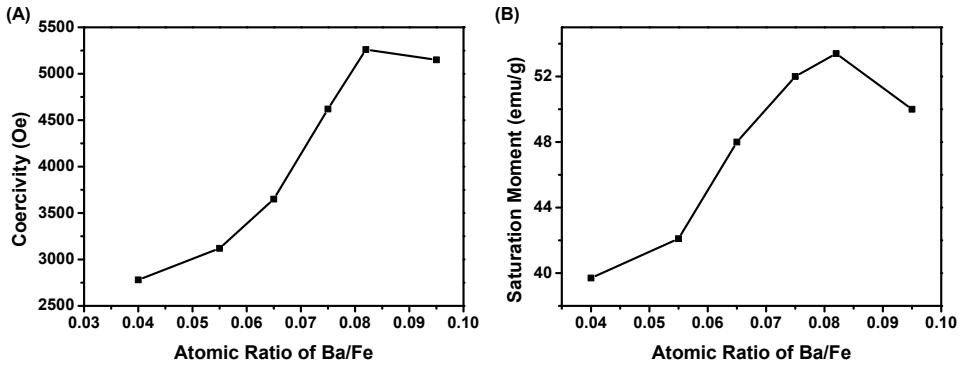

Fig. S4 The change of magnetic coercivity and saturation moment of the annealed Ba-Fe-O NPs with different Ba compositions.

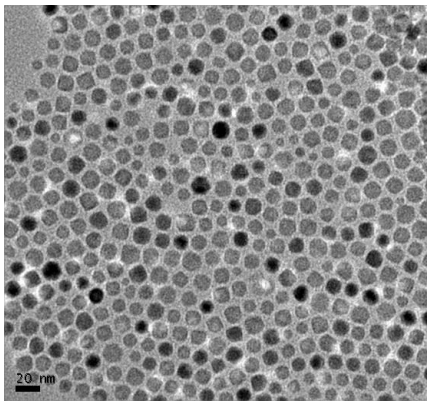

Fig. S5 TEM image of the as-synthesized Sr-Fe-O NPs with Sr/Fe composition of 0.078.

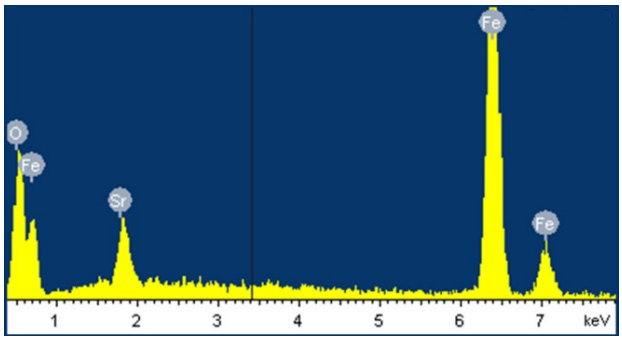

Fig. S6 EDX spectrum of the $Sr_{0.078}$-Fe-O NPs deposited on a Si substrate.

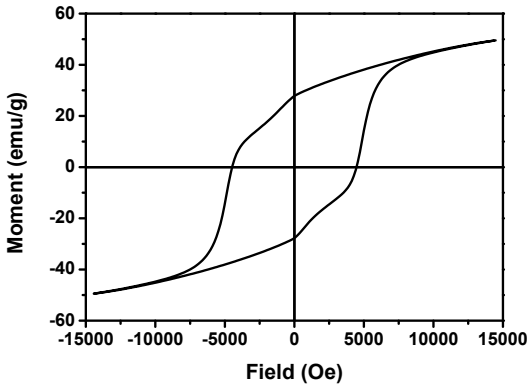

Fig. S7 Hysteresis loop of the $Sr_{0.078}$-Fe-O NPs after annealing in O_2 at 700 ^oC for 1 h.

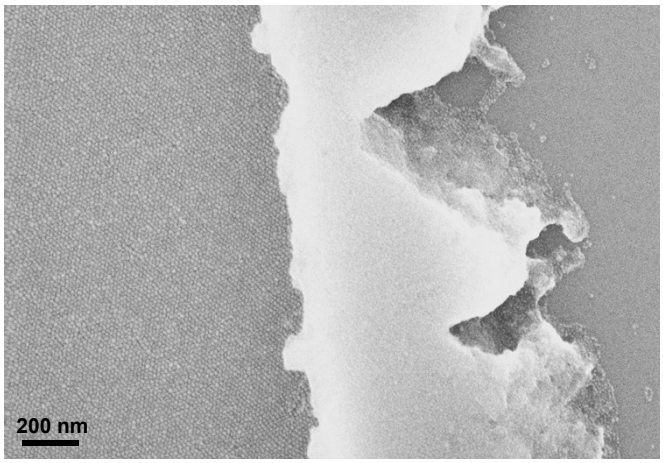

Fig. S8 SEM image of the scratched multilayer assembly of the $Ba_{0.082}$-Fe-O NPs, showing multilayer arrays of the NPs.