

## Supporting Information

### Chemical Synthesis of Nd<sub>2</sub>Fe<sub>14</sub>B/Fe-Co Nanocomposite with High Magnetic Energy Product

Hieu Minh Ngo,<sup>a</sup> Gyutae Lee,<sup>b</sup> Syed Kamran Haider,<sup>a</sup> Umapada Pal,<sup>a\*</sup> Thomi Hawari,<sup>a</sup> Kyung Min Kim<sup>c</sup>, Jongryoul Kim<sup>b</sup>, Hae-Woong Kwon<sup>c</sup>, and Young Soo Kang<sup>a,†</sup>

<sup>a</sup> *Department of Chemistry, Sogang University, #1 Shinsu-dong, Mapo-gu, Seoul 121-742, Republic of Korea*

<sup>b</sup> *Department of Materials Science & Chemical Engineering, Hanyang University, #320, 55, Hanyangdaehak-ro, Sangnok-gu, Ansan, Kyeonggi-do, Korea, 426-791, Republic of Korea*

<sup>c</sup> *Department of Materials science and engineering, Pukyong National University, Busan, Republic of Korea 48513*

<sup>†</sup> *Corresponding author, E-mail: [yskang@sogang.ac.kr](mailto:yskang@sogang.ac.kr)*

*\*On leave from Instituto of Physics, Autonomous University of Puebla, Mexico.*

## ***Materials and method***

### ***Materials.***

Iron acetylacetonate (97%), cobalt(II) acetylacetonate (97%), oleic acid (70%), oleylamine (70%), tetramethylammonium hydroxide solution (TMAOH, 25 wt% in water), neodymium nitrate hexahydrate ( $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.9%), iron nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , > 97%), citric acid (99.5%), ethylene glycol (99%) and 1,2-hexadecanediol (90%) were purchased from Aldrich. Ethanol (99.5%), acetone (95%) and hexane (95%) were purchased from Samchun, Korea. Boric acid ( $\text{H}_3\text{BO}_3$ , 99%) was purchased from Katayama Chemicals. Calcium hydride ( $\text{CaH}_2$ , 99.5%) was purchased from Alfa-Aesar. Ammonia solution (28%  $\text{NH}_3$  in water) was purchased from Junsei. Deionized (DI) water from a Milli-Q IQ 7000 system ( $\rho > 18.2 \text{ M}\Omega \cdot \text{cm}$ ) was utilized for solution preparation.

***Synthesis of cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) NPs.*** Cobalt ferrite NPs of ~ 5 nm average size were prepared following previous reports.<sup>1-5</sup> Oleyl amine, oleic acid and 1,2-hexadecanediol were used as surfactants to control the size of the  $\text{CoFe}_2\text{O}_4$  NPs. In a typical synthesis process, iron acetylacetonate (0.265 g, 0.75 mmol) and cobalt acetylacetonate (0.129 g, 0.5 mmol) were added to a 100 mL capacity three-necked round-bottom flask in 3:2 molar ratio. About 0.387 g (1.5 mmol) of 1,2-hexadecanediol, 5 mL of oleic acid, and 5 mL of oleylamine were added to the prepared mixture. The mixture was stirred at 110 °C for 30 min for degassing and then refluxed at 300 °C for 2 h (5 °C/min heating rate) under Ar atmosphere. After cooling to room temperature, the product was precipitated by adding a mixture solution of hexane (10 mL) and ethanol (30 mL) and separated. The process was repeated for three times to eliminate the surfactant and unreacted precursors (if any). After

separation and washing, the sample was re-dispersed in 30 mL of hexane and stored at room temperature for further use.

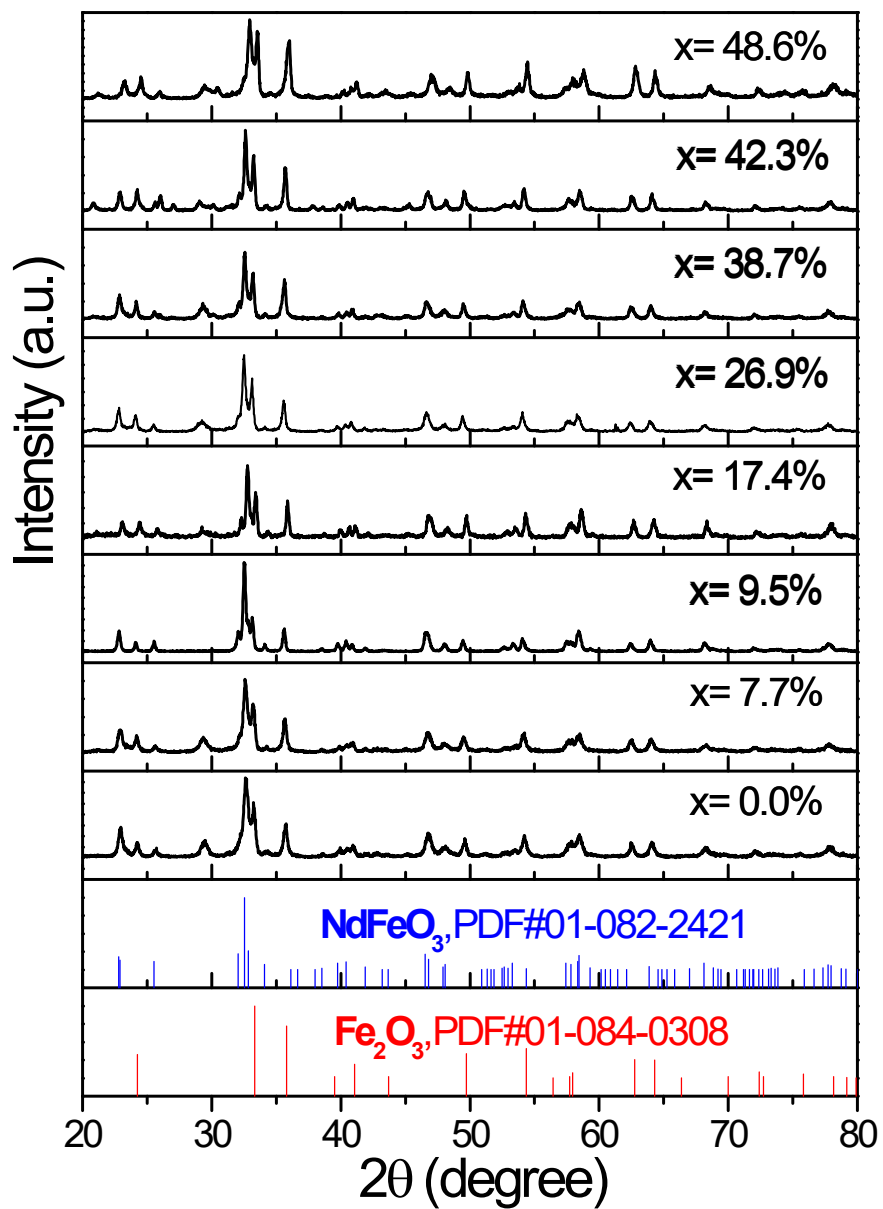
***Surface modification CoFe<sub>2</sub>O<sub>4</sub>NPs with TMAOH.*** As-synthesized Fe-Co oxide NPs were washed with a solution of ethanol and hexane mixture (3:1, v/v) three times by centrifugation (8000 rpm, 10 min). The supernatant was discarded, and the precipitate was re-dispersed in 2 mL of TMAOH under sonication. 5 mL of water was added into the solution and sonicated for 10 min to obtain a stable soft-phase solution. Concentration of the oxide nanostructures in colloidal solution was calculated to be 0.07 mol/L).

***Synthesis of Nd-Fe-B/Fe-Co hard-soft phase oxide nanocomposites.***

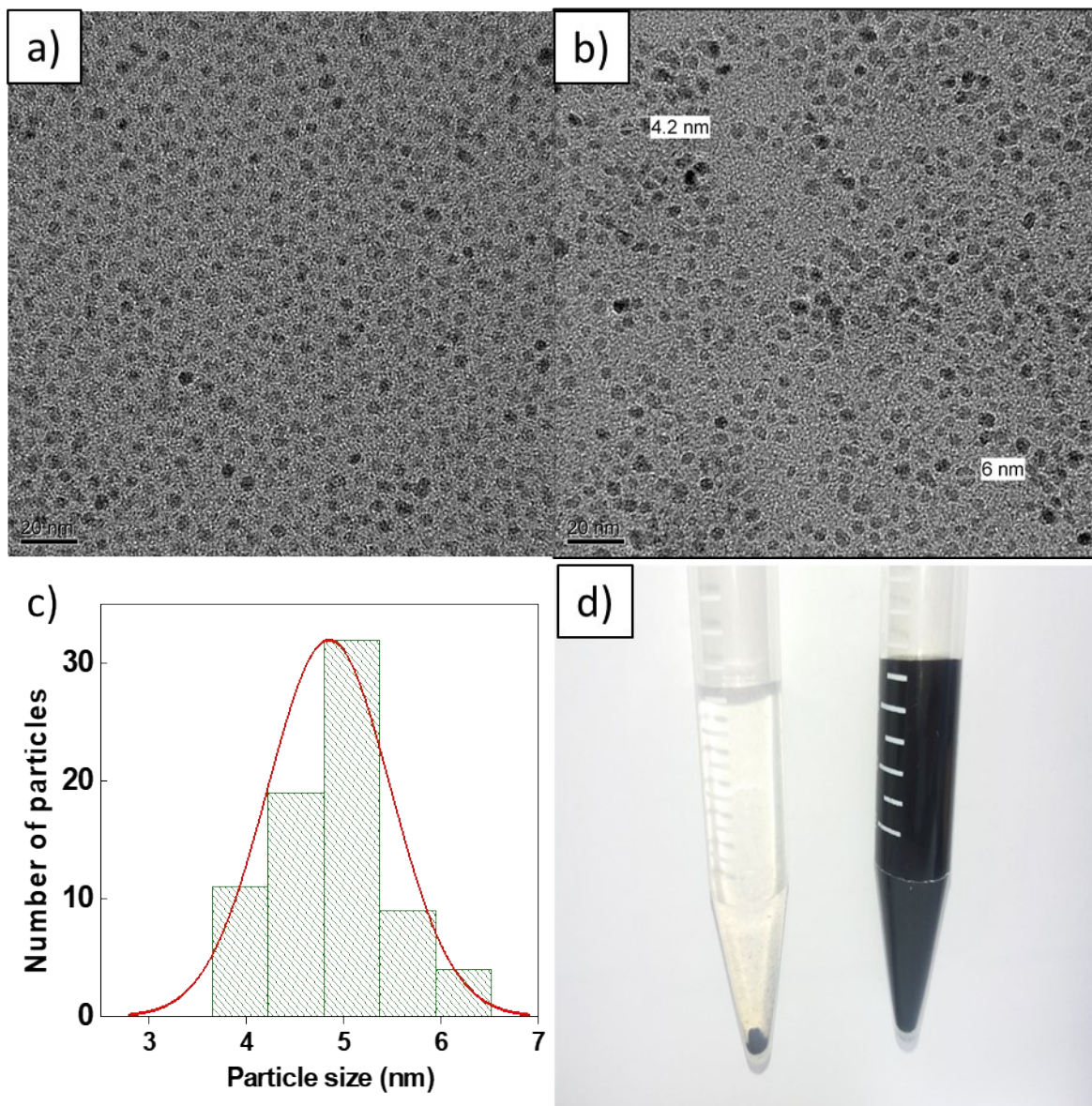
The hard phase Nd-Fe-B oxide nanostructures were fabricated using gel-combustion process, following the procedure reported by Ma et al.<sup>6</sup> with some modification. In a typical synthesis process, about 1.391 g (3.0 mmol) Nd(NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O, 4.358 g (10 mmol) Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O, 0.100 g (1.5 mmol) H<sub>3</sub>BO<sub>3</sub>, 5.920 g (29 mmol) citric acid, 1.7 mL (29 mmol) ethylene glycol, and 15 mL H<sub>2</sub>O were mixed together in a glass vial. The mixture was stirred vigorously for 1 h to obtain a homogeneous black solution. pH of the sol was adjusted to 7.0 by adding aqueous ammonia solution. Then a specific volume of the soft-phase solution (colloidal solution of the surface modified Fe-Co oxide NPs) was added to it and ultrasonicated for 5 min. The Fe-Co oxide NP-dispersed sol was then heated overnight at 90 °C to remove water from it, obtaining a grey color gel. The gel was heated further to 200 °C, which ignited the combustion, producing the composite of Nd-Fe-B oxide and Fe-Co oxide nanostructures. The obtained product was ground in an agate mortar, and air-annealed at 400 °C for 2 h and 800 °C for 2 h, successively. For the reduction of this oxide composite, obtained powder was mixed with CaH<sub>2</sub> (105 mg CaH<sub>2</sub>/100 mg sample)

inside a glove box, and pelletized (12 mm diameter) by cold pressing (300 Kg.cm<sup>-2</sup>, 1 min). The pellet was ground to powder with 5 mL of ethanol and washed repeatedly with DI water until the supernatant becomes transparent. The final product was collected by magnetic separation, washed 2 times with acetone, and stored in hexane.

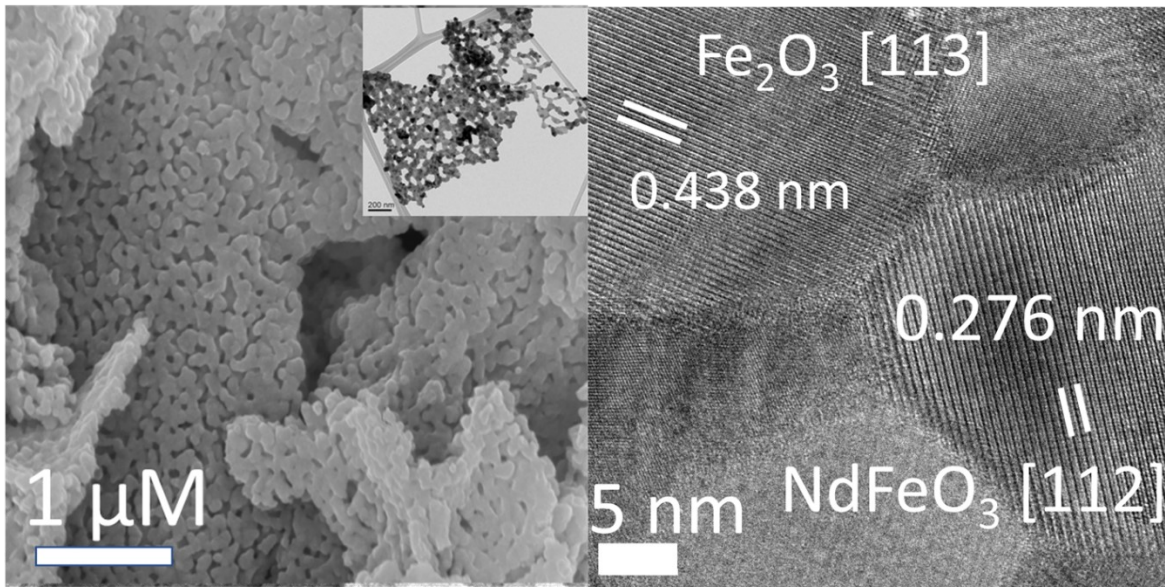
**Sample characterization.** To evaluate the crystallinity and structure of the oxides and reduced nanocomposites, their X-ray diffraction (XRD) patterns were recorded in a Rigaku D-Max 2500PC diffractometer operating at 40 kV accelerating voltage and 200 mA filament current, utilizing Cu K $\alpha$  ( $\lambda$ = 1.5406 Å) radiation. A Jeol-JSM-6700F scanning electron microscope (SEM) operating at 15 kV was utilized for inspecting the morphology of the samples. Crystallinity, inter-grain structure and elemental distribution in the nanocomposites were analyzed in a JEOL JEM-2100F transmission electron microscope (TEM), coupled with a Bruker XFlash6T|60 energy dispersive spectroscopy (EDS) analytical system operating at 200 kV accelerating voltage. A Quantum Design Physical Property Measurement system (PPMS, Evercool II – 9T) was utilized to record the magnetization curves of the nanocomposites at room temperature in -3T to 3T range of applied magnetic field. The Henkel plot ( $\delta M(H) = m_d(H) - [1 - 2m_r(H)]$ ) was used to confirm the interaction between soft and hard magnetic phases. On the demagnetized samples, the isothermal remanent magnetization (IRM) and the DC demagnetization remanent magnetization (DCD) curve were measured respectively to obtain  $m_r(H)$  and  $m_d(H)$  values using a vibrating sample magnetometer (VSM, Lake shore, VSM 7410, USA).<sup>7</sup>



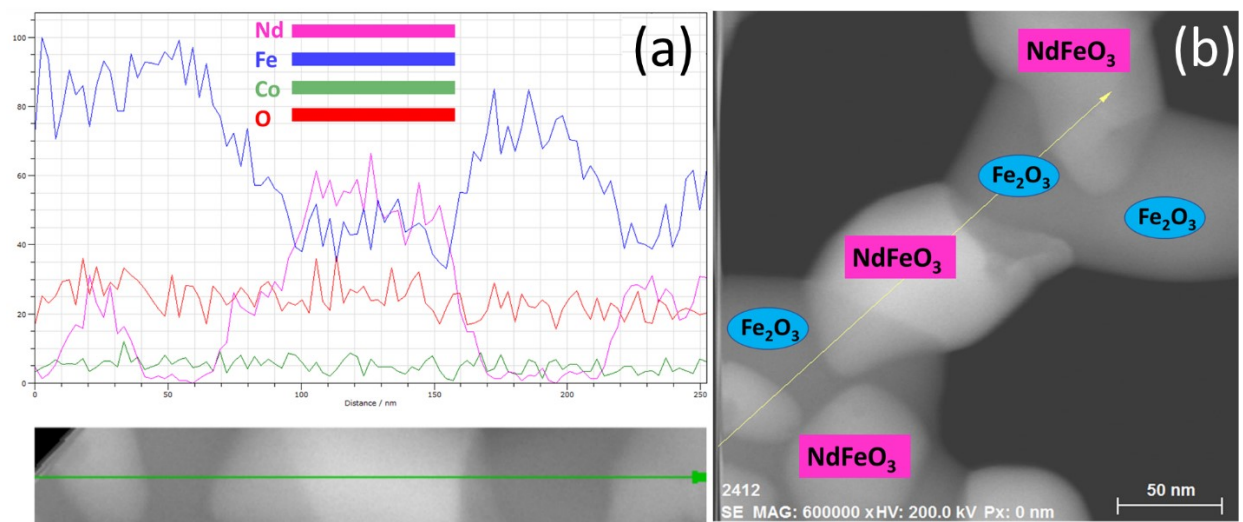
**Figure S1.** XRD patterns of the  $(100-x\%)\text{Nd-Fe-B}/x\%\text{Fe-Co}$  composite oxides with different  $\text{CoFe}_2\text{O}_4$  (Fe-Co oxide) contents after annealing at 800 °C for 2 h.



**Figure S2.** Typical (a) TEM images of Fe-Co oxide dispersed in hexane, (b) TEM image of Fe-Co oxide dispersed in water after phase transfer process, (c) Particles distribution, (d) Image of Fe-Co oxide particles dispersed in water before (left) and after (right) phase transfer modification.

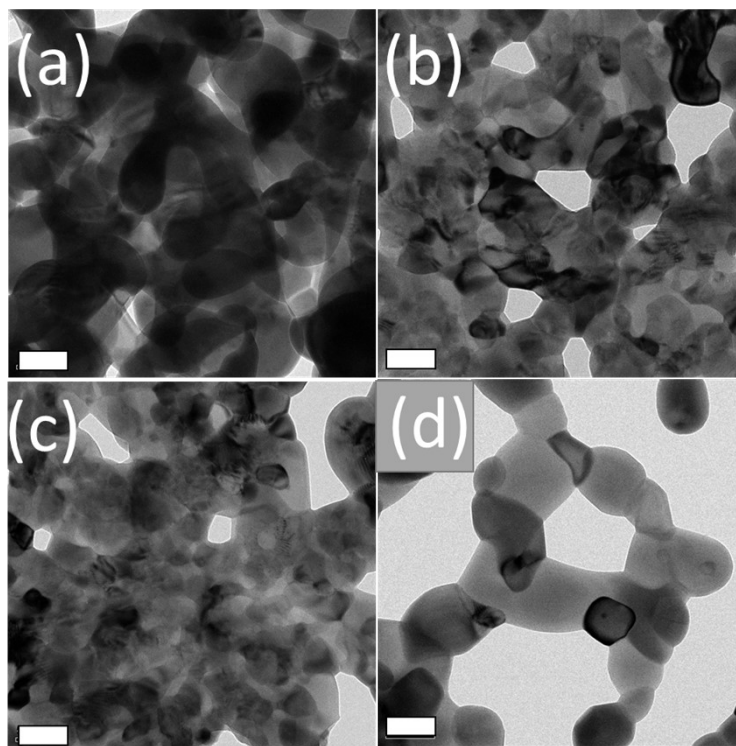


**Figure S3.** Typical (a) SEM (inset TEM), (b) HRTEM images of Nd-Fe-B oxide after annealing at 800 °C for 2 h.

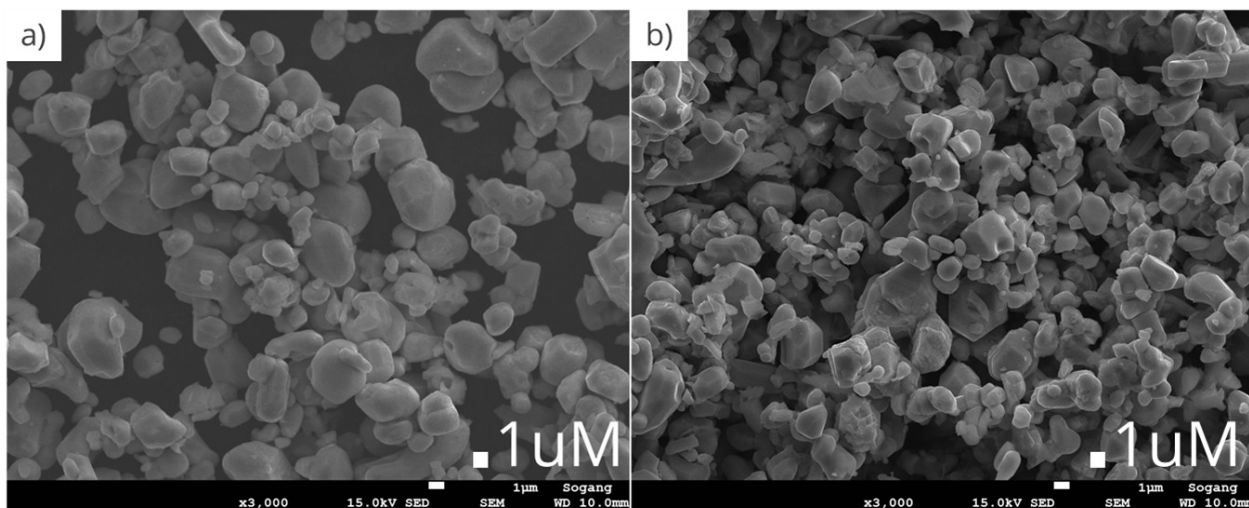


**Figure S4:** TEM-EDS line scanning (a) and HAADF-STEM (b) of a region of NdFeB oxide. The image shows an interconnected region between NdFeO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>

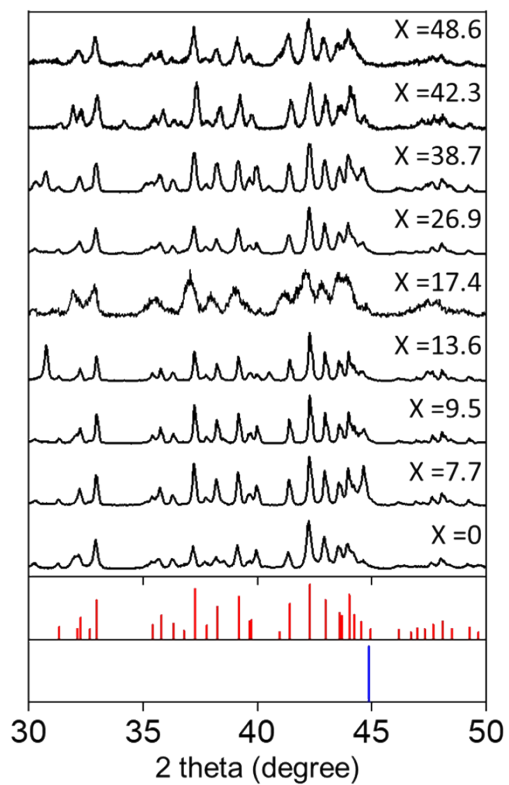




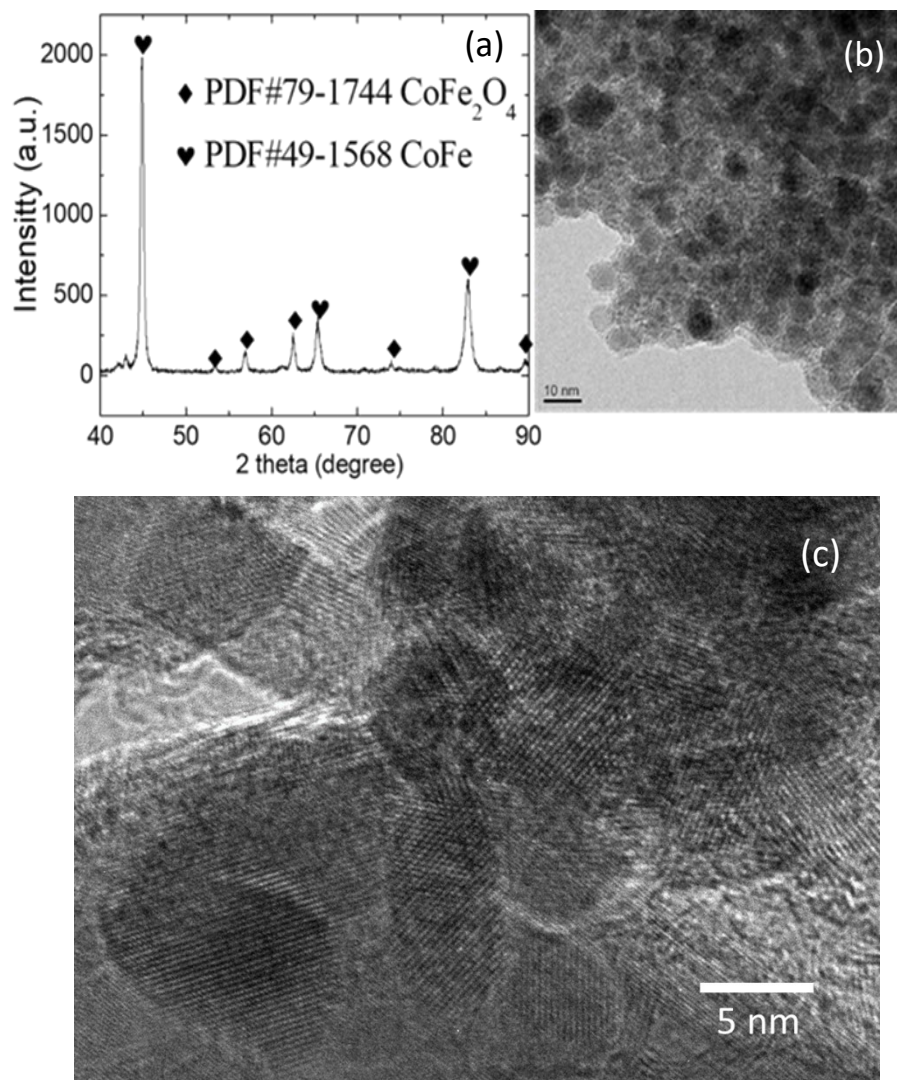
**Figure S5:** TEM images of a region of NdFeB (100-X%)/FeCo X% with (a) X= 0, (b) X =7.7, (c) X=9.5, (d) X = 26.9. The scale bar (white) is 50 nm.



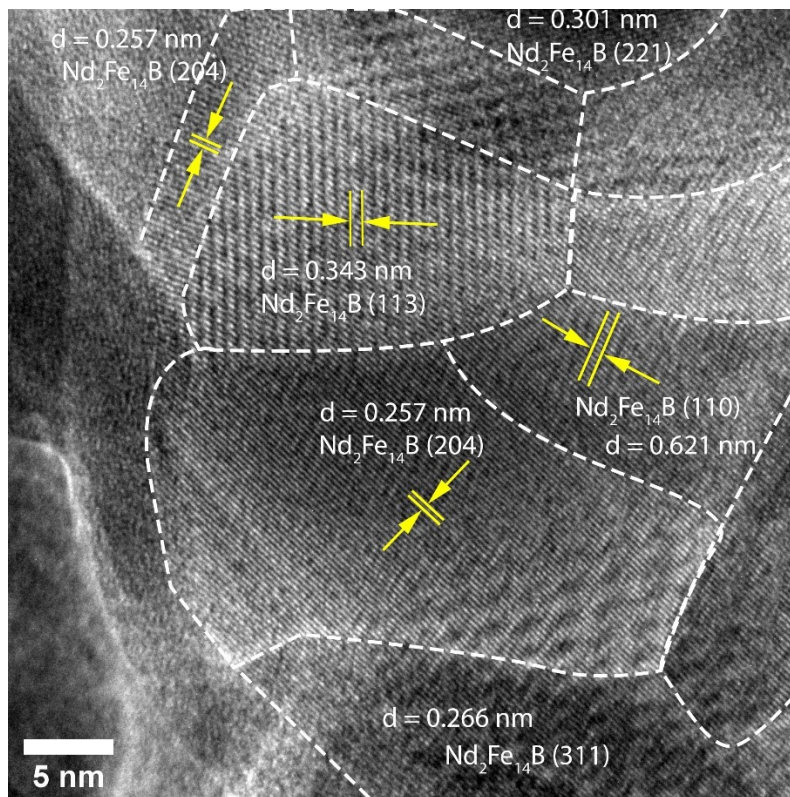
**Figure S6.** Typical SEM of (a) NdFeB 100% sample and (b) NdFeB92.3%/FeCo7.7% obtained after the reduction Nd-Fe-B oxide with  $\text{CaH}_2$  at 900 °C for 2 h and subsequent washing in water.



**Figure S7.** XRD patterns of the (100-X%)Nd-Fe-B/X%Fe-Co composite oxides containing different mol% (X) of Fe-Co oxide particles after reduction-diffusion treatment and subsequent washing with water. (Red pattern denotes ref #01-070-1385Nd<sub>2</sub>Fe<sub>14</sub>B and blue pattern denotes ref #00-049-1568 FeCo)



**Figure S8.** (a) XRD pattern and (b) typical TEM image and (c) typical HRTEM image of the CoFe<sub>2</sub>O<sub>4</sub> nanoparticles after CaH<sub>2</sub> assisted reduction at 500 °C in Ar atmosphere. Formation of well-crystalline Fe-Co alloy particles is clear in the HRTEM image (b).



**Figure S9.** HRTEM image of the Nd<sub>2</sub>Fe<sub>14</sub>B nanoparticles after CaH<sub>2</sub> assisted reduction at 900 °C in Ar atmosphere

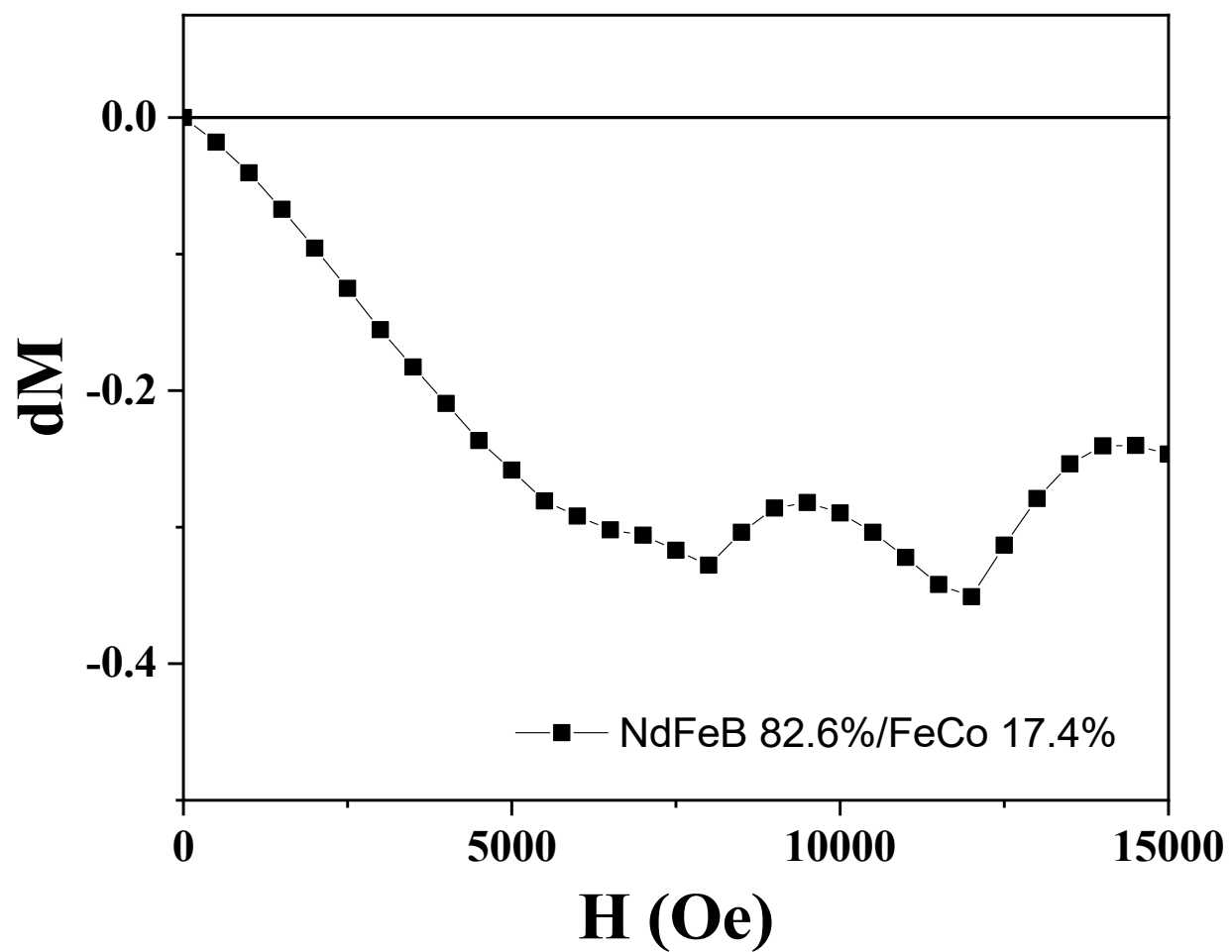


Figure S11. Henkel plot of NdFeB 82.6%/FeCo 17.4%

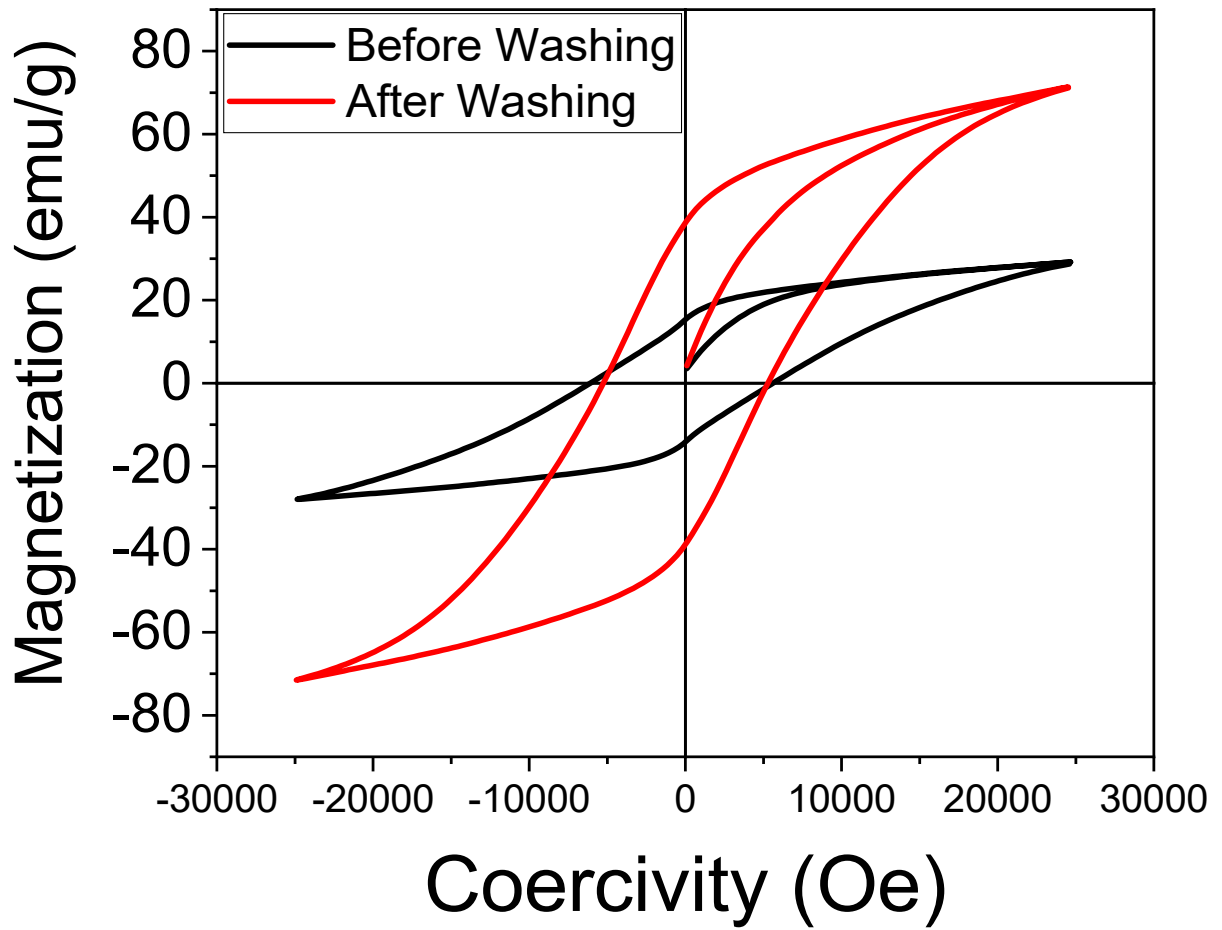


Figure S12. VSM data of NdFeB (100-x) %/FeCo x% with x = 17.4% before and after washing

Thermo calculation data:

Thermo calculation data was calculated from Thermochemical Data of Pure substance, Ihsan Barin<sup>8</sup>

**Table S2. Free Energy Changes  $\Delta G$  for the Reduction Reactions**

No.	Reaction	$\Delta G$ (kJ mol <sup>-1</sup> ) at 600K	$\Delta G$ (kJ mol <sup>-1</sup> ) at 900K	$\Delta G$ (kJ mol <sup>-1</sup> ) at 1200K
1	$\text{CaH}_2 = \text{Ca} + 2\text{H}$	472.544	397.666	321.376
2	$\text{B}_2\text{O}_3 + 3\text{Ca} = 2\text{B} + 3\text{CaO}$	-603.468	-583.434	-553.9877
3	$\text{B} + \text{H} = \text{BH}$	201.563	188.505	176.732
4	$2\text{H} = \text{H}_2$	-375.28	-342.264	-308.058
5	$\text{NdFeO}_3 + 3\text{Ca} = \text{Nd} + \text{Fe} + 3\text{CaO}$	-523.027	-515.515	-505.5067
6	$\text{Nd}_2\text{O}_3 + 3\text{Ca} = 2\text{Nd} + 3\text{CaO}$	-81.169	-71.741	-59.0127
7	$\text{Nd} + 2\text{H} = \text{NdH}_2$	-480.005	-400.432	-317.828
8	$2\text{B} + 6\text{H} = \text{B}_2\text{H}_6$	-981.723	-820.424	-654.313
9	$\text{Fe}_2\text{O}_3 + 3\text{Ca} = 2\text{Fe} + 3\text{CaO}$	-1054.762	-1038.641	-1018.2027
10	$\text{CoFe}_2\text{O}_4 + 4\text{Ca} = \text{Co} + 2\text{Fe} + 4\text{CaO}$	-1413.57	-1391.143	-1381.4686



**Table S3. Free Energy Changes  $\Delta G$  for the Reduction Reactions**

No.	Reaction	$\Delta G$ ( $\text{kJ mol}^{-1}$ ) at 600K	$\Delta G$ ( $\text{kJ mol}^{-1}$ ) at 900K	$\Delta G$ ( $\text{kJ mol}^{-1}$ ) at 1200K
1	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{BH} + 3\text{CaO} + 2\text{H}_2$	466.73	302.046	147.4883
2	$\text{NdFeO}_3 + 3\text{CaH}_2 = \text{Nd} + \text{Fe} + 3\text{CaO} + 3\text{H}_2$	-231.235	-349.309	-465.5527
3	$\text{Nd}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{Nd} + 3\text{CaO} + 3\text{H}_2$	210.623	94.465	-19.0587
4	$\text{Nd}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{NdH}_2 + 3\text{CaO} + \text{H}_2$	1.173	-21.871	-38.5987
5	$\text{Fe}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{Fe} + 3\text{CaO} + 3\text{H}_2$	-762.97	-872.435	-978.2487
6	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 = \text{B}_2\text{H}_6 + 3\text{CaO}$	-167.559	-210.86	-244.1727
7	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{B} + 3\text{CaO} + 3\text{H}_2$	-311.676	-417.228	-514.0337
8	$\text{CoFe}_2\text{O}_4 + 4\text{CaH}_2 = \text{Co} + \text{Fe} + 4\text{CaO} + 4\text{H}_2$	-1024.514	-1169.535	-1328.1966

## References

1. G. S. Chaubey, C. Barcena, N. Poudyal, C. Rong, J. Gao, S. Sun and J. P. Liu, *J Am Chem Soc*, 2007, **129**, 7214-7215.
2. S. Sun and H. Zeng, *J Am Chem Soc*, 2002, **124**, 8204-8205.
3. T. Lu le, N. T. Dung, D. Tung le, C. T. Thanh, O. K. Quy, N. V. Chuc, S. Maenosono and N. T. Thanh, *Nanoscale*, 2015, **7**, 19596-19610.
4. S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang and G. Li, *J Am Chem Soc*, 2004, **126**, 273-279.
5. C. Moya, P. Morales Mdel, X. Batlle and A. Labarta, *Phys Chem Chem Phys*, 2015, **17**, 13143-13149.
6. H. X. Ma, C. W. Kim, D. S. Kim, J. H. Jeong, I. H. Kim and Y. S. Kang, *Nanoscale*, 2015, **7**, 8016-8022.
7. R. W. Gao, D. H. Zhang, W. Li, X. M. Li and J. C. Zhang, *Journal of Magnetism and Magnetic Materials*, 2000, **208**, 239-243.
8. I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft mbH, 1995.