

## *Electronic Supplementary Information (ESI)*

### **Chemical Synthesis of Nd<sub>2</sub>Fe<sub>14</sub>B/Fe<sub>3</sub>B Nanocomposites**

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#### **1. Experimental**

Neodymium(III) 2, 4-pentanedionate Nd(acac)<sub>3</sub> (99.9+%), Triethylamineborane (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NBH<sub>3</sub>(95%), 1-Octadecene (ODE, 90%), were purchased from Alfa Aesar. Oleylamine (OAm, >70%) was purchased from Aldrich. Iron (III) acetylacetonate (Fe(acac)<sub>3</sub>) was from Beijing Yili Fine Chemical. Iron pentacarbonyl (Fe(CO)<sub>5</sub>, 98%) was from Xin Ding Peng Fei Chemical Co. in China Anhydrous ethyl alcohol (99.9%), and hexane (99.0%) were purchased from Beijing Chemicals. All syntheses were carried out under air-free conditions, using a standard Schlenk-line setup.

##### *1.1. Synthesis of α-Fe NPs:*

20 mL ODE and 0.3 mL OAm were degassed at 120 °C for 2 h to remove moisture and impurity. 0.3 mL (2.25 mmol) Fe(CO)<sub>5</sub> was quickly injected into the solution and kept for 2 min, then increased to 180 °C at a heating rate of 12 °Cmin<sup>-1</sup> and kept for 5 min. The α-Fe NPs were precipitated by adding 20 mL ethanol and washed three times with ethanol, then dispersed in hexane.

##### *1.2. Synthesis of α-Fe@Fe<sub>3</sub>B nanoalloys:*

α-Fe@Fe<sub>3</sub>B nanoalloys was synthesized with injection of Fe(CO)<sub>5</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NBH<sub>3</sub> at molar ration 3: 1 in the as-prepared α-Fe NPs, and kept at 180 °C for 15 min before cooling down to room temperature. Finally, it can tune a final molar ratio of α-Fe:

Fe<sub>3</sub>B at 5: 1, 3: 1 and 1: 1. The nanoalloys were washed three times by hexane and ethanol, then dispersed in hexane for further characterization.

### *1.3. Synthesis of $\alpha$ -Fe@Fe<sub>3</sub>B@Nd-Fe-B-oxide precursor:*

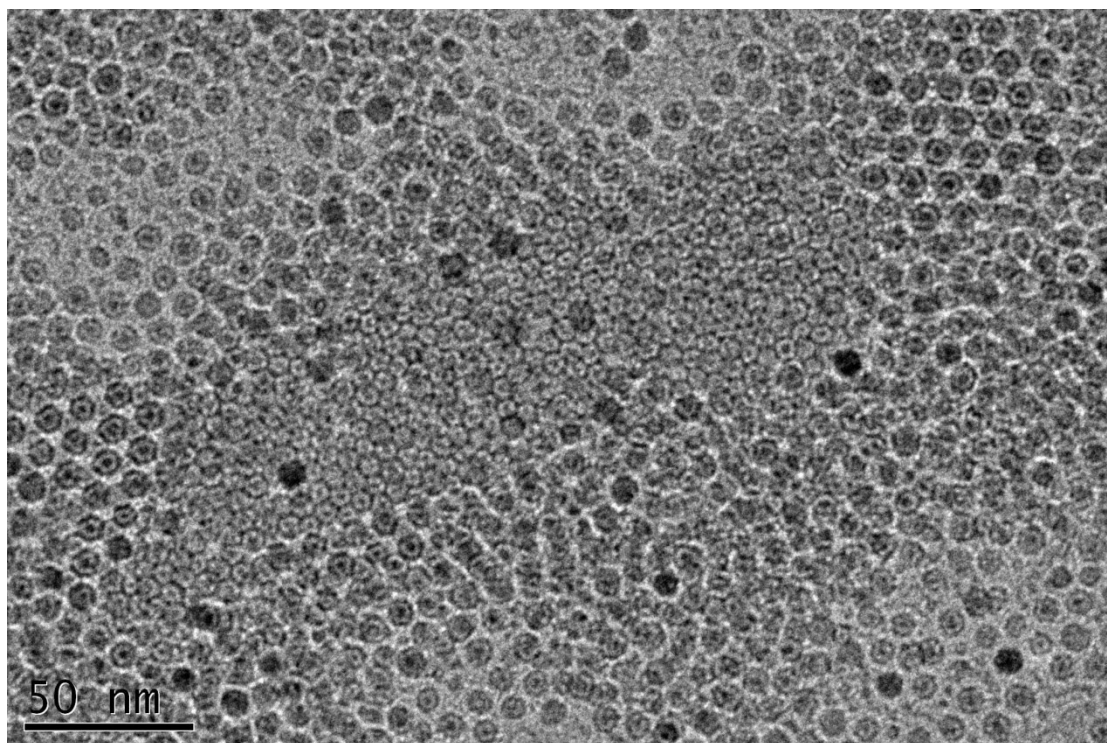
For total Nd/Fe molar ratio at 2.5/10 was prepared: 1.266 g (2.5 mmol) Nd(acac)<sub>3</sub> and 0.79 mL (6 mmol) Fe(CO)<sub>3</sub> was dissolved in 30 mL OAm. The solution was degassed at 120 °C for 1 h. As-prepared  $\alpha$ -Fe@Fe<sub>3</sub>B nanoalloys (1 mmol) with molar ratio of  $\alpha$ -Fe: Fe<sub>3</sub>B at 1: 1 were dispersed in 10 mL hexane before added into the solution. The solution was kept at 120 °C for 1 h to remove hexane. Then, 100  $\mu$ L (0.6 mmol) (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NBH<sub>3</sub> was quickly injected. Subsequently, the mixture was heated to 350 °C at a heating rate of 10 °Cmin<sup>-1</sup> and kept for 1 h before cooling to room temperature. The Nd-Fe-B-oxide/FeB precursor, with total Nd/Fe ratio tuned by addition of different amount of Nd, Fe precursors and  $\alpha$ -Fe@Fe<sub>3</sub>B, was precipitated by ethanol and separated by centrifuging at 10000 rpm for 6 min. The as-prepared composites were dispersed in hexane for further characterization.

### *1.4. Synthesis of Fe<sub>3</sub>B@Nd<sub>2</sub>Fe<sub>14</sub>B nanocomposites:*

A typical procedure for the synthesis of Nd<sub>2</sub>Fe<sub>14</sub>B nanocomposites is as follows: the as-prepared composites were first reduced with stainless steel crucible under Ar + 5% H<sub>2</sub> at 800 °C for 1 h at a heating rate of 20 °Cmin<sup>-1</sup>. Then, 500 mg of Ca powder was ground together with 170 mg of above powder and Nd<sub>2</sub>O<sub>3</sub> nano-powder for compensation of neodymium evaporation in glove box. The mixture was wrapped and quickly transferred to a quartz tube that had been flushed with Ar. After that, a reduction & diffusion reaction was carried out at 850 °C for 1.5 h in argon atmosphere and the powder was furnace cooled to room temperature. To remove the CaO and un-reacted Ca, the sample was washed twice with 5% acetic acid solution, and then with cold distilled water to remove any traces of acetic acid. Finally, the sample was rinsed with ethanol and dried in vacuum.

### *1.5 Nanocomposites Characterization:*

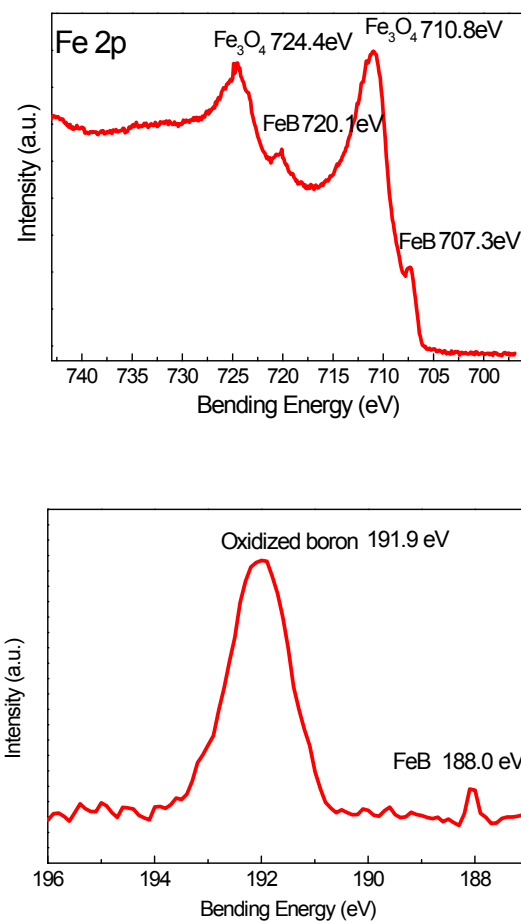
The samples were studied by transmission electron microscopy (TEM, TECNAI T20, 300 kV), high-resolution transmission electron microscope (HRTEM, FEI TECNAI F30, 300 kV), field-emission scanning electronic microscopy (SEM, JEOL JSM-7600F, 10 kV), X-ray powder diffraction (XRD, Rigaku D/MAX-2000, Cu K $\alpha$ ) and X-ray Photoelectron Spectroscopy (XPS, Kratos Axis Ultra). Magnetic studies were performed using a Quantum Design SQUID instrument with a field upto 30 kGs. The compositions of the samples were characterized by energy-dispersive X-ray spectroscopy (EDS).



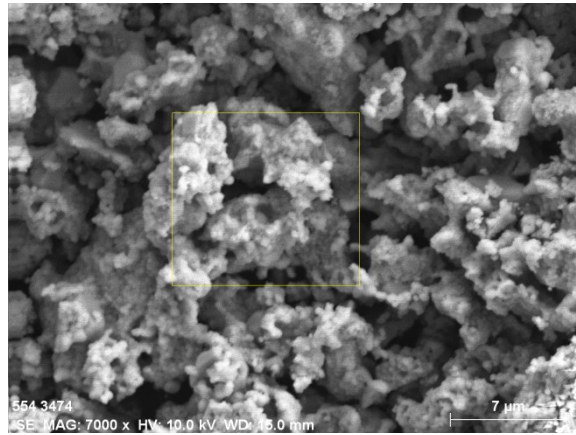
**Figure S1.** The magnification image of Figure 1d.

For  $\alpha$ -Fe@Fe<sub>3</sub>B nanoalloys with  $\alpha$ -Fe: Fe<sub>3</sub>B at 1: 1 were analyzed by XPS spectra for Fe/B molar ratio at 3.82/1 (in Figure S2). Two peaks of iron with binding energies of 710.8 and 724.4 eV can be attributed to the Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> levels, respectively, which was consistent with the values for Fe<sub>3</sub>O<sub>4</sub> on nanoalloys surface[1]. The relative areas of the main and smaller peaks of the Fe 2p<sub>3/2</sub> level suggest that iron is mainly in forms of oxide state on the surface, it was attributed to the oxide surface on the NPs. In addition, a smaller peak at 707.3 eV for Fe 2p<sub>3/2</sub> was assigned to the metallic state

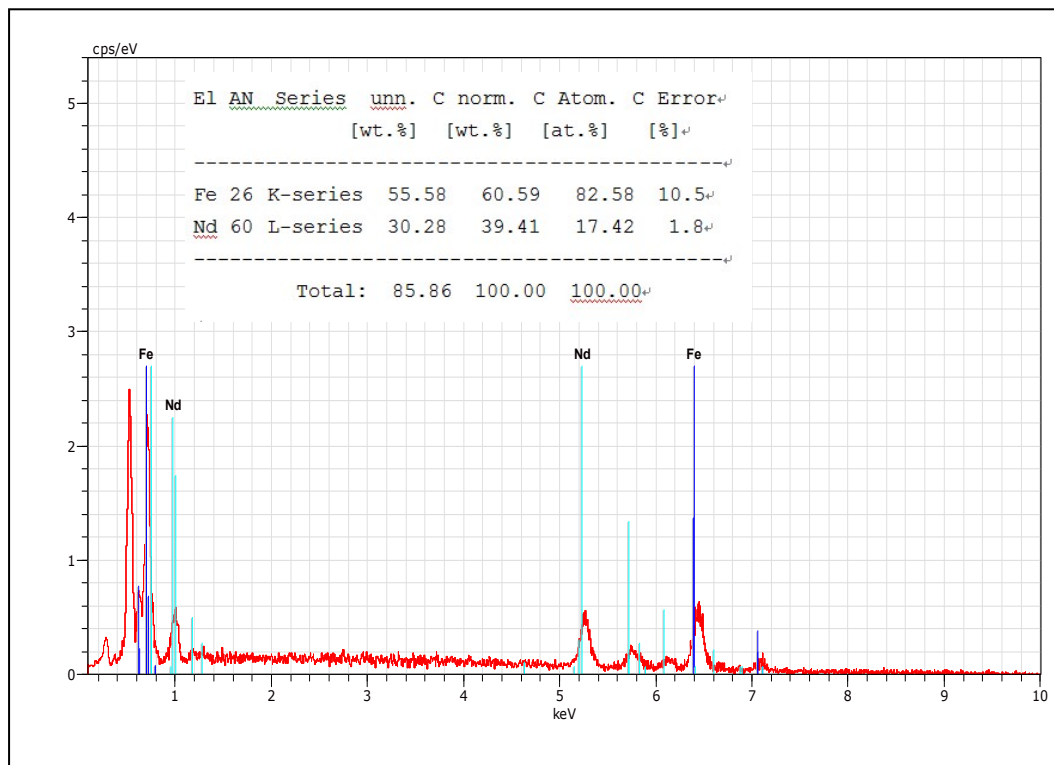
of FeB nanoalloys. The peak at 191.9 eV for B 1s is corresponding to oxidized boron species. In comparison with pure boron (187.3 eV) [2], the binding energy at 188.0 eV in FeB nanoalloys positively shifted about 0.7 eV [3], which indicated electron transferred from boron to iron.



**Figure S2.** XPS spectra of  $\alpha$ -Fe@Fe<sub>3</sub>B nanoalloys with  $\alpha$ -Fe: Fe<sub>3</sub>B at 1: 1. (a) Fe 2p spectrum, which indicates the existence of Fe<sub>3</sub>O<sub>4</sub> phase on the FeB surface [1], (b) B 1s spectrum, which indicates boron oxide on the FeB surface [3].



a)



b)

**Figure S3.** a) SEM images of  $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$  nanocomposite powder with total Nd/Fe ratio of 2.5/10. b) EDS analysis results show the molar ratio of Nd to Fe=2.11:

## Reference

- [1] T. Yamashita, P. Hayes, *Appl. Surf. Sci.* 2008, 254: 2441-2449.
- [2] Y. Okamoto, Y. Nitta, T. Imanaka, S. Teranishi, *J. Chem. Soc. Faraday Trans 1* 1979, 75: 2027-2039.
- [3] S. Ma, P. Z. Si, Y. Zhang, B. Wu, Y. B. Li, J. J. Liu, et al. *Scr. Mater.* 2007, 57: 265-268.