

# Electronic Supporting Information

## for

### Chemical Synthesis of Hard Magnetic SmCo Nanoparticles

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#### Experimental Section:

Cobalt(II) acetate tetrahydrate,  $\text{Co}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$  (98%), samarium(III) acetate hydrate,  $\text{Sm}(\text{ac})_3 \cdot x\text{H}_2\text{O}$  (99.9%), and calcium acetate monohydrate,  $\text{Ca}(\text{ac})_2 \cdot \text{H}_2\text{O}$  (98%) were purchased from Strem Chemicals. Oleic acid (90%), 1-octadecene (90%), and benzyl ether (98%) were purchased from Aldrich. n-hexadecyltrimethylammonium hydroxide (HTMA-OH, 25% in methanol) was purchased from TGI America. All chemicals were used without further purification.

*Synthesis of  $\text{SmCo}_{3.6}\text{-O}$  NPs:* 0.498 g of  $\text{Co}(\text{ac})_2$  and 0.220 g of  $\text{Sm}(\text{ac})_3$  were dissolved in a mixture of 17.5 ml of octadecene and 2.5 ml of oleic acid in a 50 ml four-neck flask. Under a nitrogen flow, the mixture was stirred magnetically and heated to 120 °C, with the solution color changed from pink to blue. The solution was kept at this temperature for 1 h to remove the trace amount of moisture and oxygen and 9 ml n-hexadecyltrimethylammonium hydroxide methanol solution was injected, after which the mixture was kept at 120 °C for 1 h. Under a static  $\text{N}_2$  atmosphere, the solution was heated to 320 °C. The reaction was kept 320 °C for 1.5 h until the color of the solution became brown. The solution was cooled down to room temperature by removing the heating source. The  $\text{SmCo}_{3.6}\text{-O}$  NPs were precipitated by adding 50 ml of isopropanol and centrifuged at 8000 rpm for 8 min. The precipitates were redispersed in 30 ml of hexane, and 40 ml of ethanol was added to precipitate the NPs again. Finally, the  $\text{SmCo}_{3.6}\text{-O}$  NPs were re-dispersed in hexane.

The molar ratio of Co/Sm in the as-prepared  $\text{SmCo}_n\text{-O}$  NPs was controlled by varying the ratio of  $\text{Sm}(\text{ac})_3$  to  $\text{Co}(\text{ac})_2$ . For example,  $\text{SmCo}_n\text{-O}$  NPs with Co/Sm ratios of 1:6.5, 1:5.1, and 1:3.6 were synthesized by using 0.13, 0.18, and 0.22 g  $\text{Sm}(\text{ac})_3$ , respectively, along with 0.498 g  $\text{Co}(\text{ac})_2$ .

*Synthesis of CaO-coated NPs:* Under a gentle  $\text{N}_2$  flow and magnetic stirring, 0.352 g of

$\text{Ca}(\text{ac})_2$  was dissolved in 30 ml of benzyl ether and 100 mg of  $\text{SmCo}_{3.6}\text{-O}$  NPs (dispersed in hexane) were added to the mixture. The solution was heated to 120 °C and kept at this temperature for 30 min to remove hexane. 6.2 ml of n-hexadecyltrimethylammonium hydroxide methanol solution was added into the solution. The mixture was kept at 120 °C for 1 h to remove methanol and other low boiling impurities. Under a static  $\text{N}_2$  atmosphere, the solution was heated to 300 °C and kept at 300 °C for 1 h before it was cooled down to room temperature by removing the heating source. The  $\text{SmCo}_{3.6}\text{-O}/\text{CaO}$  particles were precipitated by adding 20 ml of isopropanol and centrifuged at 6000 rpm for 6 min. The precipitates were washed again with a mixture of 15 ml of hexane and 25 ml of isopropanol. The yellow  $\text{SmCo}_{3.6}\text{-O}/\text{CaO}$  particles were kept in 10 ml hexane.

*Synthesis of  $\text{SmCo}_5/\text{Sm}_2\text{Co}_{17}$  NPs:*  $\text{SmCo}_{3.6}\text{-O}/\text{CaO}$  NPs in 5 ml of the hexane dispersion was precipitated out by adding ethanol and dried under air. The dried powder was transferred to an argon glove box and was ground with 200 mg of anhydrous KCl and 350 mg of Ca granules. The mixture was then transferred to a covered stainless steel boat and the boat was quickly transferred to a ceramic tube flushed with a gas mixture of 95% Ar +5%  $\text{H}_2$ . The tube was heated to 120 °C for 45 min to remove traces of air and moisture absorbed on the inner wall of the tube and then to 960 °C at a rate of 20 °C/min. The tube was kept at this temperature for 2 h under the gas mixture of 95% Ar +5%  $\text{H}_2$  and was cooled down to room temperature by turning off the heating furnace. The sample could be characterized at this point. For further purification, the annealed product was washed under a  $\text{N}_2$  atmosphere with degassed DI water twice at room temperature to remove extra Ca, CaO and KCl. Finally, the powder was washed twice by degassed ethanol and dried in a vacuum chamber. The NPs were kept in a nitrogen glove box for further characterization.

*NP characterization:* The size and morphology of the NPs were characterized by using a Philips EM 420 (120 kV) and a JEOL 2010 (200 kV) transmission electron microscope. Powder X-ray diffraction patterns of the NPs were recorded on a Bruker AXS D8-Advanced diffractometer with Cu  $\text{K}\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). Magnetic studies were performed using a Quantum Design Superconducting Quantum Interface Device (SQUID) with a field up to 70 kOe and a Vibrating Sample Magnetometer (VSM) with a field up to 1.55 kOe. The NP compositions were characterized by Oxford energy-dispersive X-ray spectroscopy (EDS).

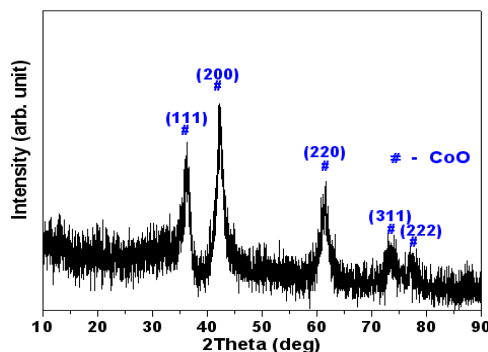
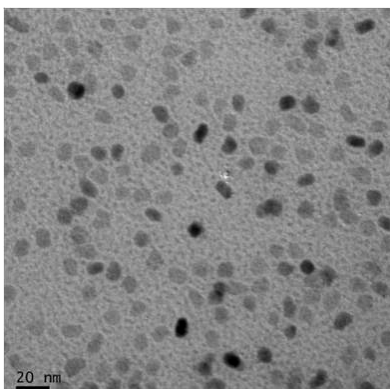
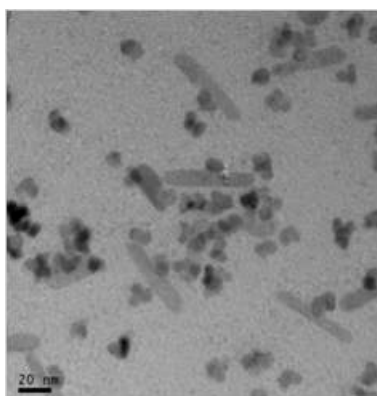


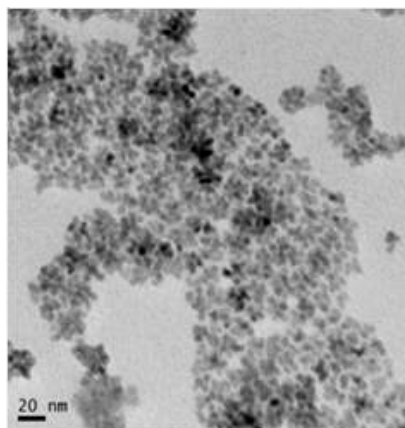
Fig. S1. XRD pattern of the as-synthesized  $\text{SmCo}_{3.6}\text{-O}$  NPs.



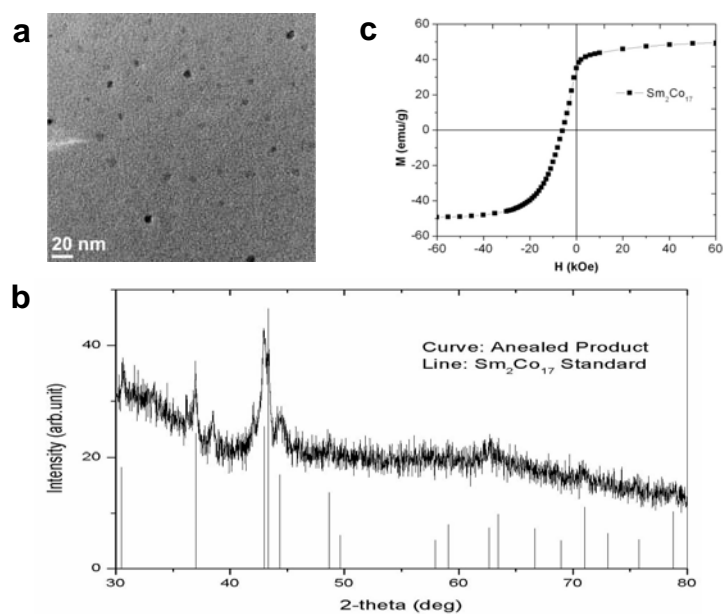
**Fig. S2.** TEM image of the as-synthesized CoO and Sm<sub>2</sub>O<sub>3</sub> NPs without the injection of n-hexadecyltrimethylammonium hydroxide.



**Fig. S3.** TEM image of the as-synthesized SmCo-O NPs obtained by a slow heating rate with oleic acid/octadecene volume ratio of 1:3.



**Fig. S4.** TEM image of the flower-like SmCo-O NPs obtained by a fast heating rate with oleic acid/octadecene volume ratio of 1:3.



**Fig. S5.** (a) TEM image of the Sm<sub>2</sub>Co<sub>17</sub> NPs, (b) XRD of the Sm<sub>2</sub>Co<sub>17</sub> NPs, and (c) room temperature hysteresis loop of the Sm<sub>2</sub>Co<sub>17</sub> NPs.