

## Electronic Supporting information

### Experimental Section

#### Synthesis from reverse micelles:

**8.3-nm Amorphous Co Nanoparticles:** the synthesis and characterization of Co polycrystals coated with dodecanoic acid have been described in a previous paper: reverse micelles of  $5 \times 10^{-2}$  M Co(AOT)<sub>2</sub> form an isotropic phase. The amount of water added in solution is fixed to reach a water concentration defined as  $w = [\text{H}_2\text{O}]/[\text{AOT}] = 32$ . Sodium borohydride, NaBH<sub>4</sub>, added to the micellar solution reduces the cobalt ions. The sodium borohydride content is defined as  $R = [\text{NaBH}_4]/[\text{Co}(\text{AOT})_2] = 4$ . Immediately after NaBH<sub>4</sub> addition, the micellar solution color changes from pink to black, indicating the formation of colloidal Co nanoparticles. After the synthesis, 312  $\mu\text{L}$  Oleic acid (99%, Sigma-Aldrich) was added into the Co colloidal solution to extract the Co nanoparticles. The nanoparticles coated with oleic acid (C<sub>17</sub>H<sub>34</sub>COOH) are washed and centrifuged several times with ethanol to remove all the AOT surfactant and the black powder obtained is dispersed in hexane. In order to eliminate the largest nanoparticles formed, the solution is again centrifuged and only the upper part containing the smallest sized nanoparticles is collected. At the end of the synthesis, 8.3 nm Co nanoparticles coated with oleic acid with a  $\sim 9\%$  size distribution are produced. The entire synthesis is carried out in an N<sub>2</sub> glove box using de-oxygenated solvents to prevent particle oxidation.

To obtain a smaller sized nanoparticles, e.g. 7.9 nm, all the synthetic parameters were kept except for a slight increase amount of the NaBH<sub>4</sub>, where R is increased to 5.

**HCP single domain nanocrystals:** After deposition of the amorphous Co nanoparticles solution on the TEM grids, the samples were loaded into the oxidation apparatus, which is illustrated in Scheme S1. The oxidation apparatus was based on a modified Schlenk line, including high-vacuum pump, source of inert gas (Ar) and

source of oxygen gas ( $O_2$ ). After loading into the apparatus, the samples were submitted to the vacuum pump-Ar flow three times in order to remove the air. The heating setup was pre-adjusted to 250 °C to anneal the samples. The annealing process takes place under an argon flux, whose rate is determined by gas bubbles (2 bubbles/s). After 60 min aging at 250°C, the heating setup was removed in order to stop the annealing process. After annealing treatment, a slight increase of size takes place compared to the native amorphous Co nanoparticles. The 8.3-nm Co nanoparticles results in the 8.4-nm hcp Co nanocrystals, and the 7.9-nm Co nanoparticles leads to the formation of 8.2-nm hcp Co nanocrystals.

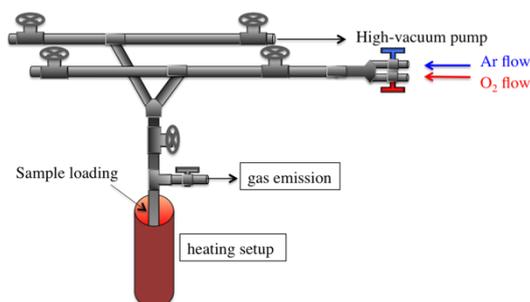
**Synthesis of Polycrystal fcc-Co Nanocrystals by thermal decomposition:** 0.3 mL of oleic acid and 0.5 mL of dioctylamine were dissolved in 20 mL of dodecane. The mixture was heated at 100 °C for 1 h under flowing nitrogen and then cooled to room temperature. 0.54 g of  $Co_2(CO)_8$  was quickly added into the above solution. The solution was heated up to 100 °C for 30 min and subsequently to 200 °C. After 60 min of stirring, the reaction system was cooled down to room temperature. After the synthesis, the Co nanocrystals were washed through ethanol-hexane cycles. Additional oleic acid (200  $\mu$ L) was added into the colloidal solution, and the excess oleic acid was further washed by ethanol.

**Synthesis of Single Crystal  $\epsilon$ -Co Nanocrystals:** 0.1 g of trioctylphosphine oxide (TOPO) and 0.15 mL of oleic acid (OA) were dissolved in 15 mL of 1,2-dichlorobenzene (DCB). The solution is heated to 180 °C under flowing nitrogen. In the glove box, 0.54 g of  $Co_2(CO)_8$  is dissolved in 3 mL of DCB under vigorous stirring. The solution was moved out from glove box by a syringe and rapidly injected into the hot solution containing TOPO and OA. The brown solution immediately turned black indicating the formation of cobalt nanoparticles. The reaction was held at 180 °C for 20 min and then cooled to room temperature. After the synthesis, the Co nanocrystals were washed through ethanol-hexane cycles. Additional oleic acid (200  $\mu$ L) was added into the colloidal solution, and the excess oleic acid was further washed by ethanol.

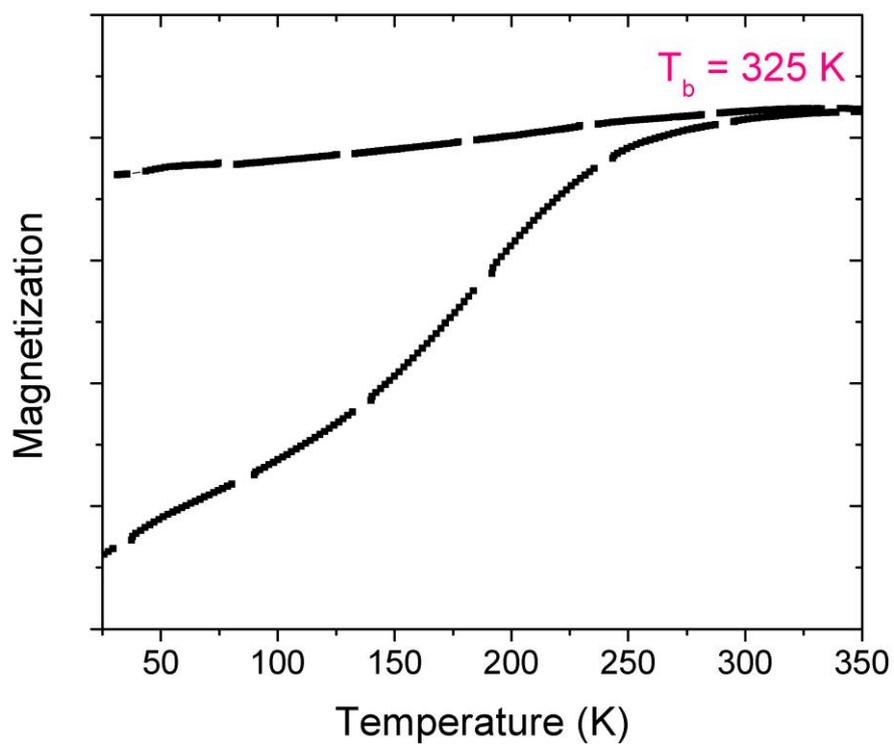
## Oxidation Process

When the samples were subjected to pure oxygen, the heating setup was pre-adjusted to 200 °C (or 260 °C). After 10 min, the heating setup was removed and the oxygen flow was replaced by Ar flow in order to stop the oxidation immediately. After cooling by argon flow to room temperature, the samples are characterized by TEM.

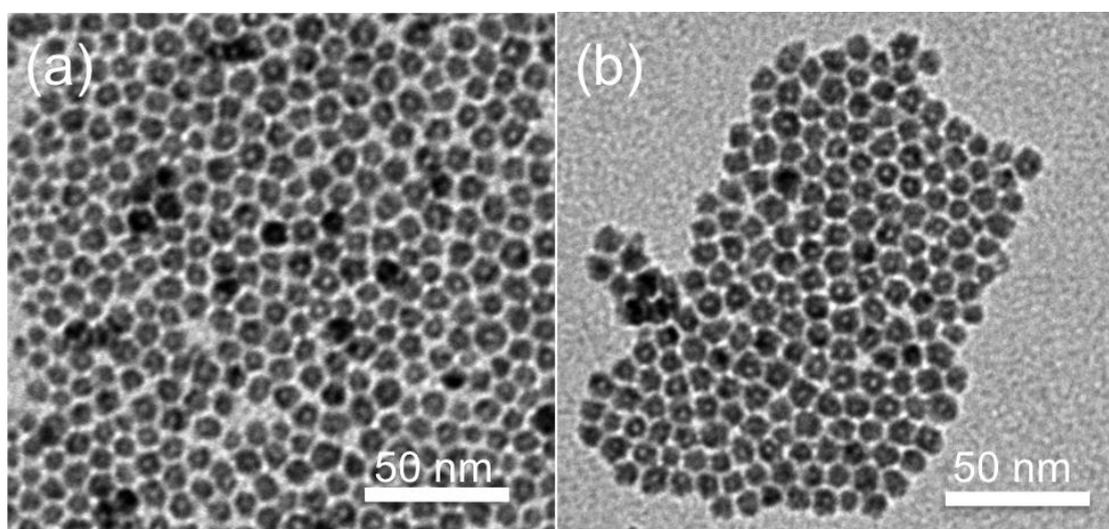
**Apparatus:** Conventional transmission electron microscopy (TEM) was performed using a JEOL 1011 microscope at 100 kV. High-resolution transmission electron microscopy was performed using a JEOL 2010 microscope at 200 kV.



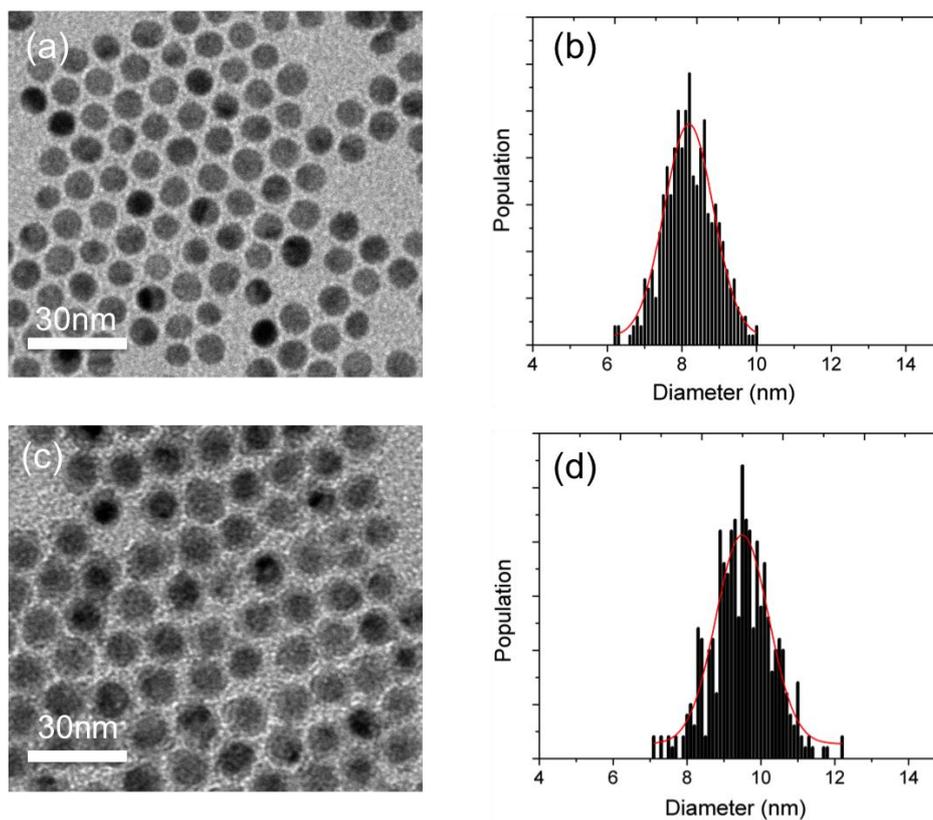
**Scheme S1.** Modified Schlenk line setup applied for the air-free annealing or oxidizing the samples



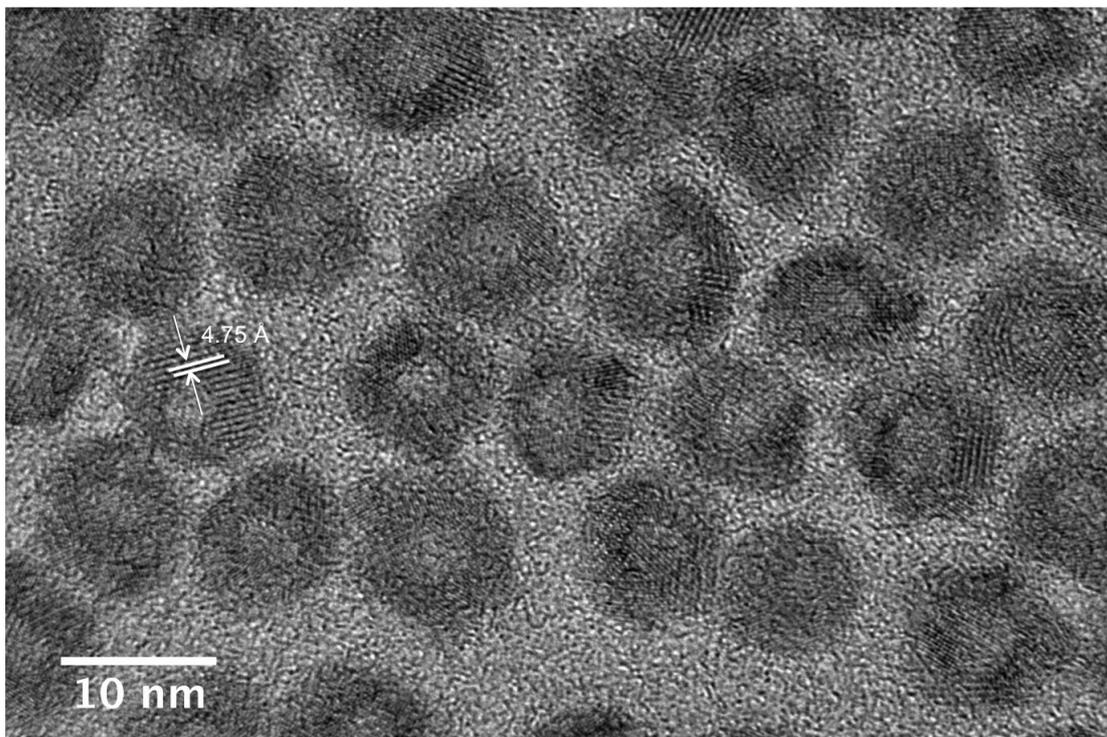
**Fig. S1** ZFC/FC curve of 8.4 nm Co<sub>HCP</sub> nanocrystals.



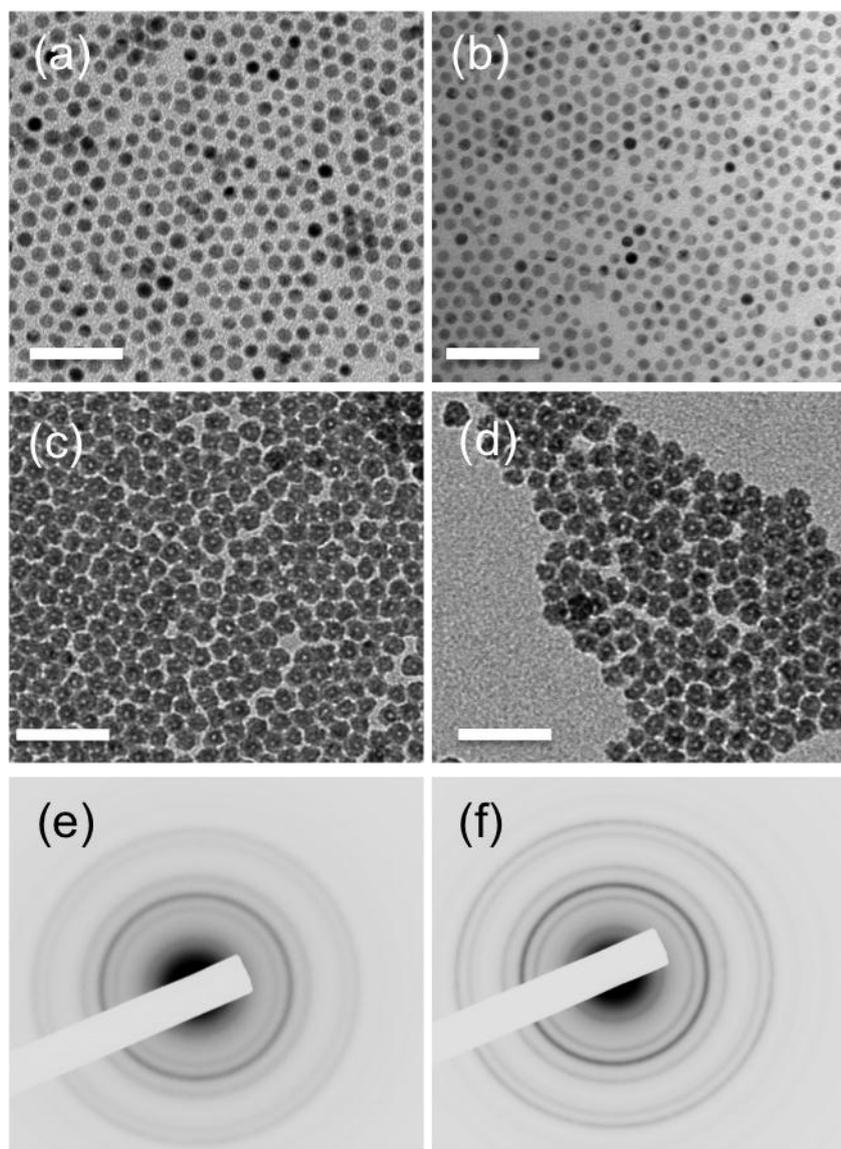
**Fig. S2** TEM images of oxidation of 7 nm Co<sub>HCP</sub> nanocrystals coated with dodecanoic (a) and oleic acid (b). (oxidation conditions: 200°C for 10 min)



**Fig. S3** TEM images of 8.2-nm hcp Co nanocrystals before (a) and after oxidation (c) at 200°C for 10min; (b) and (d) are the corresponding size histogram. The size and size distributions of the nanocrystals before and after oxidation are 8.2nm, 9%, and 9.5nm, 10%, respectively.



**Fig. S4** HRTEM image of  $\text{Co}_3\text{O}_4$  nanoparticle produced after oxidation of Co nanoparticles: the case of  $\text{Co}_6$ .



**Fig. S5** TEM images of oxidation process of 7-nm  $\text{Co}_{\text{HCP}}$  nanocrystals produced both in dry system (a, c, e) and in solution (b, d, f): (a,b) before oxidation; (c,d) after oxidation at 260 °C for 10 min; (e,f) is the corresponding SAED from (c,d). Scale bars inserted in TEM images are 50 nm.