

Supporting Information for

Unconventional morphologies of CoO nanocrystals via controlled oxidation of cobalt oleate precursor

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Experiment

In a typical synthesis, 238 mg cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 1 mmol, Sinopharm Chemical Reagent Co., 99%) and 1.212 g sodium oleate (NaOA, 4 mmol, TCI Co., >97%) were dissolved in the mixed solvent of 8 mL ethanol, 6 mL distilled water, and 14 mL n-hexane. The solution was heated to 70 °C and kept for 5.5 h. The solution was then washed with 10 mL distilled water and then rinsed with 5 mL ethanol in a separatory funnel. The recovered organic phase solution was treated with rotary evaporator to remove the n-hexane to collect the blue purple Co (II) oleate complex precursor. The as-prepared precursor was added 13 mL 1-octadecene (ODE, Acros Organics, 90%) and then kept in the ambient condition for 10 min / 60 min / 6 h to obtain a slightly oxidized purple / partly oxidized red / mostly oxidized brownish green color clear precursor solution or 12 h to collect a green color one. Each precursor solution was then added 315 μL oleic acid (TCI Co., >85%) and degassed at room temperature for 30 min under vacuum, and then heated to 320 °C at a heating rate of 15 °C / min, and kept at for two hours with vigorous stirring. The final dark green color solution was cooled to room temperature, and washed with n-hexane/isopropanol.

Supporting Figures

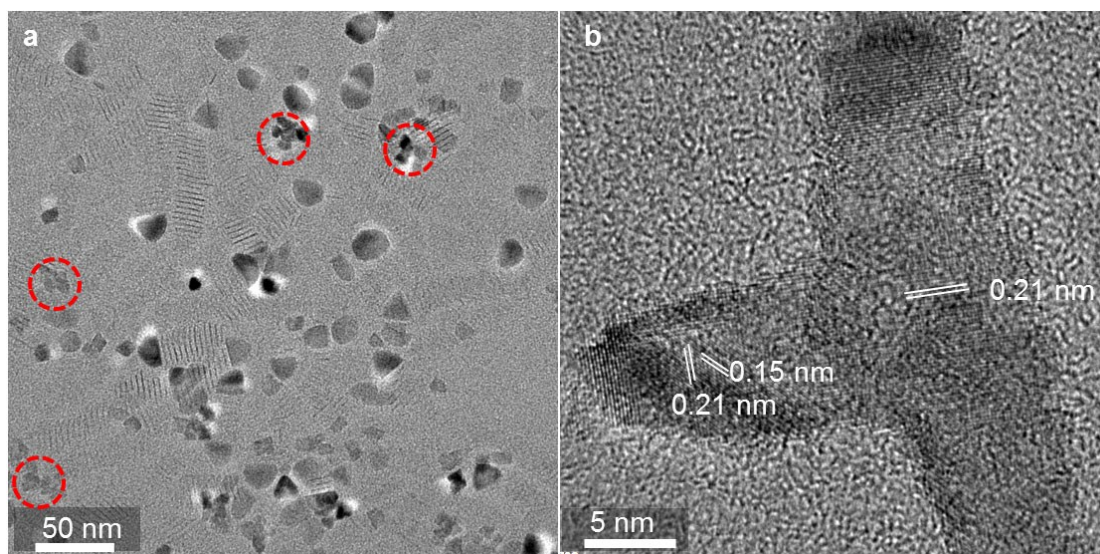


Figure S1. TEM (a) of the product from oxidized precursor. CoO NCs in cubic phase are highlighted with red dash circles. HRTEM (b) of one c-CoO NC with lattice fringe spacings 0.21 and 0.15 nm indexed to (200) and (220) planes.

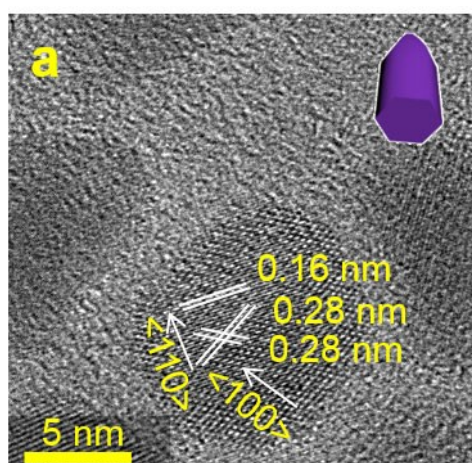


Figure S2. HRTEM image of the basal plane of one typical CoO nanorod.

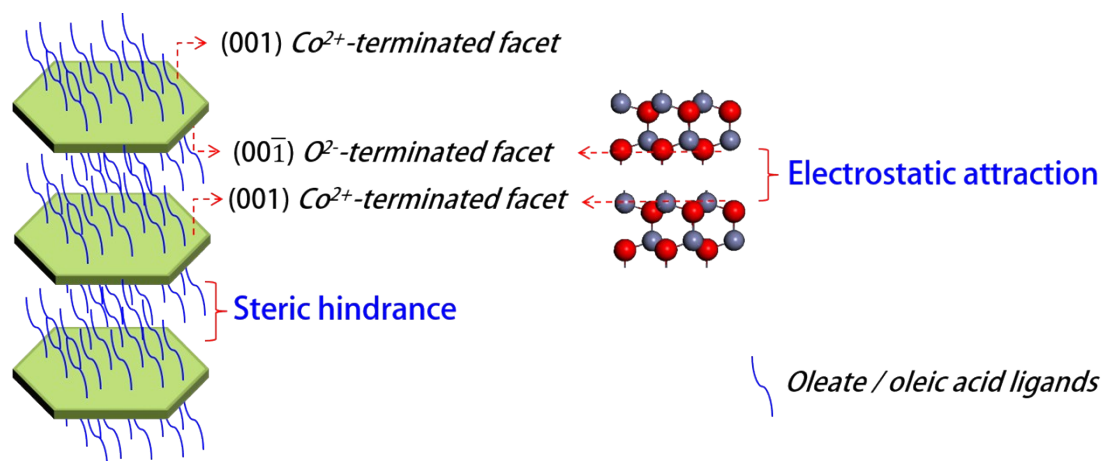


Figure S3. Schematic illustration for the interactions between nanosheets in the assembly.

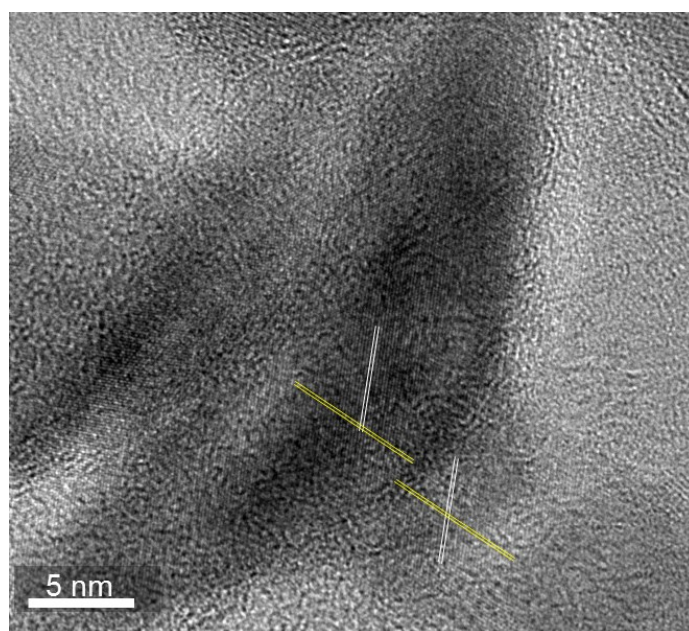


Figure S4. HRTEM of the connection part of a nanorod and a nanoplate of one typical 1D/2D structure.

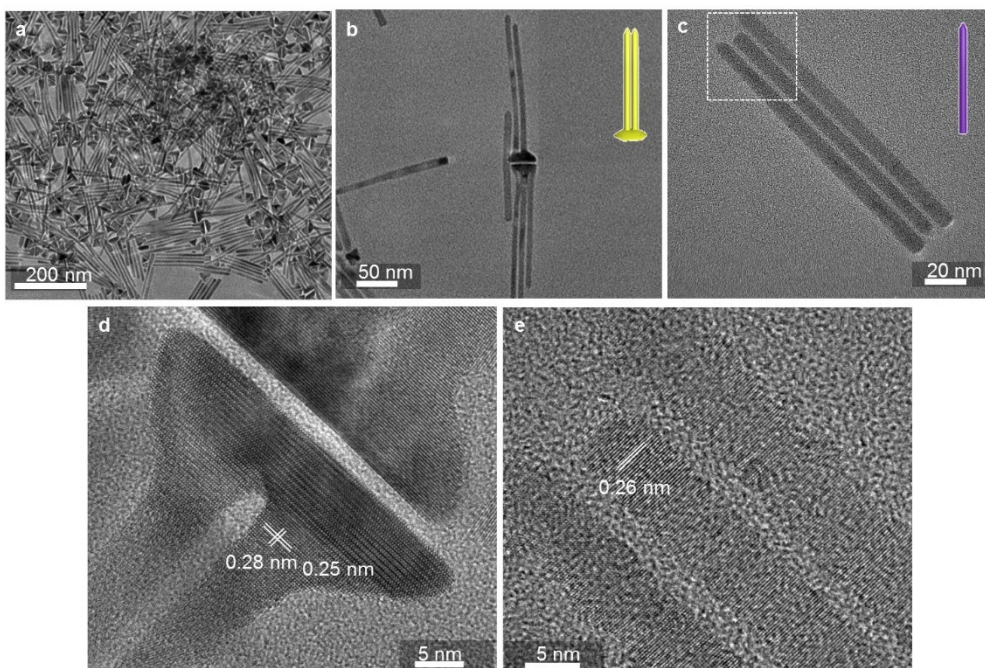


Figure S5. TEM images (a - c) and HRTEM images (d, e) of CoO NCs obtained from slightly oxidized precursor.

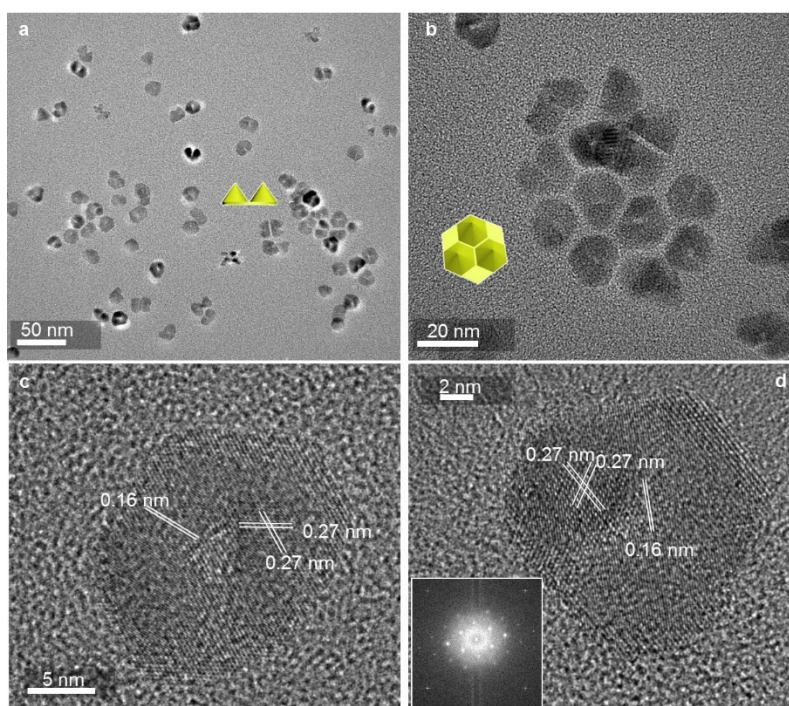


Figure S6. TEM images (a, b), HRTEM images (c, d) and SAED (d inset) of CoO NCs obtained from mostly oxidized precursor.

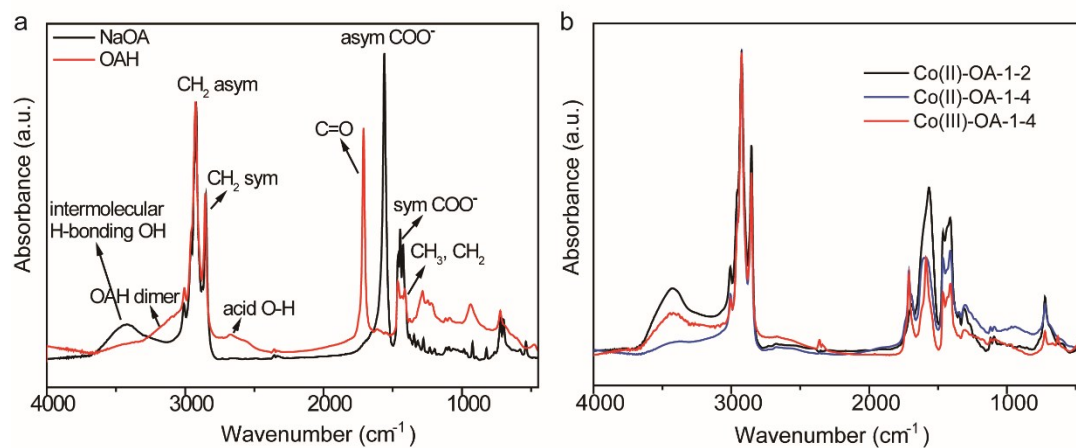


Figure S7. FTIR spectra of OAH and NaOA in (a) and cobalt oleate precursors in (b).

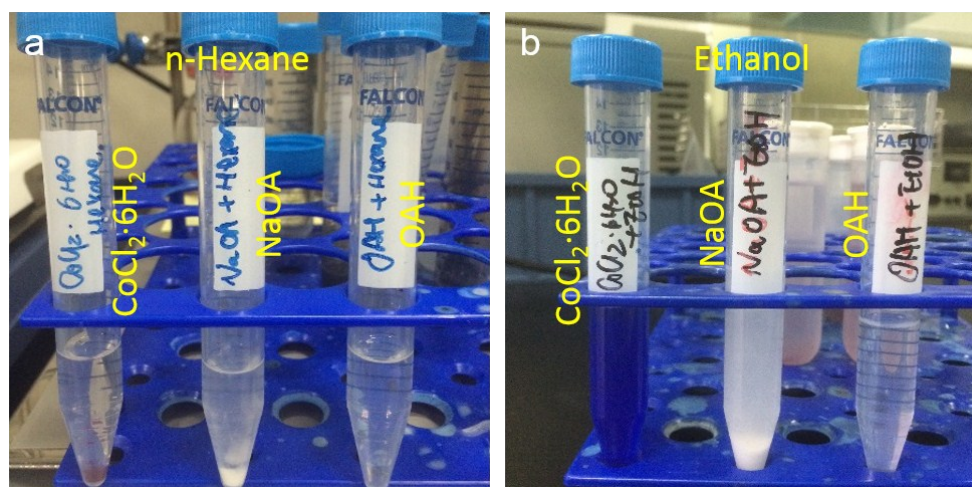


Figure S8. Solubility of CoCl₂·6H₂O, NaOA and OAH in (a) n-hexane and (b) ethanol at room temperature. CoCl₂·6H₂O and NaOA were not dissolved well in n-hexane and ethanol.

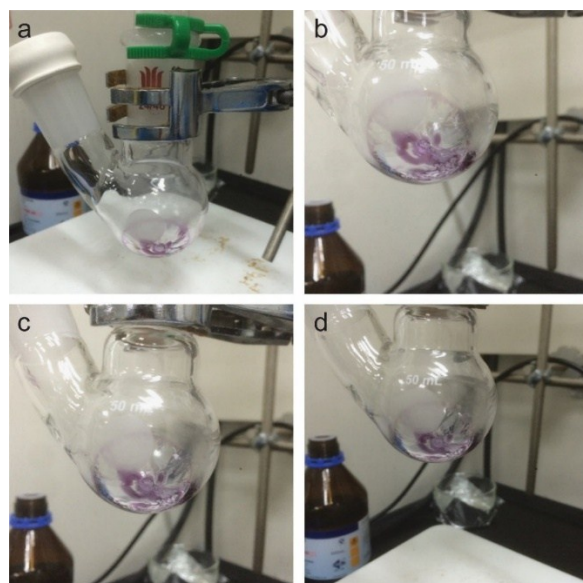


Figure S9. (a – d) Pictures of the purple precursor in the N_2 atmosphere for 0, 10, 20, and 30 min. This indicates atmospheric N_2 does not initiate the change in the precursor.

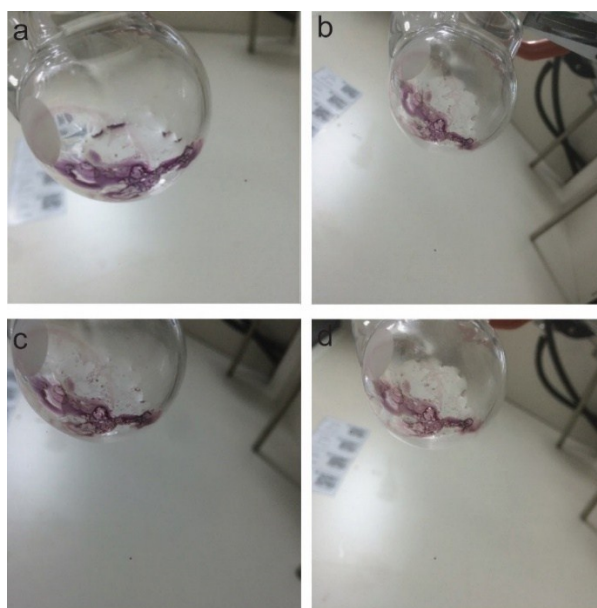


Figure S10. (a – d) Pictures of the purple precursor in the H_2O-N_2 atmosphere for 0, 10, 20, and 30 min. This indicates atmospheric H_2O does not initiate the change in the precursor.

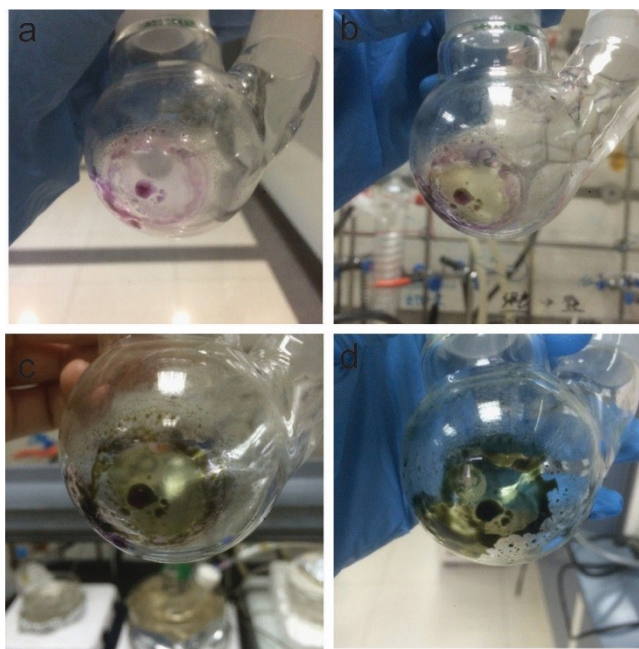


Figure S11. (a – d) Pictures of the purple precursor in the O₂ atmosphere for 0, 20, 60 min and 12h. This indicates the color change of the precursor is caused by the atmospheric O₂ most probably oxidizing the cobalt ions.

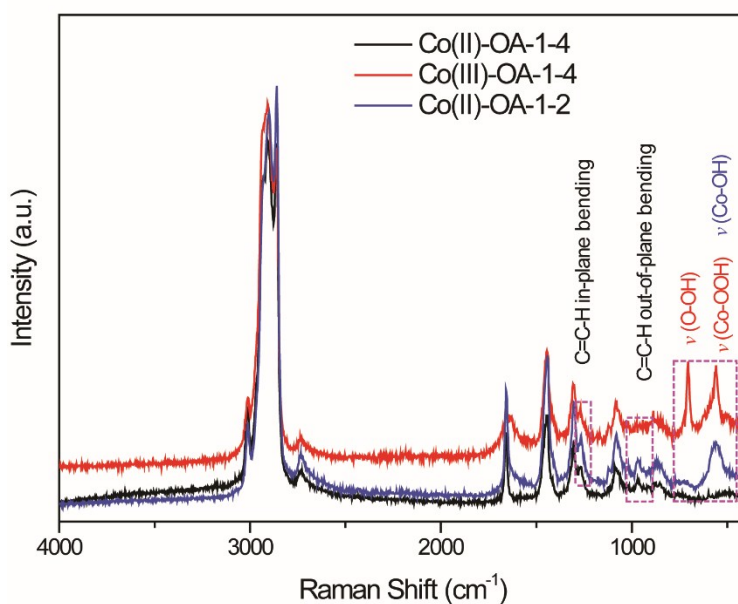
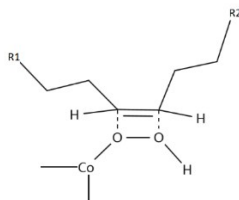


Figure S12. Resonance Raman spectra of Co(II)-OA-1-4, Co(III)-OA-1-4 and Co(II)-OA-1-2. The band at 560 cm^{-1} was assigned to $\nu(\text{Co-OOH})$ in Co(III)-OA-1-4^[S1] and $\nu(\text{Co-OH})$ in Co(II)-OA-1-2^[S2, 3]. The band at 706 cm^{-1} was assigned to $\nu(\text{O-OH})$ vibration mode in Co(III)-OOH linkage^[S1, 4] and Co(III) hydroperoxo complexes.^[S5] It was observed that Co(III)-OA-1-4 had a decreased C=C-H out-of-plane bending mode (971 cm^{-1}) and a similar C=C-H in-plane bending mode (1262 cm^{-1}), compared with Co(II)-OA-1-2 and Co(II)-OA-1-4. This might be because of the interaction of Co-OOH with C=C in oleate and oleic acid as below. (Raman spectra were measured with 532 nm excitation at 25 °C.)



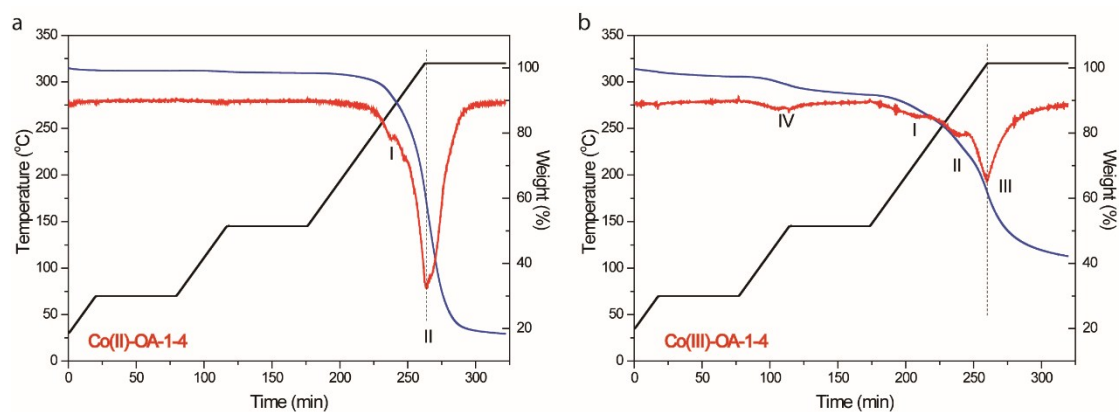


Figure S13. Thermogravimetric analysis of (a) Co(II)-OA-1-4 and (b) Co(III)-OA-1-4 precursors (pure precursors without solvents) in N₂ atmosphere, with a heating rate of 2 °C/min. Black line for temperature, blue for TGA, red for DTG.

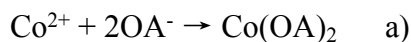
Table S1. Estimated structural change of precursor during the thermal decomposition.

	<i>Proposed molecular formula / M.W.</i>	<i>Proposed structure after TGA test / M.W.</i>	<i>Calculated retained weight %*</i>	<i>Experimentally retained weight %**</i>
<i>Co(II)-OA-1-4</i>	Co(II)(OA) ₂ / 622	Co-O / 75	6 ~ 8 %	13 %
<i>Co(III)-OA-1-4</i>	Co(III)(OOH)(OA) ₂ / 655	O-Co···OA / 356	29 ~ 38 %	49 %***

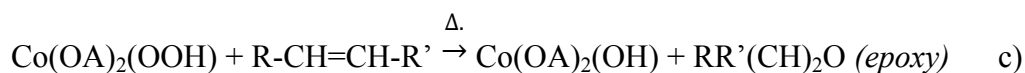
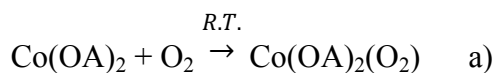
* The presence of oleic acid molecules in the precursor has been taken into account. The molar ratio of Co:OAH is 1 ~ 2.

** Weight % of H₂O in the sample was taken into account for calculation.

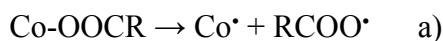
*** The discrepancy with calculated value may be caused by incomplete oxidation.



Eqn. S1. (a) In the ligand exchange reaction, the $\text{CoCl}_2:\text{NaOA}$ ratio was 1:2. (b) Hydrolysis of excessive amount of NaOA during ligand exchange to produce OAH .



Eqn. S2. The room temperature autoxidation of Co(II) oleate is proposed to go through the formation of Co(III) oleate superoxo complex intermediate (a), which further reacts with OAH to generate Co(III) oleate hydroperoxo complex and RCOO^\bullet (b). This reaction process corresponds to our experimental observations that the color changing reaction of Co(II) oleate is sensitive to the temperature as well as the amount of OAH mixed with Co(II) oleate precursor. (c) The Co(III) oleate hydroperoxo complex can epoxidize^[S6] the C=C bonds at certain elevated temperatures. (d) With the presence of H_2O and oleic acid, the epoxy converts to diol^[S6] or other alcohol species, depending on the amount of H_2O . These alcohols can reduce Co^{3+} to Co^{2+} at certain temperature during the thermal decomposition process.



Eqn. S3. (a,b) The thermal decomposition process of Co(II) oleate first generates free radicals at an elevated temperature which can propagate the further decomposition reactions.^[S8]

Reference

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