

## Supporting Information:

# Morphology Effects of $\text{Co}_3\text{O}_4$ Nanocrystals Catalyzing CO Oxidation in a Dry Reactant Gas Stream

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## 1. Experimental Section

### 1. Synthesis of $\text{Co}_3\text{O}_4$ NCs with different morphologies

Nanocrystalline  $\text{Co}_3\text{O}_4$  samples with plate-like, rod-like, cubical, and roughly spherical  
morphologies were synthesized by using the same cobalt salt and with or without the same capping  
20 reagent under hydrothermal conditions.

### 1.1. Plate-like $\text{Co}_3\text{O}_4$ NCs (P- $\text{Co}_3\text{O}_4$ ):

Ten mmol  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Wako, 99.0%) and 50 mmol PVP (Wako, K25, molecular weight,  $M_w = 35\,000$ ) calculated in terms of monomeric unit were dissolved in 30 ml of distilled water to form a red solution (solution 1). An aqueous solution consisting of 20 mmol KOH (Nacalai Tesque, 85%) dissolved in 20 ml distilled water (solution 2) was then added to solution 1 to form a greenish-blue suspension. After 30 min of stirring at room temperature, the suspension was aged at 293 K for 12 h in a Teflon-lined autoclave in which was maintained a reductive environment produced by adding 1g of hydrazine ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , Wako, 98%) in another container kept over the reaction solution. The pink hexagonal plate-like  $\text{Co}(\text{OH})_2$  NCs thus obtained were centrifuged, washed first with distilled water and then with ethanol, dried at 333 K for 12 h, and were finally calcined in air at 573 K for 2 h by raising the temperature at a rate of 373 K/h to produce plate-like  $\text{Co}_3\text{O}_4$  NCs.

### 1.2. Rod-like $\text{Co}_3\text{O}_4$ NCs (R- $\text{Co}_3\text{O}_4$ ):

Ten mmol  $\text{K}_2\text{CO}_3$  (Rare Metallic, 99.9%) dissolved in 20 ml distilled water was added to solution 1 to make a blue suspension. After 30 min of stirring at room temperature, the suspension was aged at 373 K for 12 h in a Teflon-lined autoclave in a similar manner to that reported in the literature.<sup>[11]</sup> The purple rod-like  $\text{CoOH}(\text{CO}_3)_{0.5} \cdot 0.11\text{H}_2\text{O}$  NCs thus obtained were then treated by the same procedures described above.

### 1.3. Cubical $\text{Co}_3\text{O}_4$ NCs (C- $\text{Co}_3\text{O}_4$ ):

Twenty mmol KOH and 5 mmol  $\text{KClO}_3$  (Nacalai Tesque, 99.5%) dissolved in 20 ml distilled water was added to solution 1 to make a blue suspension. After 30 min of stirring at room temperature, the greenish-blue suspension was aged at 393 K for 18 h in a Teflon-lined autoclave in a manner similar to that described in our previous report.<sup>[23]</sup> The black cubical  $\text{Co}_3\text{O}_4$  precipitates obtained were then treated by the same procedures as those used to produce plate-like  $\text{Co}_3\text{O}_4$  NCs.

#### 1.4. Spherical $\text{Co}_3\text{O}_4$ NCs (S- $\text{Co}_3\text{O}_4$ ):

Ten mmol  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Wako, 99.0%) was dissolved in 30 ml of distilled water to form a red solution (solution 3). Twenty mmol KOH and 5 mmol  $\text{KClO}_3$  (Nacalai Tesque, 99.5%) dissolved in 20 ml distilled water was added to the solution 3 to make a blue suspension. After 30 min of stirring at room temperature, the greenish-blue suspension was aged at 393 K for 18 h in a Teflon-lined autoclave in a manner similar to that described in our previous report.<sup>[12]</sup> The spherical black  $\text{Co}_3\text{O}_4$  precipitates thus obtained were then treated by the same procedures used to produce plate-like  $\text{Co}_3\text{O}_4$  NCs.

#### 2. Characterization of differently shaped $\text{Co}_3\text{O}_4$ NCs

Samples were characterized by powder X-ray diffraction (XRD) with a Rigaku RINT 2500 with Cu  $\text{K}\alpha$  radiation ( $\lambda = 0.15418$  nm), by electron diffraction with a JEOL JEM-4000EX, and by TEM with a JEOL JEM1010D electron microscope operating at 100 keV. The BET specific surface areas were measured at Shimadzu Techno Research Co. (Kyoto, Japan) by using the multipoint method with a Micromeritics ASAP-2400 apparatus.

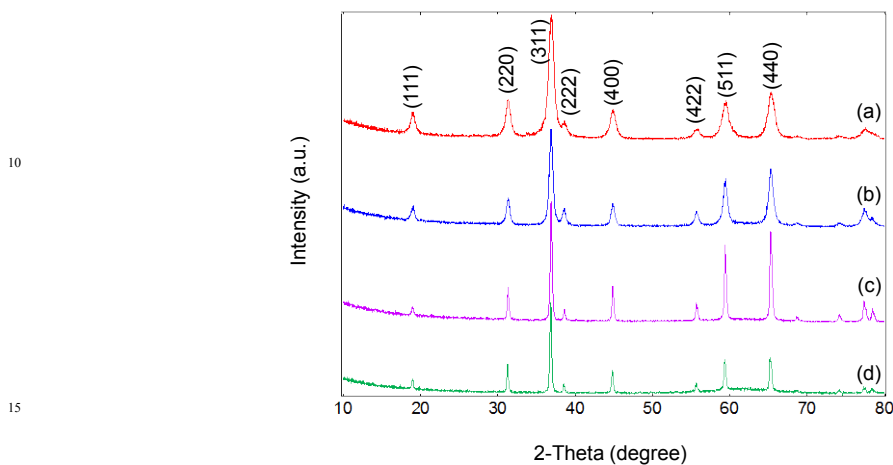
#### 3. Measurement of catalytic activity

Catalytic activity for CO oxidation was measured by using a flow-type fixed-bed Pyrex reactor (i.d. = 5 mm) with a “U” shape as described in the literature.<sup>[16]</sup> In general, a standard gas containing 1.0 vol% CO and 21 vol%  $\text{O}_2$  balanced with He was passed through a molecular sieve 3A trap cooled to 273 K and then the reactor filled with a catalyst sample in an amount corresponding to  $3.6 \text{ m}^2$  of surface area (40–60 mesh, 100 mg for cube morphology) at a rate of flow of 50 ml/min (space velocity =  $30\,000 \text{ h}^{-1}$  ml  $\text{g}_{\text{-cat}}^{-1}$  for sphere morphology) under atmospheric pressure. All samples were pretreated at 573 K for 30 min before catalytic tests and then cooled to a starting reaction temperature in the same stream of 21 vol%  $\text{O}_2$  in He. The concentrations of CO,  $\text{O}_2$ , and  $\text{CO}_2$  in the inlet and outlet streams were measured by using a gas chromatography system (GL Science Inc.) equipped with an active carbon column and TCD

and FID detectors. An automatic gas sampling interval of 15 min was used to measure the steady-state conversion of CO at a fixed catalyst temperature, usually after the reaction had been in progress for 30 min. Experiments at temperatures below 273 K were conducted by using an ether/liquid nitrogen or methanol/dry ice cooling solution.

Kinetic measurements for CO oxidation over the four kinds of  $\text{Co}_3\text{O}_4$  NCs were carried out in the temperature range of 178 to 239 K at CO conversions below 15% (differential reactor assumption) by changing the space velocity in the range of  $3 \times 10^4$  to  $2.4 \times 10^5 \text{ h}^{-1} \text{ ml g}_{\text{-cat}}^{-1}$ .

## 2. X-ray diffraction (XRD) patterns



**Fig. 1S** XRD patterns for  $\text{Co}_3\text{O}_4$  NCs with (a) plate-like, (b) rod-like, (c) cubical, and (d) roughly spherical shapes.