## **Supporting Information for:**

# TEMPO-Mediated, Room Temperature Synthesis of Pure CoO Nanoparticles

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**1. Experimental procedure for the synthesis of CoO nanoparticles.** To a solution of dicobalt octacarbonyl (0.200 g; 0.526 mmol) and oleic acid (175  $\mu$ L; 0.530 mmol) (Note a) in degassed THF (10 mL) under Ar (Schlenk line), a solution of 2,2,6,6-tetramethylpiperidine-1-oxyl (0.336 g; 2.106 mmol) in degassed, anhydrous (<10 ppm H<sub>2</sub>O) THF (4 mL) was added dropwise at room temperature, gas evolution being observed during *ca.* 10 min (Note b). After a short time, the purple nanoparticles (*ca.* 0.1 g) were precipitated by acetone addition (Note c) and characterized by TEM.

#### Notes:

**Note a:** Trioctylphosphine oxide (TOPO) can optionally be employed as a further additive (0.042g, 0.11 mmol).

**Note b:** Both CO and CO<sub>2</sub> are evolved from the reaction mixture.<sup>2</sup> 2,2,6,6-Tetramethylpiperidine is formed as the only by-product, as analyzed by EI-MS and <sup>1</sup>H NMR. **Note c:** The purple nanoparticles can also be precipitated by acetone addition if the preparation is peformed in *o*-dichlorobenzene. Alternatively, product isolation can be performed by centrifugation at 4400 rpm (90 min), separation of the supernatant, redispersion in hexane and centrifugation (three times).

Experiments aimed to the determination of the influence of the solvent on the size of the nanoparticles aggregates: 0.2 ml/min addition (2 mL, 10 min addition) of 8 eq of TEMPO to  $Co_2(CO)_8$  (0.14M) in the presence of 1 eq of oleic acid and 0.2 eq of TOPO at room temperature followed by a 60 min. thermal treatment at 50 °C. After this time, the solution was kept at -30 °C until it was analyzed by TEM. Mean diameter with standard deviation of the aggregates: 88±39 nm (o-DCB); 186±105 nm (toluene); 625±218 nm (dioctyl ether).

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#### 2 In-Situ FTIR monitoring of the reaction

For the IR measurements, a ReactIR 4000 (Mettler-Toledo AutoChem ReactIR<sup>TM</sup>) with a silicon probe (SiComp, optical range = 4400-650 cm<sup>-1</sup>) was used. In a typical experiment, the specified amount of TEMPO was added to a solution of dicobalt octacarbonyl (0.200 g, 0.526 mmol) in 2 ml of degassed *o*-dichlorobenzene containing oleic acid (0.152 g, 0.526 mmol) and, in some cases (see Figure S1), TOPO (0.042 g, 0.11 mmol) under argon atmosphere, where the silicon probe was submerged. The evolution of the absorption intensity of the different carbonyl bands was monitored from the injection time to complete disappearance. We have represented in Figure S1 the evolution with time of the band at 2022 cm<sup>-1</sup>, the last in disappearing from the spectra.



**Figure S1.** FT-IR monitoring of the disappearance of the carbonyl band at 2022 cm<sup>-1</sup> of  $Co_2(CO)_8$  under different experimental conditions. Absorbances have been volume-corrected and normalized.

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## 3. Characterization of the CoO nanoparticles

# 3.1 Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS) and Selected Area Electron Diffraction (SAED).

Nanocrystal size and morphology were investigated using a Hitachi 800MT Transmission Electron Microscope (200 KeV) provided with a Gatan Multiscan chamber. For sample preparation, nanocrystals suspended in dichloromethane were placed onto a Holey formvar® carbon-coated copper grid (200 mesh) and the solvent was allowed to evaporate to dryness.



**Figure S2**. Top left, SAED analysis of the disperse nanoparticles obtained in the reaction of  $Co_2(CO)_8$  with TEMPO in the presence of oleic acid, after fast quenching of the reaction. Bottom left, TEM image of the nanoparticles (Scale bar, 100 nm). Top right, SAED analysis of the nanoparticles aggregates obtained in the reaction of  $Co_2(CO)_8$  with TEMPO in the presence of oleic acid, after aging. Bottom right, TEM images of the ca. 100 nm nanoparticles aggregates.(Scale bar is 200 nm).

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The most relevant TEM images are presented in the body of the manuscript. TEM images of disperse nanoparticles, obtained by fast quenching of the reaction mixture, and their corresponding SAED pattern are shown in Figure S2, as well as of nanoparticles aggregates exhibiting the same but diffuse SAED pattern. The electron diffractions obtained by SAED on discrete nanoparticles and on aggregates can be indexed to cubic CoO.<sup>3</sup> The distances (in Å) and their indexation are presented in Table S1:

d (Å)	hkl
2.49	111
2.13	200
1.53	220
1.27	311
1.06	400
0.96	331
0.87	422

 Table S1 Indexation of the SAED diffractograms.

An EDS spectrum of the aggregates indicates that oxygen and cobalt are the only elements present in the specimen (besides Cu and C from the copper grid which the background subtraction did not completely remove) (Figure S4).



Figure S4. An EDS spectrum of CoO nanoparticles.

# 3.2 High Resolution Transmission Electron Microscopy (HR-TEM) and Electron Energy Loss Spectroscopy (EELS)

Specimens were prepared by placing a drop of nanoparticles suspension in dichloromethane onto a Holey formvar® carbon-coated copper grid (200 mesh) and allowing the solvent to evaporate. The sample was treated with a 5%O<sub>2</sub>/Ar plasma for 15 seconds to eliminate most of the organic matter. High-resolution transmission electron microscopy measurements were performed on a Jeol JEM 2010F provided with a high resolution digitalizing chamber at 200keV and equipped with a field emission gun. Electron energy loss spectroscopy (EELS) was performed using Gatan Image Filter (GIF).

Electron Energy Loss Spectroscopy (EELS) analysis shows only the presence of cobalt and oxygen in the samples. The presence of two bands at 541 and 562 eV and their relative intensities indicate the presence of mainly oxygen attached to  $Co^{2+}$  (the O-K fine edge structures of  $Co_3O_4$  and CoO are completely different). The sharper shoulder at 532 eV originates from the oxygen of oleic acid, and from oxygen adsorbed on the carbon film.<sup>4</sup> The quantitative analysis shows a Co/O ratio of 0.6 and the relative intensity of cobalt L<sub>3</sub> and L<sub>2</sub> bands strongly supports the exclusive presence of  $Co^{2+}$  (Figure S5).<sup>5,6</sup>



**Figure S5.** EELS analysis of the nanoparticles obtained in the reaction of  $Co_2(CO)_8$  with TEMPO in the presence of oleic acid.

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### 3.3 Magnetic measurements

Magnetic data of the solid samples (Figures S6 and S7) were collected with a Quantum Design MPMS SQUID susceptometer (AC and DC modes and maximum static field of  $\pm$  5 T) in liquid helium, after cooling in zero magnetic field (ZFC) or by cooling in a field of 50 Oe (FC).



**Figure S6.** Plots of magnetization against applied field at 2K of the nanoparticles obtained in the reaction of  $Co_2(CO)_8$  with TEMPO in the presence of oleic acid.



**Figure S7.** Magnetic susceptibility of the CoO samples. Zero field cooled – field cooled curves measured at 10 Oe.

#### 3.4 XPS measurements

The XPS studies (Figure S8) were carried out with a Perkin-Elmer PHI 5500 spectrophotometer using MgK $\alpha$  radiation. In depth measurements were obtained by recording the spectra after sputtering the samples to different depths with an Ar+ ion beam at 4 keV.



**Figure S8.** XPS analysis of the nanoparticles obtained in the reaction of  $Co_2(CO)_8$  with TEMPO in the presence of oleic acid.

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#### 3.5 Thermogravimetric and elemental analysis

A Mettler thermobalance, SDTA851e model, with a precision of ± 0.25% and 1600 °C maximum temperature was used for thermogravimetric studies.

The TG curve recorded under nitrogen (Figure S9, grey) shows a weight loss of oleic acid, centered at 350 °C, corresponding to a 68.5% of the initial weight. A second weight loss, at *ca.* 540 °C, corresponds to a 7.1% of the initial weight and is assigned to thermal decomposition of surface or near-surface CoO into Co. Note that for a full-shell cluster made of approx. 5 shells (see below, 4.2), *ca.* 74% of the total CoO units are in the two more external spheres.

The TG curve recorded under air (Figure S9, red) does not show the reduction peak at 530 °C.



**Figure S9.** TG analysis of the nanoparticles obtained in the reaction of  $Co_2(CO)_8$  with TEMPO in the presence of oleic acid under N<sub>2</sub> (dark trace) and under air (light trace).

The elemental analysis of CoO nanoparticles, identical to those employed for the TGA studies, gave the following composition: C; 55.01%, H; 9.97%, N; 0.00%, S; 0.00%. If all carbon in the sample came from oleic acid (C; 76.54%, H; 12.13%, O; 11.33%), the amount of oleic acid in the sample would be 71.9%, in good agreement with value determined from TGA measurements.

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## 4. Topology of the nanoparticles

In a CoO fcc unit cell the Co-O distance is 213 pm, and the cell unit is 426 pm,

therefore, its volume is 0.077 nm<sup>3</sup>.

8 Co atoms in the cube edges: 1 at.

6 Co atoms in the face center: 3 at

Total: 4 atoms of Cobalt per unit cell.



In an spherical NP of 3.0 nm diameter, the volume is  $(4/3\pi 1.5^3) = 14.14 \text{ nm}^3$ . therefore we have:

14.14/0.077 = 184 units cell per particle and 184 x 4 = 736 atoms of Co per particle

For a full-shell cluster built up by cubic (ccp, fcc) close-packed atoms, the number of concentrical shells, the total number of atoms, and the % of surface atoms can be easily calculated, the number of atoms per shell being  $10n^2+2.^7$  A graphical representation of the % of surface atoms *vs.* total number of atoms is presented in Figure S10.



Figure S10. Surface Co atoms (%) vs. total number of Co atoms in a cubic (fcc) CoO

Simple interpolation indicates, for a cluster comprising 736 Co atoms, 42% of surface cobalt atoms. In addition, a number of shells between 5 and 6 is predicted.

<sup>1</sup> J. R. Fish, S. G. Swarts, M. D. Sevilla, and T. Malinski, *J. Phys. Chem.*, 1998, **92**, 3745-3751

 $^2$  CO $_2$  was observed by IR when monitoring the reaction by react-IR. The presence of CO was checked with an electrochemical cell CO detector.

<sup>3</sup> D. Grier, G. McCarthy, North Dakota State University, Fargo, North Dakota, USA, ICDD Grant-in-Aid (1991) <sup>4</sup> J. S. Yin,and Z. L. Wang, *Phys. Rev. Lett.*, 1997, **79**, 2570-2573.

<sup>5</sup> Z. L. Wang, J. S. Yin, W. D. Mo, and Z. J. Zhang, *J. Phys. Chem. B*, 1997, **101**, 6793-6798.

<sup>&</sup>lt;sup>6</sup> Z. L. Wang, J. S. Yin, Y. D. Jiang, *Micron*, 2000, **31**, 571-580.

<sup>&</sup>lt;sup>7</sup> Nanoscale Materials in Chemistry, Klabunde, K. J., Ed. Wiley-Interscience, New York, 2001.