Supporting Information for

Two-step synthesis of Fe_2O_3 and Co_3O_4 nanoparticles: Towards a general method for synthesizing nanocrystalline metal oxides with high surface area and thermal stability

Junjiang Zhu,[a,b,]* Xiaoying Ouyang,[c] Ming-Yung Lee,[b] Ryan C. Davis,[c] Susannah L. Scott,[b,c,]*
Anna Fischer[a] and Arne Thomas[a]
[a] Department of Chemistry, Technical University of Berlin
[b] Department of Chemical Engineering, University of California, Santa Barbara
[c] Department of Chemistry & Biochemistry, University of California, Santa Barbara

Table of contents

Experimental section

Sample preparation:

Synthesis of metal oxide nanocrystalline materials (NCMs): In a general procedure, 2 g of metal nitrate ($Fe(NO_3)_3\cdot9H_2O$ or $Co(NO_3)_2\cdot6H_2O$) was first dissolved in 6 mL de-ionized water and deposited by wet impregnation onto 2 g activated carbon (ABCR, surface area: 1300 ~ 1400 m^2/g), then dried in a static air oven at 110 ºC overnight. The resulting materials were subsequently transferred to a muffle oven, flushed with argon, and thermally treated at 350 ºC for 2 h (heating rate of 2 °C/min), to generate the supported metal oxide NCMs. Finally, the samples were reheated in air at a heating rate of 5 ºC/min to 500 ºC and kept at this temperature for 2 h, to remove the AC template and recover the metal oxide NCMs.

Preparation of Fe_2O_3 *using one-step method* (Fe_2O_3*_one step)*: The synthesis procedure is the same as described above, except that the treatment in argon was omitted.

Preparation of Fe_2O_3 *in organic solvent* (Fe_2O_3*_Org)*: 4.04 g $Fe(NO_3)_3\cdot9H_2O$ was dissolved in 5 g ethanol, then mixed with 10 g ethanol containing 1 g P123 ($M_{av.}$ = 5800, Sigma Aldrich). The mixture was stirred at 80 °C until all the solvent evaporated. The resulting solid was calcined at 350 °C for 4 h.

Characterization:

Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer, using Cu $K\alpha_1$ irradiation. Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai G² 20 S-TWIN instrument (200 keV) equipped with a GATAN MS794 P CCD-Kamera, using carbon-coated copper grids (specimens were loaded directly on the copper grids; no solvent dispersion was used). N_2 sorption isotherms were determined at -196 ºC with a Quantachrome Autosorb-1 apparatus. Prior to the measurement, each sample was degassed at 150 ºC overnight. TGA measurements were carried out on a STA6000 (PerkinElmer) under pure N_2 or O_2. The gas flow rate was 20 mL/min and the temperature ramp was 10 °C/min. XPS analysis was performed with a Kratos Axis Ultra X-ray Photoelectron Spectrometer using Al Kα radiation. The charging effect was corrected using the C 1*s* signal (285.0 eV) as a reference.

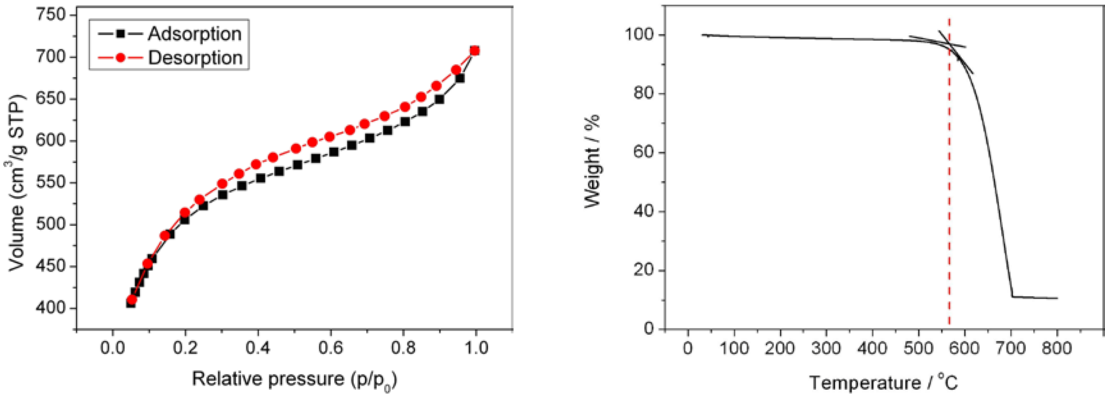
X-ray Absorption Spectroscopy

EXAFS spectra were recorded at the Co and Fe K-edges (7709 and 7112 eV, respectively) at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam lines 4-1 and 4-3. Samples were mounted at a 45° angle to the beam in order to collect transmission and fluorescence spectra simultaneously. The intensity of the incident beam was measured with a N_2-filled ionization chamber installed in front of the sample. Fluorescence from the sample was recorded at right angles to the beam, using an Ar-filled Lytle detector with a Soller slit and a PIPS detector on beamlines 4-1 and 4-3, respectively. Co and Fe foils were placed between the second and third ionization chambers and the data collected was used to ensure proper calibration of the edge energy.

A single data sweep (collection time: 20 min) was sufficient to obtain a good signal-to-noise ratio in the fluorescence channel. Subsequent data sweeps showed no change due to sample decomposition. Fluorescence data generally showed better signal-to-noise ratios and were used in subsequent data analyses instead of transmission data. EXAFS spectra were analyzed in k-space using IFeffit (Athena). The data were first background-corrected by subtracting a linear fit to the pre-edge region extrapolated the entire length of the spectrum, then normalized by a third-degree polynomial fitted to the post-edge region. EXAFS spectra were k^3-weighted and fitted with a polynomial spline between 2 and 14 Å-1.

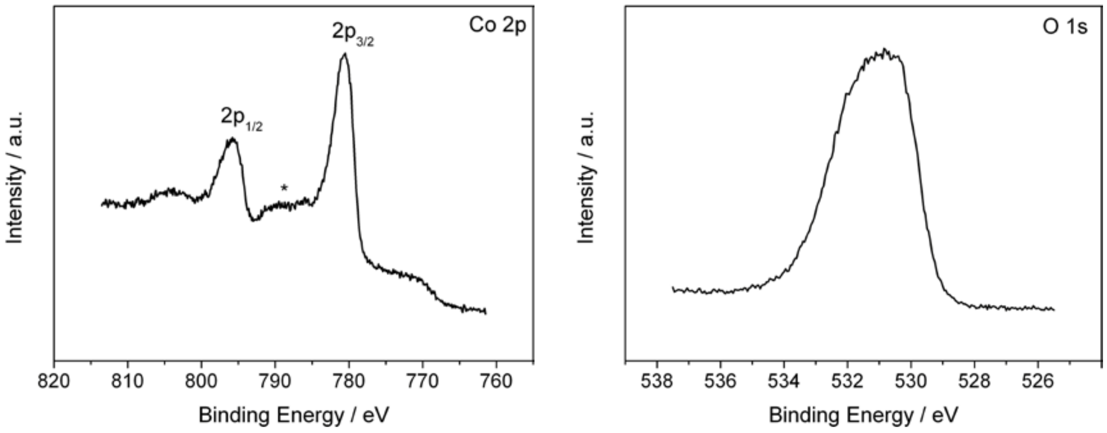
Catalytic testing

Activity testing was carried out in a Hiden Catlab micro-reactor, equipped with a Hiden quadrupole mass spectrometer (HPR20). The catalyst (50 mg) was placed on a quartz wool bed in a quartz tube, which was inserted into a vertical furnace equipped with a temperature controller. The reactant gas (4000 ppm CO, 10 % O_2 in argon) was passed through the catalyst bed at a total flow rate of 50 mL min^{-1}. The temperature was raised from 50 to 350 ºC with a heating rate of 5 ºC/min. The composition of the outlet gas stream was monitored with the HPR20 MS, detecting components with mass-to-charge ratios (m/e) of 28 (CO) and 44 (CO_2). The catalyst was pretreated in air at 350 ºC for half an hour before the measurement. The activity was calculated based on the CO_2 yield.



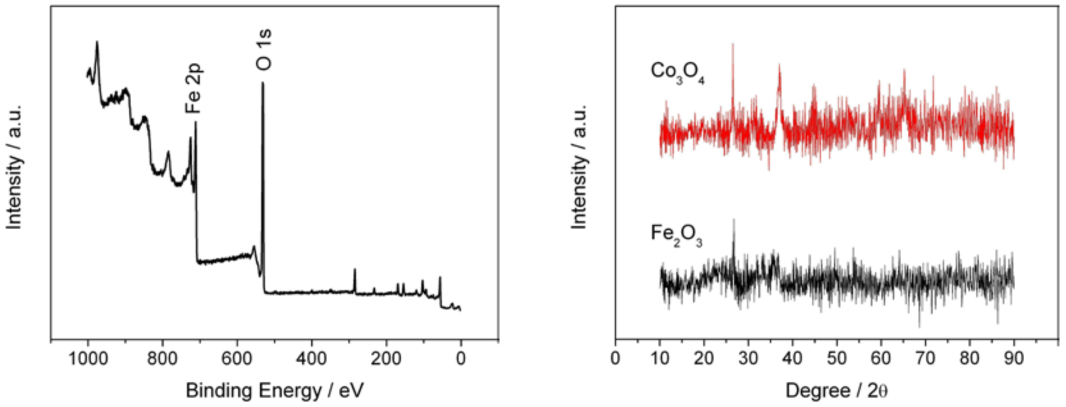
(A) (B)

Figure S1. N_2-sorption isotherms (A) and TGA profile recorded in O_2 (B) for the activated carbon used in this study.



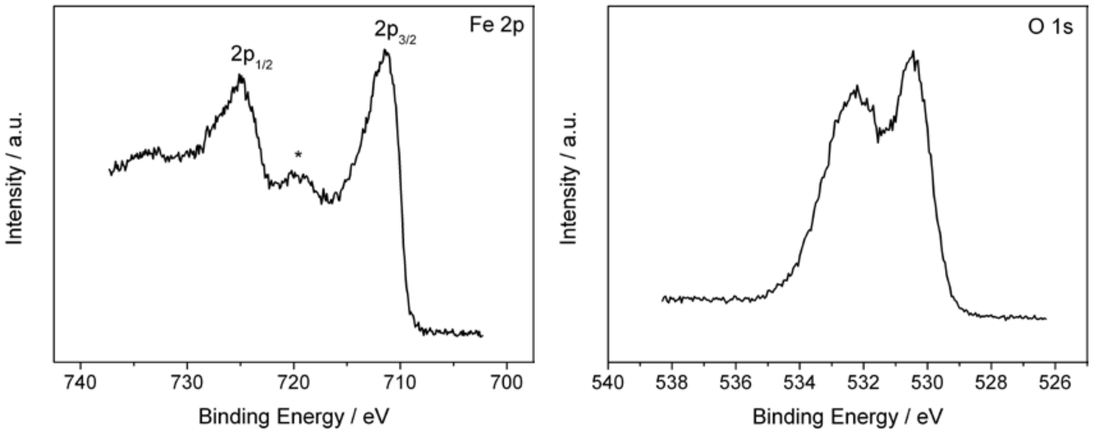
(A) (B)

Figure S2. High resolution XPS spectra of the Co_3O_4_NCMs, in the Co 2*p* (A) and O 1*s* (B) regions.



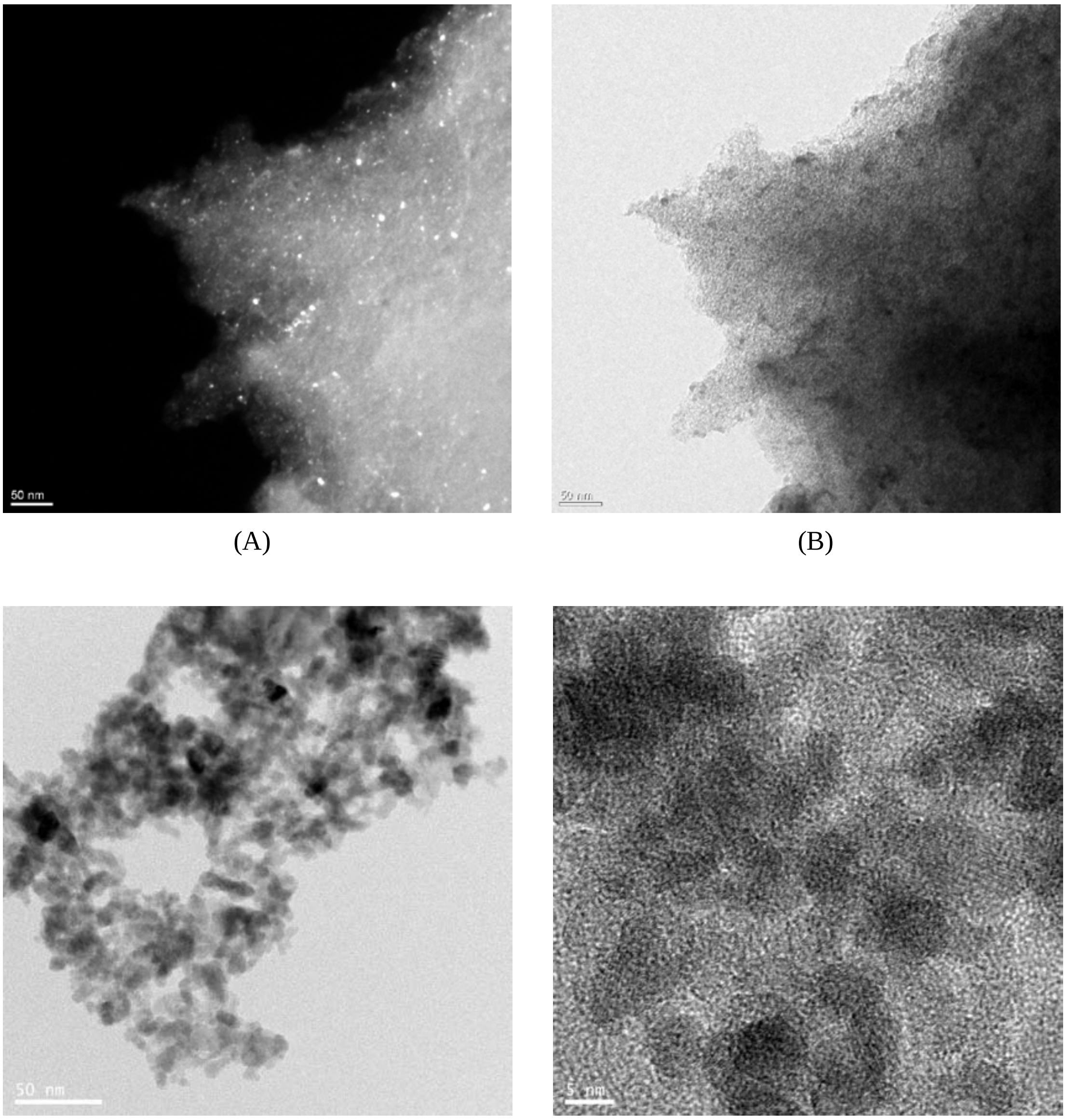
(A) (B)

Figure S3. (A) XPS survey spectrum of the Fe_2O_3_NCMs, and (B) powder XRD patterns of the unsupported Co_3O_4_NCMs and Fe_2O_3_NCMs.



(A) (B)

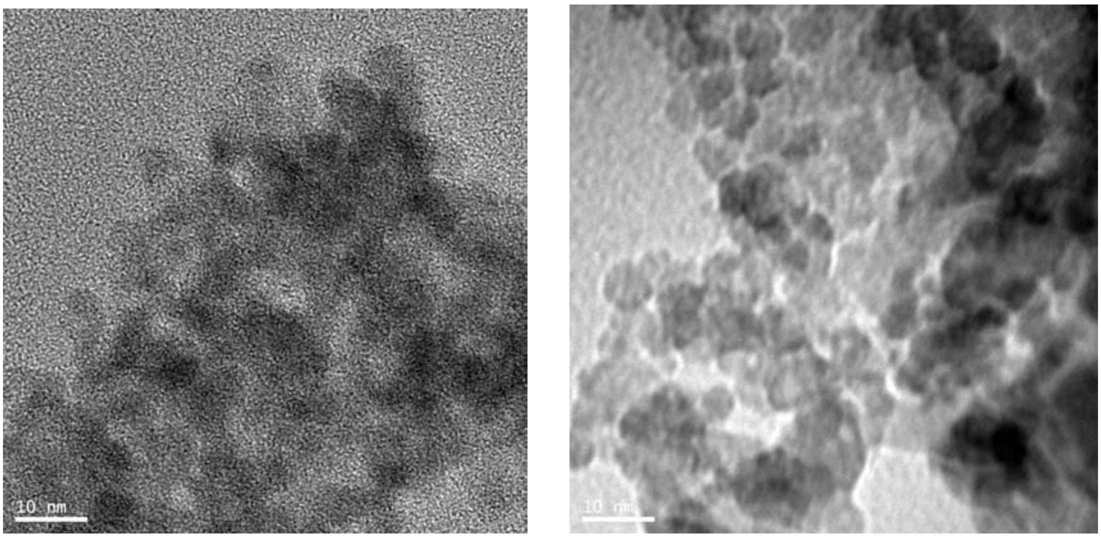
Figure S4. High resolution XPS spectra of the Fe_2O_3_NCMs, in the Fe 2*p* (A) and O 1*s* (B) regions.



(A) (B)

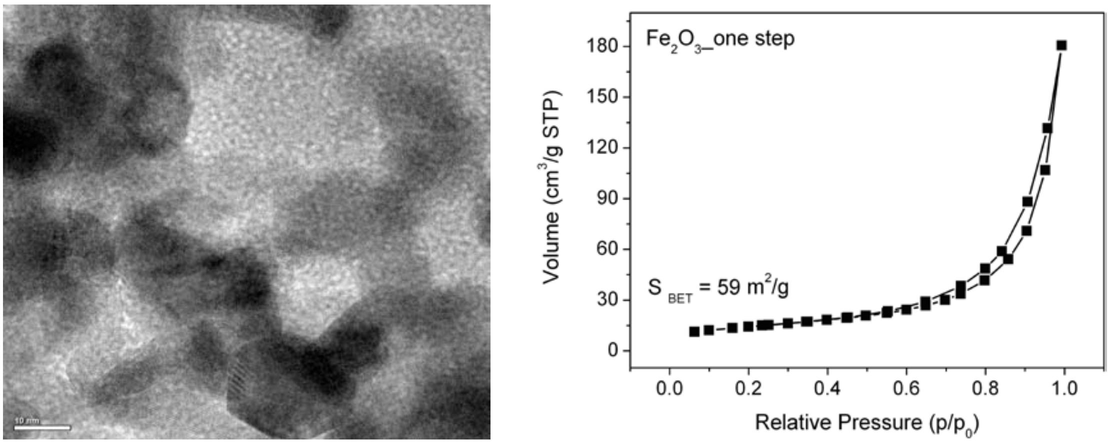
(C) (D)

Figure S5. TEM images for AC-supported Fe_2O_3 NCMs, obtained in the first step: (A) dark-field and (B) bright-field; and unsupported Fe_2O_3 NCMs obtained in the second step: (C) and (D), bright-field.



(A) (B)

Figure S6. TEM images of the Fe_2O_3_NCMs, before (A) and after (B) their use in CO oxidation



(A) (B)

Figure S7. TEM images (A) and N_2 sorption isotherms (B) for the Fe_2O_3 nanoparticles prepared by a one-step method (Fe_2O_3_one step), which indicate particle size of ca. 20 nm and surface area of 59 m^2/g.