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Supercritical CO_2-Facilitating Large-Scale Synthesis of CeO_2 Nanowires and Their Application for Solvent-free Selective Hydrogenation of Nitroarenes

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Preparation of Pt-CeO_2

20 mg ceria nanowires (after subject to 500 °C heat treatment for 5 h) was dispersed in 20 mL ethanol under 1 min tip sonication. In the following step, 1 mL $H_2PtCl_6{\cdot}6H_2O$ ethanol solution (conc. at 1 mg/mL) was slowly dropped into the nanowire suspension under 2 min tip sonication. Then 1 mL $NaBH_4$ ethanol solution (conc. at 0.4 mg/mL) was slowly dropped into the mixed dispersion under 2 min tip sonication in a similar manner as above. The products were subsequently washed with ethanol and vacuum-dried at 60 °C overnight for catalytic reaction use.

Preparation of conventional Pt-CeO_2 through an incipient wetness method

20 mg ceria particles (obtained under the same experimental conditions as ceria NWs except at 2MPa CO_2) was dispersed in 2 mL $H_2PtCl_6{\cdot}6H_2O$ ethanol solution (conc. at 0.5 mg/mL). The dispersion was kept magnetic-stirring for 5 h and dried at 60 °C overnight. The collected precipitate was then reduced under H_2 bubbling at 300 °C for 2 h and cooled to ambient temperature for catalytic use. TEM characterization shows that Pt NPs with sizes at about 5 nm deposited on the outer surfaces of ceria particles (Figure S8).

Solvent-free hydrogenation of nitroarenes (nitrobenzene, o-chloronitrobenzene)

Typically, 1.23 g nitrobenzene (NB) or o-chloronitrobenzene (o-CNB) and 10.2 g catalyst (Pt-CeO_2 at 1.80 wt% Pt loading) were added into a reactor followed by which the reactor was sealed and flushed with H_2 three times to remove the air in the reactor. Then the reactor was heated up to 333 K and H_2 was introduced up to desired pressure (i.e. 2 MPa for NB and 3 MPa for o-CNB). The hydrogenation reaction was conducted with magnetic stirring (625 r. p. m.). The H_2 pressure was kept constant by replenishing H_2 as the reaction proceeded. The resulting product after removing the catalyst and water content by ultracentriguge was analyzed by gas chromatograph (Agilent 4890D) with a capilary column. The conversion of NB and o-CNB reached 92.0% and 99.0 % after a time scale of 27 min and 58 min, respectively.

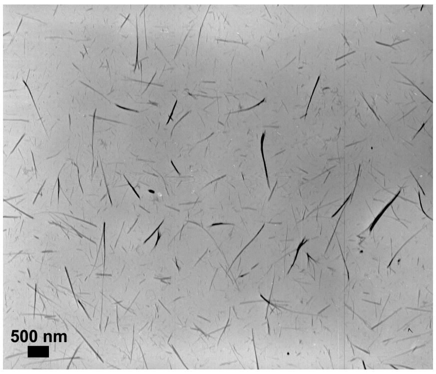


Figure S1. TEM image of the ceria nanowire-ethanol dispersion after subject to 10 min bath-sonication.

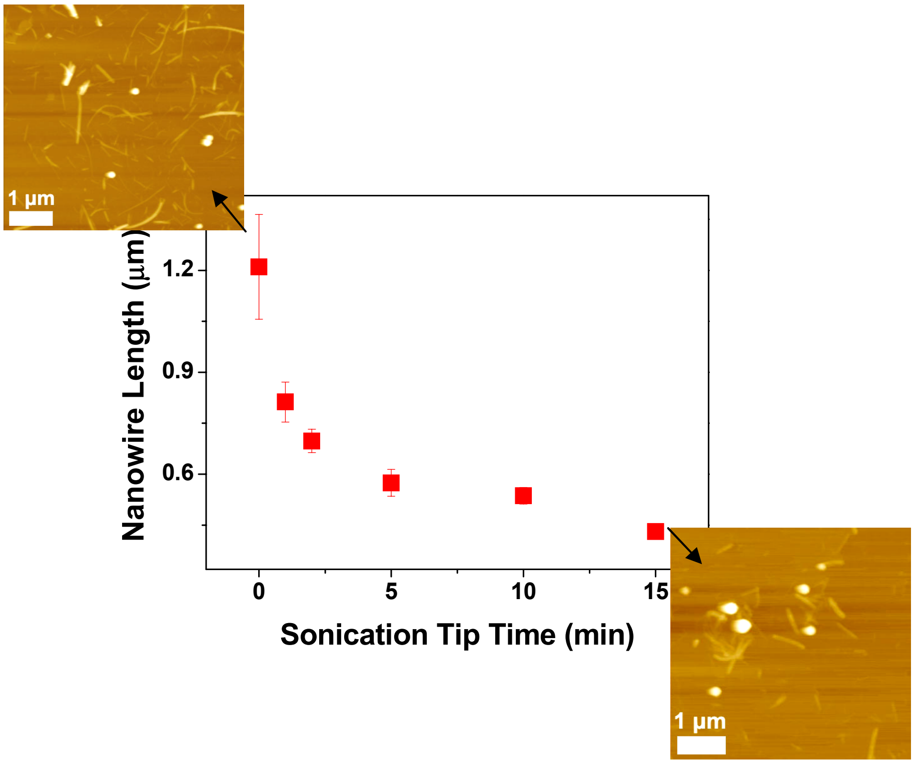


Figure S2. Graph of ceria nanowire length as a function of tip-sonication time. Top and lower inset correspond to typical AFM images for ceria nanowires after subject to 0 and 15 min tip sonication.

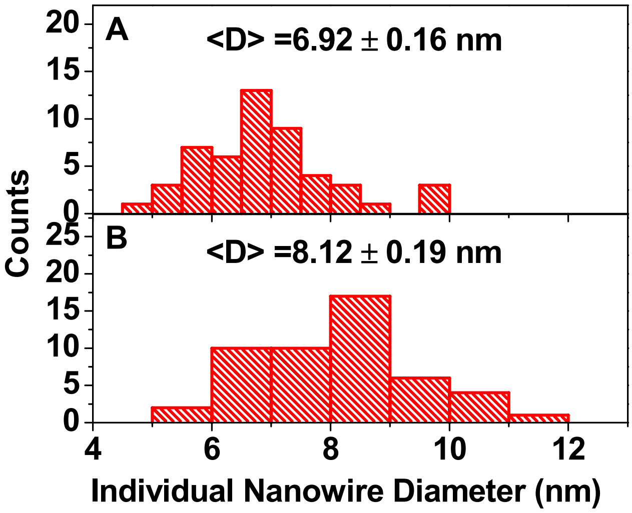


Figure S3. The diameter histograms of the ceria nanowires prepared under varying precursor concentrations: (A) 10 mg/mL, and (B) 40 mg/mL. Note that the diameter distributions were obtained for each sample from 50 randomly chosen individual nanowires in their typical HRTEM images.

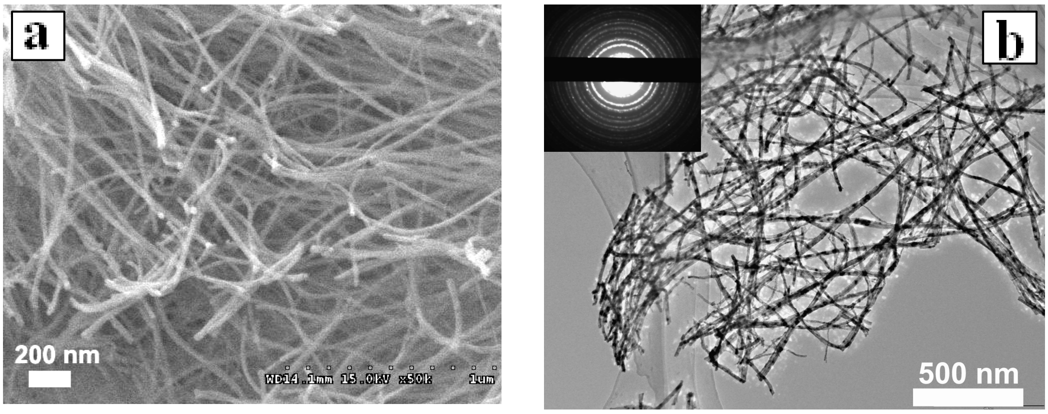


Figure S4. (a) SEM and (b) TEM images of the ceria nanowires after treated at 500 °C for 5 h, inset in b is the electron diffraction pattern of the nanowires in the image view.

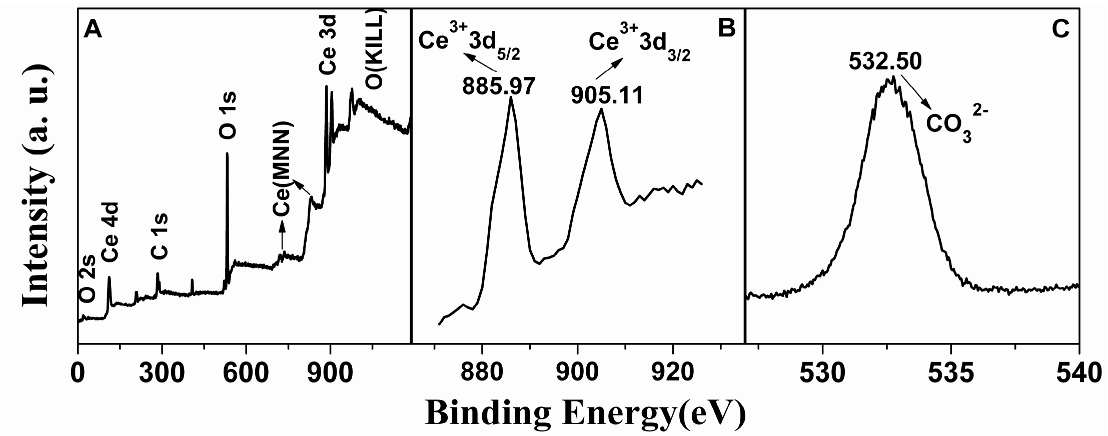


Figure S5. (A), (B), (C) correspond to wide-survey, Ce 3d level, and O 1s XPS spectra of the sample obtained at 150 °C for 1 h, respectively. The prominent doublet with binding energies of Ce 3d$_{3/2}$ at 905.11 eV and Ce 3d$_{5/2}$ at 885.97 eV can be ascribed to Ce^{3+}.[1] The O1s XPS peak centered at 532.50 eV corresponds to CO$_3^{2-}$ species.[2]

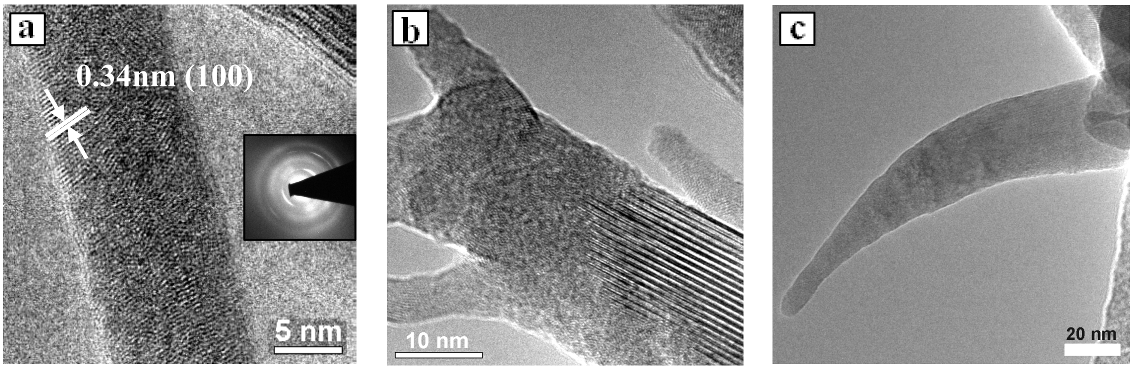
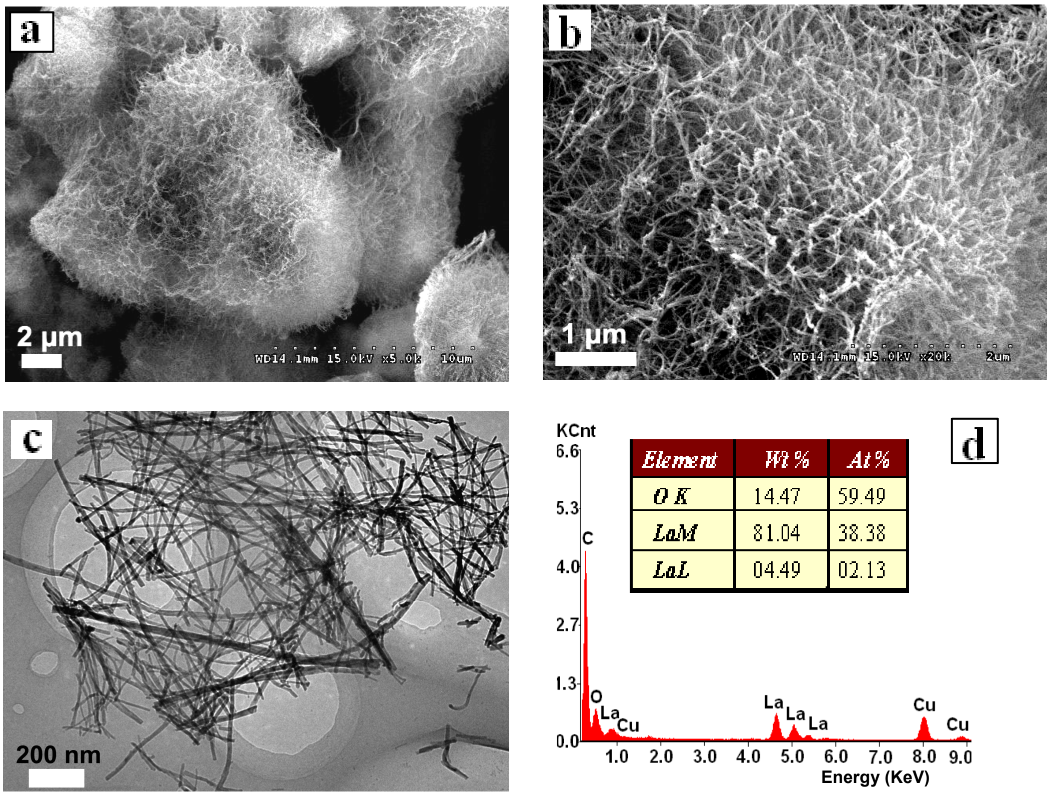


Figure S6. HRTEM images of (a) an individual, (b) branched- and (c) tapering lanthanum oxide nanowire. Inset in a is the SAED pattern of the nanowire.



Element	Wt %	At %
O K	14.47	59.49
LaM	81.04	38.38
LaL	04.49	02.13

Figure S7. (a) SEM, (b) high-magnification SEM, and (c) TEM images of lanthanum oxide nanowires after subject to 500 °C for 5 h. (d) EDS pattern of the nanowires shown in c.

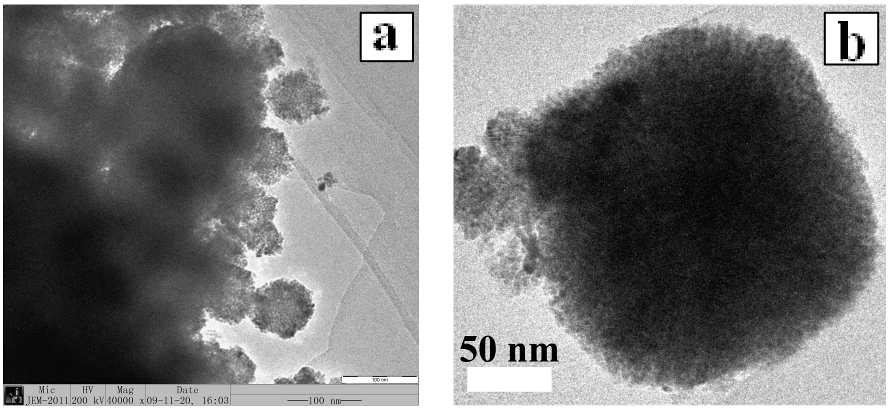


Figure S8. Typical TEM images of conventional Pt-CeO_2 prepared by an incipient wetness method: (a) at low magnification and (b) at high magnification.

References:

[1] J. Z. Shyu, W. H. Weber, H. S. Gandhi, *J. Phys. Chem.* **1988**, *92*, 4964.

[2] G. Beamson, D. Briggs, High Resolution XPS of Organic Polymers, The Scienta ESCA 300 Database: John Wilev & Sons: New York. **1992**.