Electronic Supplementary Information (ESI)

A General Method for Ultrathin 1D Oxide Nanomaterials

Yuxin Zhao,[a] Shi Hu,*[b] Bing Sun, [a] Shucai Zhang,[a] Lin Wang,[a] Miao Zhang,[c] Quanzhen Liu,[a] Shanjun Mu,[a] Ziyang Huo*[d]

[a] *State Key Laboratory of Safety and Control for Chemicals, SINOPEC Research Institute of Safety Engineering, No. 339, Songling road, Laoshan District, Shandong Qingdao, China.*
[b] *Department of Chemistry, School of Science, Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, 300072, Tianjin, China.*
[c] *Queensland Micro and Nano Centre, Griffith Uinversity, Australia, Brisbane 4111.*
[d] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, University of California-Berkeley, Berkeley CA 94720*
** Address correspondence to:* rychushi@gmail.com and ziyanghuo@gmail.com

Experiment Details:

General preparation of ultrathin 1D oxides materials

All chemicals were purchased from Aldrich and used without further purification. Oleic acid and oleylamine were dried at 120 °C under vacuum before use. Ultrathin 1D oxides materials were prepared under similar conditions as the cerium oxide nanoribbons by using lanthanum (III) acetate hydrate, niobium (V) ethoxide, vanadium(V) oxytriethoxide, tungsten (VI) hexachloride titanium (IV) butoxide and indium (III) acetate hydrate as precursors. In general, 1-2 mmol of precursors were dissolved in a mixture of 5-6 mL of oleic acid and 20~25 mL of oleylamine under vigorous string at 85 °C for more than 30 min. The transparent solution shortly became cloudy, which indicated the mesostructures had started to form. Some lyotropic liquid crystal phase could then be observed, as shown in the movie. The reaction was then heated at 230 °C for more than 6 h under nitrogen atmosphere. For the synthesis of tungsten oxide and vanadium oxide, the reaction temperature needs to be increased to 280 °C in order to obtain crystalline products. Before reaching the reaction temperature, some solution containing intermediates was transferred from the flask to a small vial. This vial was then put into the freezer to solidify the solution for low angle XRD test. After high-temperature synthesis, some solids were suspended in the solution. The final products could be obtained from the bulk solution after centrifugal separation at 3000 rpm. Hexane and ethanol were used to wash the products to remove the excess surfactants. After the washing, the products could be readily dispersed in non-polar (weakly polar) solvents, such as hexane, toluene or chloroform.

Preparation of CeO_2 nanorods

The CeO_2 nanorods were prepared by a control precipitation reaction. The as-received 1.3g of cerium (III) nitrate hexahydrate was dissolved into 10ml H_2O. 12g of NaOH (beads) was dissolved into 40ml H_2O and then mixed with the above aqueous $Ce(NO_3)_3$ solution. The generated white slurry was aging for 1h then transferred into autoclave for hydrothermal process at 100C. After 16h reaction, the precipitate was collected from the bottom and washed by EtOH and water. The collected products were further baked at 200 °C in vacuum oven. For surface treatment, the catalysts were placed into stainless steel chamber with oxygen plasma generator which was pre-evacuated for 15min until the pressure reach at 5×10^{-3} Torr. The air flow was kept at 10-20 sccm. The treatment gas pressure was set to 10^{-2} Torr where the power density is ca 10~15W. The plasma treated catalyst were then transfer to reaction tube for catalytic reaction test.

Catalytic reaction assessment

The catalytic reaction of CO oxidation was process in a flow reactor. Gas flows were regulated using calibrated mass-flow controllers. Temperature was controlled using a thermocouple (K type) and the PID control box. The as-prepared CeO_2 catalysts (25mg) were mixed with inert quartz sand (high temperature treated and washed with Acid) to form the test powder and then loaded into quartz reaction tube. CO conversion rates were acquired in 40 Torr CO and 100 Torr O_2 with a balance (carrier gas) of Helium. The resulted gas products were analyzed with a thermal conductivity detector (TCD) on an HP gas chromatograph.

Characterizations

Powder X-ray diffraction (XRD) patterns (low-angle) were recorded by a Rigaku. D/max 2500Pc X-ray diffractometer (XRD) with Cu Kα radiation (λ=1.5418 Å). The operation voltage and current were kept at 40 kV and 250 mA, respectively. XRD patterns (high-angle) were carried out with a GADDS Hi-Star D8 diffractometer (Bruker). XRD samples were prepared by depositing the precipitated samples on a silicon plate. The sizes and morphologies of the as-obtained nanocrystals were examined with a FEI Tecnai G^2 S-Twin transmission electron microscope at an accelerating voltage of 200 kV and a Hitachi H9500 transmission electron microscope at an accelerating voltage of 300 kV. The samples were prepared by casting the dilute colloidal solution onto carbon-coated copper TEM grids. Energy dispersive X-ray

Spectroscopy (EDS) measurements were performed with a Gatan parallel detection spectrometer attached to the electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were measured by a Perkin-Elmer PHI 5300 XPS spectrometer located in an ultrahigh vacuum chamber with a base pressure of 10^{-9} Torr. The XPS spectrometer was operated using Al Kα X-ray source at an accelerating voltage of 15 kV and a power of 350 W. XPS samples were prepared by drop casting the colloidal solution on a silicon wafer.

Supporting Figures:

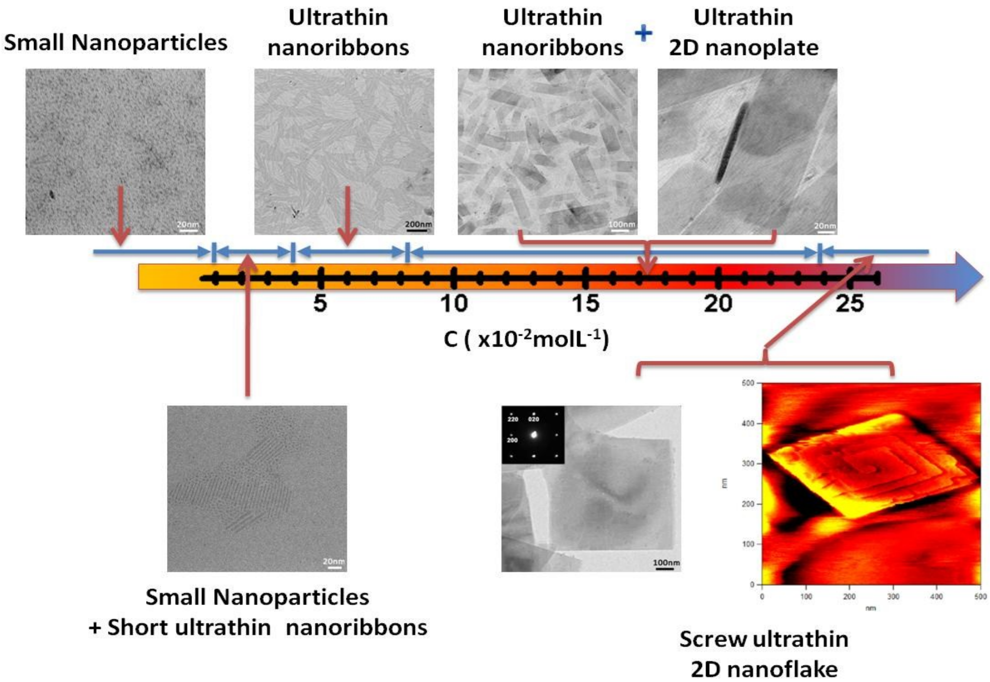

Fig. S1 TEM images of as-prepared CeO_2 nanostructures under different conditions. The concentration of inorganic species shows dramatic influence on shape evolution. The ultra-small dimensions of the as-generated products are always consistent until the very high concentration was set up in the experiment. Even under the very high concentration when the soft mesostructures cannot prevent the growth of the inorganic crystal, the ultrathin features could still be found in the large crystalline flakes. The screw height in the flake is still around 2 nm. Furthermore, the screw direction (100) shows the same orientation with the ultrathin 1D nanoribbons.

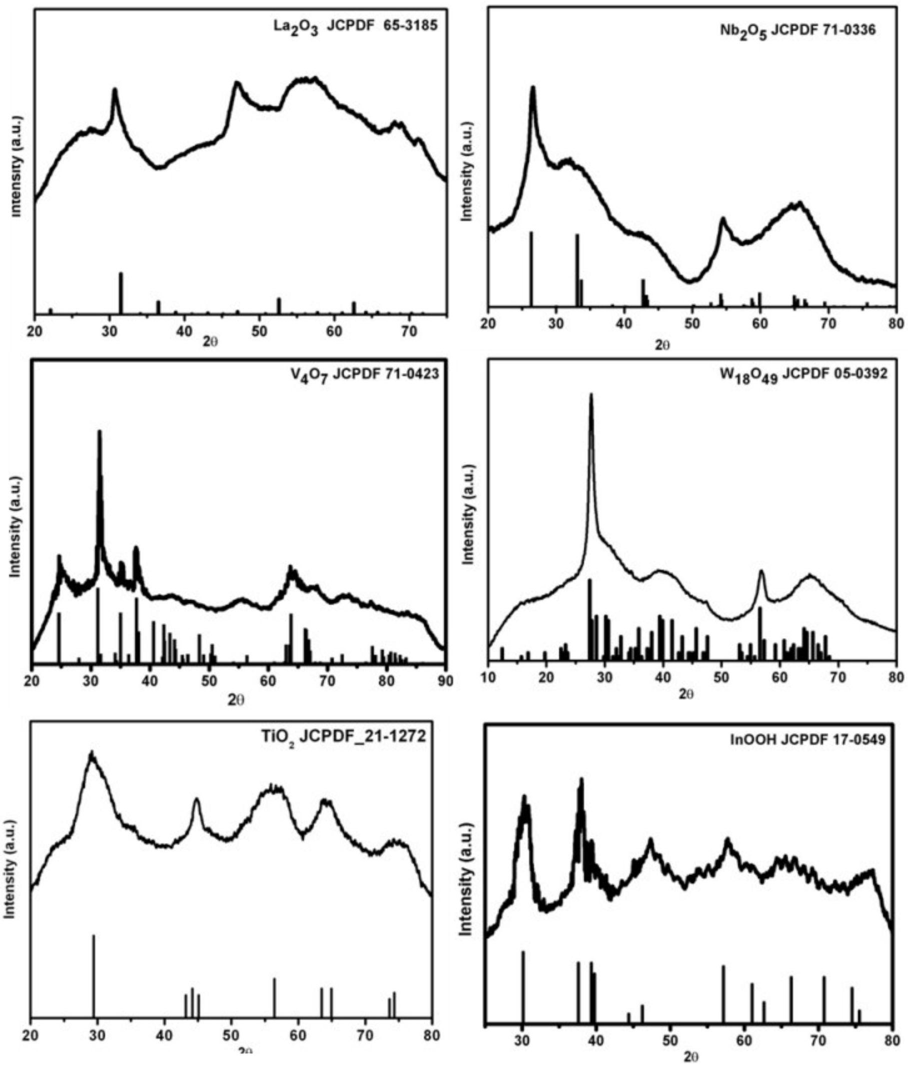

Fig. S2 XRD patterns of as-prepared ultrathin oxides. The broad diffraction peaks are very common in these patterns, and the shape of diffraction peaks always reveals the orientation of the ultrathin crystal.

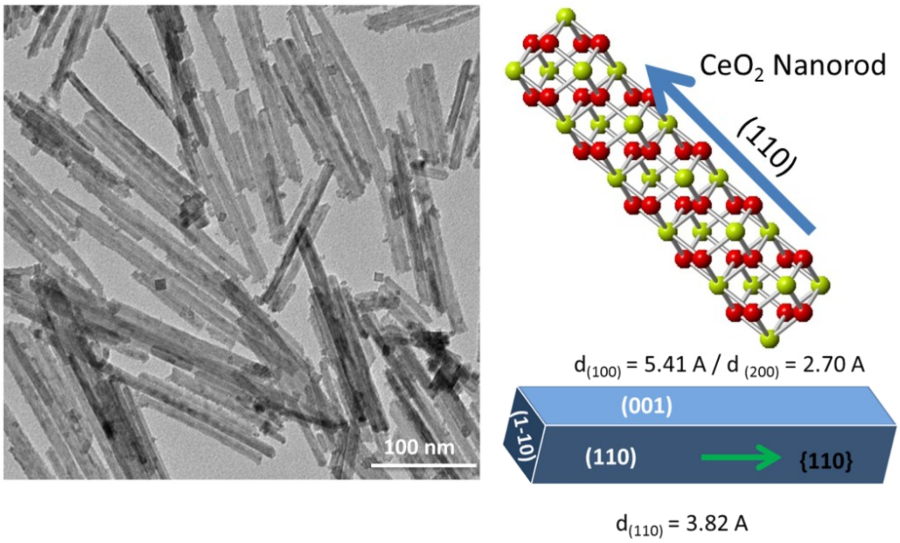

Fig. S3 TEM image of as-prepared CeO_2 nanorods and corresponding 110 oriented CeO_2 crystal structure. The CeO_2 nanorods with (110) crystal plane was reported as highly active catalyst in CO oxidation reaction.

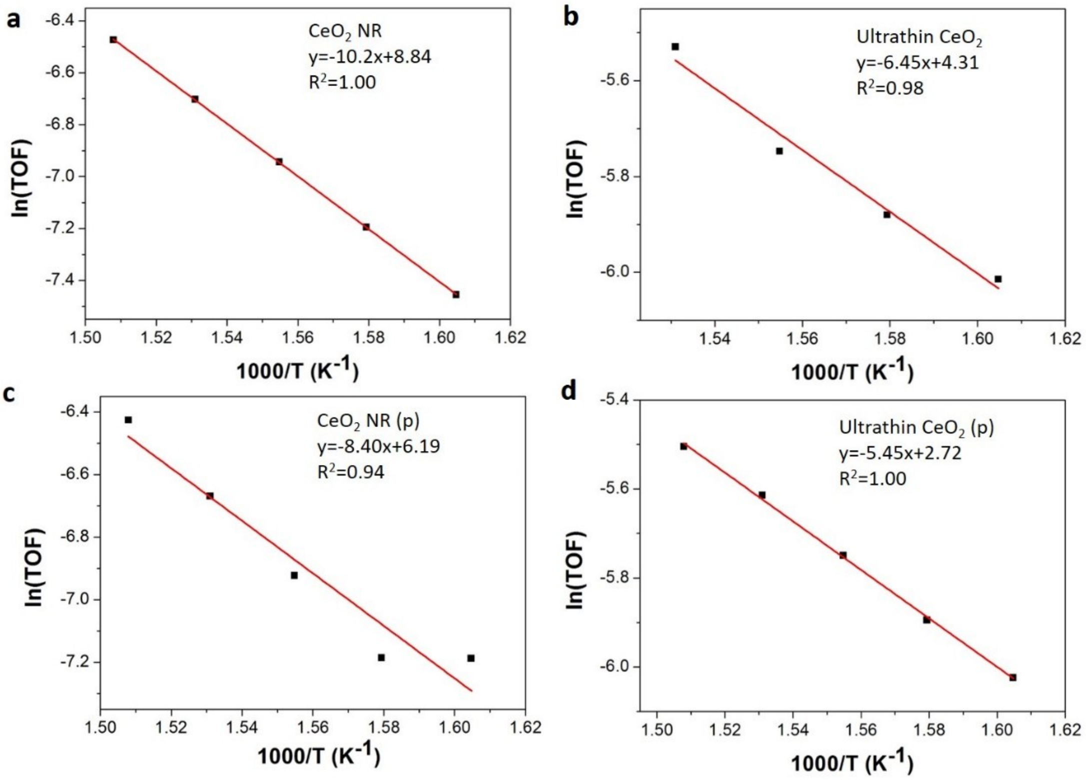

Fig. S4 Catalytic performance of various CeO_2 nanostructures as a function of reaction temperature: (a) CeO_2 NR, (b) Ultrathin CeO_2, (c) Plasma-treated CeO_2 NR, (d) Plasma-treated ultrathin CeO_2.