

## Surface Crystal Plane Determination and Strong Metal-Support Interactions in CeO<sub>2</sub> Nanorod-Supported CuO<sub>x</sub> Catalysts

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Understanding the catalyst-support interactions provides mechanistic information about how the catalytic reaction takes place. Both CuO-CeO<sub>2</sub> and Cu-CeO<sub>2</sub> have been reported to have high catalytic activity to promote carbon monoxide oxidation, water-gas shift reaction, and methanol steam reforming. This can be attributed to the quick reversible Ce<sup>4+</sup>/Ce<sup>3+</sup> redox couple, Cu<sup>2+</sup>/Cu<sup>+</sup>/Cu<sup>0</sup> redox triple, and the CuO<sub>x</sub>-CeO<sub>2-x</sub> interactions during the redox processes [1]. The redox functionality of both catalyst and support are vital components for gas adsorption, oxygen migration at the metal-support interface and in the catalytic reactions mentioned above. To further understand CuO<sub>x</sub>-CeO<sub>2</sub> interfacial effect, we report a comparative study on CeO<sub>2</sub> nanorod-supported CuO and Cu catalysts for CO oxidation.

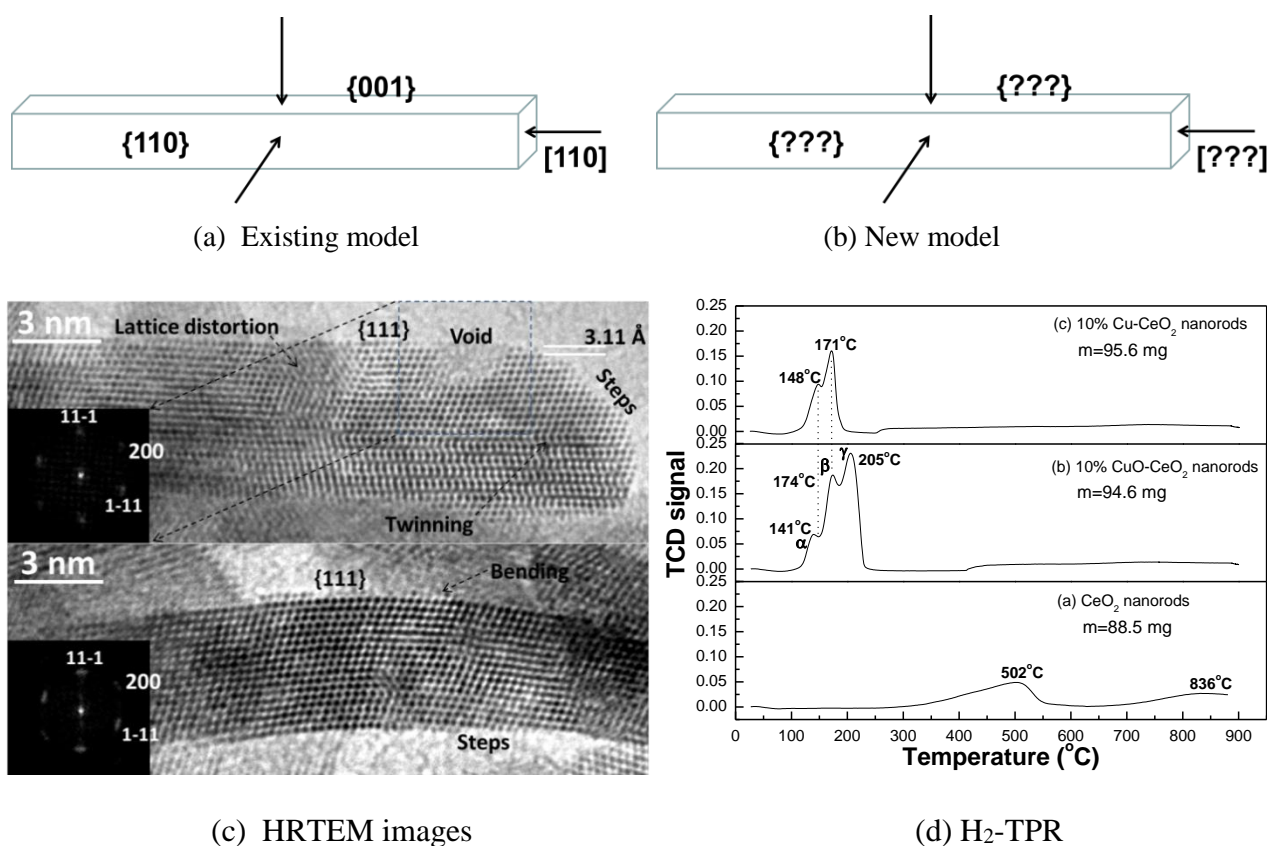
CeO<sub>2</sub> nanorods were prepared using a hydrothermal method [2-4]. Typically 0.1M Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 6M NaOH mixtures were heated to 90~130 °C and held for 48 hrs in a sealed 200 mL Teflon-lined autoclave (~50 % fill). Then the autoclave was cooled to room temperature before the solid products were recovered by suction filtration. The materials were washed thoroughly with distilled water to remove any co-precipitated salts, then washed with ethanol to avoid hard agglomeration in the nanoparticles, and dried in air at 50 °C for 12 hrs. Transmission electron microscopy (TEM) characterization was performed using a JEOL 2100 operated at 200 kV and equipped with an EDAX detector and annular dark-field detector. Hydrogen temperature programmed reduction (H<sub>2</sub>-TPR) study was examined using hydrogen chemisorption on the Quantachrome iQ and Micrometrics 2920 to explore how much hydrogen adsorbs as a function of temperature. The catalytic oxidation of CO was conducted by using a fixed bed plug flow reactor system. 1vol%CO/20vol%O<sub>2</sub>/79vol%He with a 70 mL/min flow rate was supplied through mass flow controller and passed through the catalyst bed. The catalyst (~100 mg) was mixed with quartz wool (coarse, 9 μm) and filled in the quartz tube reactor. The reaction temperature was programmed between room temperature and 350°C and monitored by thermocouple. The reactant CO and product CO<sub>2</sub> were analyzed by using an on-line gas chromatograph (SRI multiple gas analyzer GC, 8610C chassis) system.

Shown in Figure 1, the HRTEM images of CeO<sub>2</sub> nanorods clearly suggest a {111} termination surface with a significant amount of defects, including steps, voids, lattice distortion, twinning, and bending. The data thus obtained are inconsistent with those available in the literature [5], claiming a rod geometry with two {001} and two {011} surfaces, although the {001} surface was occasionally observed in the present study. By exposing these more “defected” crystal planes, CeO<sub>2</sub> nanorods have a much higher surface reduction percentage than their conventional octahedrally shaped counterparts with {111} crystal planes. H<sub>2</sub>-TPR (Figure 1) shows that a larger percentage of the reduction takes place in the lower temperature surface reduction area. Figure 1 also compares the H<sub>2</sub>-TPR profiles of the 10 w% CuO-CeO<sub>2</sub> nanorods and 10 wt% Cu-CeO<sub>2</sub> nanorods (CeO<sub>2</sub> as a reference), correlated to the three-step and two-step reduction profiles, respectively. For the CuO-CeO<sub>2</sub> sample, the three-step reduction profiles are assigned from low to high temperature as follows: CuO strongly interacting with CeO<sub>2</sub> support; highly dispersed CuO<sub>x</sub> species on CeO<sub>2</sub> support; “bulk-like” larger CuO particles. For the Cu-

CeO<sub>2</sub> sample, since only CeO<sub>2</sub> is reducible, it is reasonable to assign these two peaks to the small Cu particles ( $\alpha$ -type) that is strongly interacting with CeO<sub>2</sub> support and the well-dispersed Cu particles ( $\beta$ -type) weakly interacting with CeO<sub>2</sub> support. The H<sub>2</sub>-TPR result indicates a strong interaction via possible oxygen diffusion between the reduced metallic copper and CeO<sub>2</sub> nanorods is formed and involved in the hydrogen consumption. We will present the atomic level interfacial structure and chemical composition of CeO<sub>2</sub> nanorod-CuO<sub>x</sub> catalysts using HRTEM, EDX and EELS in details. [6]

## References

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**Figure 1.** Possible structural models (a and b) and HRTEM images (c) of the as-synthesized CeO<sub>2</sub> nanorods, and H<sub>2</sub>-TPR profiles (d) of CeO<sub>2</sub>, 10wt% CuO/CeO<sub>2</sub>, and 10wt% Cu/CeO<sub>2</sub> under a 5% H<sub>2</sub>/95% Ar gas atmosphere.