

# Ceria- and Cu-Doped Ceria Nanocrystals Synthesized by the Hydrothermal Methods

Jiacheng Wang, Qingfeng Liu, and Qian Liu<sup>†</sup>

State key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai 200050, China

**Ceria- or Cu-doped ceria nanocrystals with a uniform diameter of about 4–5 nm have been successfully synthesized directly via a hydrothermal treatment of the precipitate Ce(OH)<sub>3</sub> (purple) or Cu-doped Ce(OH)<sub>3</sub> in a strongly basic solution of sodium hydroxide at 180°C for 24 h. The formation of the nanocrystals involves the transformation of Ce (III) to Ce (IV) under the hydrothermal conditions. The as-synthesized ceria- and Cu-doped ceria crystalline nanoparticles have high specific surface areas, pore volumes, and pore sizes.**

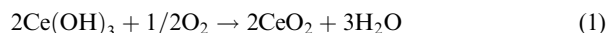
## I. Introduction

CERIA has been considered to be a useful material in applications for catalysts, catalytic supports, electrolytes, and oxygen conductors in solid oxide fuel cells.<sup>1–3</sup> These applications of CeO<sub>2</sub> emerge from its reversible oxygen storage and release capacity. If ceria was obtained in a nanosized form, it should show more effective functions resulting from a nanosize effect. To date, various methods such as template-based homogeneous precipitation,<sup>4,5</sup> hexamethylenetetramine-based homogeneous precipitation coprecipitation,<sup>6</sup> decomposition of oxalate precursors,<sup>7</sup> a hydrothermal route,<sup>8–10</sup> and a mechanical milling reaction<sup>11</sup> for the preparation of CeO<sub>2</sub> nanoparticles have been found in many papers. The as-synthesized ceria powders have a fine nanostructure (~10–50 nm).

Among these methods, worldwide focus has been on the hydrothermal route because the powders synthesized using this method possess promising characteristics including a fine size, a narrow size distribution, high purity, and good chemical homogeneity at low synthesis temperatures. Hirano and colleagues<sup>8,9,12</sup> synthesized nanocrystalline ceria powders 10–20 nm in size using Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O and urea as precursors by the hydrothermal method. Furthermore, it has been found that doping of Cu into a CeO<sub>2</sub> matrix can improve some catalytic performances. Cu/CeO<sub>2</sub> can catalyze CO oxidation at 150°C, whereas the same reaction occurs at a much higher temperature for CeO<sub>2</sub>.<sup>13,14</sup> Luo *et al.*<sup>15</sup> have demonstrated low-temperature CO oxidation for Cu-doped CeO<sub>2</sub> prepared by coprecipitation and impregnations. Bera *et al.*<sup>13</sup> synthesized Cu-doped CeO<sub>2</sub> powders through combustion methods. It can be assumed that Cu/CeO<sub>2</sub> powders with a nanosized morphology will show more excellent catalytic performance than coarse powders do. At the same time, ceria with different morphologies of nanotubes, nanorods, nanoparticles, etc. were prepared by different methods.<sup>16–22</sup>

In this communication, ceria- or Cu-doped ceria nanocrystals with a uniform diameter of about 4–5 nm have been successfully synthesized directly via hydrothermal treatment of the precipi-

tate Ce(OH)<sub>3</sub> (purple)- or Cu-doped Ce(OH)<sub>3</sub> in a strongly basic solution of sodium hydroxide at 180°C for 24 h. After the hydrothermal treatment, the resulting powder is lightly yellow, which indicates the formation of CeO<sub>2</sub>. The reaction can be expressed as follows<sup>22</sup>:



## II. Experimental Procedure

All reagents were analytical grade and were used without further purification. The synthetic procedure was as follows: Specifically, 0.87 g (0.002 mol) of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 25 mL of deionized water to obtain a Ce(NO<sub>3</sub>)<sub>3</sub> solution. Then, this solution was slowly added to a 50 mL alkali solution containing 0.65 g of NaOH under stirring at room temperature. The pH value of the colloidal precursor obtained was about 13–14. Then, the purple colloid was poured into a stainless Teflon-lined 100-mL-capacity autoclave that was maintained at 180°C for 24 h and then air cooled to room temperature. After hydrothermal treatment, the resulting light yellow products were vacuum dried, washed with water and ethanol, and then vacuum dried at room temperature. 5 mol% Cu-doped ceria nanocrystals were prepared using 25 mL of Ce(NO<sub>3</sub>)<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub> mixed solution as the precursor, which contained 0.03 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and 0.83 g of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. The percentage of CuO is 5 mol% expressed as the mole ratio [NCuO/(NCuO+NCeO<sub>2</sub>)]. The following procedure was similar to that of CeO<sub>2</sub> nanopowder above. The resulting brown product was named CeO<sub>2</sub>-Cu.

X-ray powder diffraction patterns were collected on a Rigaku D/MAX-γB (Rigaku, Tokyo, Japan) instrument using CuKα (λ = 0.15406 nm) radiation at 40 kV and 60 mA. The Specific surface areas of the powders were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen as the adsorption gas. The TEM images and HRTEM were obtained on a JEM-2010 transmission electron microscope using an accelerating voltage of 200 KV. X-ray photoelectron spectroscopy data were obtained using an ESCALab220i-XL electron spectrometer from VG Scientific (Thermo Fisher Scientific, Inc., West Sussex, England) using 300 W AlKα radiation. The base pressure was about 3 × 10<sup>-9</sup> mbar. The binding energies were referenced to the C1s line at 284.8 eV from carbon.

## III. Results and Discussion

During the synthesis of CeO<sub>2</sub> nanocrystals, the color of the mixed solution before the hydrothermal treatment was purple due to the existence of Ce(OH)<sub>3</sub>. After the hydrothermal treatment, the precipitate was slightly yellow, which indicates the production of CeO<sub>2</sub>. This also suggests the transformation of Ce (III) into Ce (IV) shown in Eq. (1).

The results of the nitrogen sorption measurements of the samples are listed in Table I. As can be seen, the CeO<sub>2</sub>

S. W. Chan—contributing editor

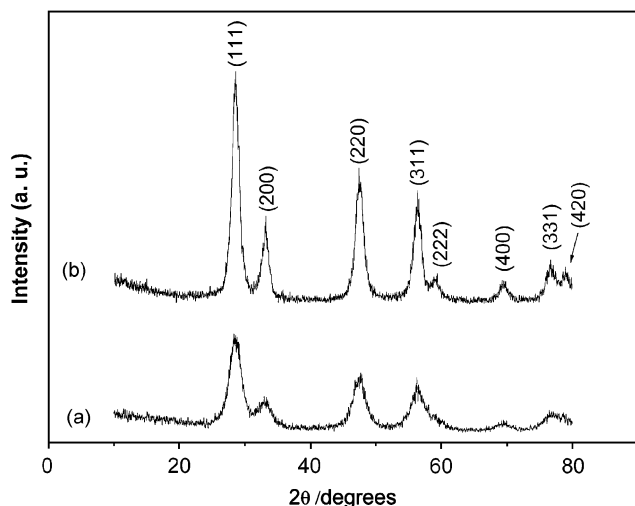
Manuscript No. 23906. Received October 26, 2007; approved February 7, 2008.

<sup>†</sup>Author to whom correspondence should be addressed. e-mail: qianliu@sunm.shcnc.ac.cn

**Table I. Specific Surface Area, Pore Volume, and Pore Diameter Measured for the CeO<sub>2</sub> and Cu-Doped CeO<sub>2</sub> Nanocrystals**

| Sample               | <sup>†</sup> Specific surface area (m <sup>2</sup> /g) | <sup>‡</sup> Pore volume (cm <sup>3</sup> /g) | <sup>§</sup> Pore diameter (nm) |
|----------------------|--------------------------------------------------------|-----------------------------------------------|---------------------------------|
| CeO <sub>2</sub>     | 125                                                    | 0.21                                          | 5.3                             |
| CeO <sub>2</sub> -Cu | 215                                                    | 0.45                                          | 6.6                             |

<sup>†</sup>Specific surface area calculated by BET methods. <sup>‡</sup>Pore volume and pore diameter calculated from the desorption isotherm.

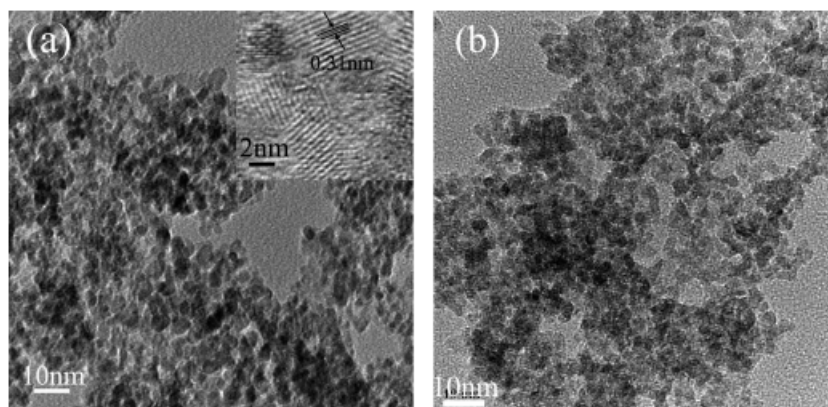
**Fig. 1.** The as-synthesized CeO<sub>2</sub> (a) and 5 mol% Cu-doped CeO<sub>2</sub> (b) nanocrystals by the hydrothermal method.

nanopowder possesses a high specific surface area of 125 m<sup>2</sup>/g, a pore volume of 0.21 cm<sup>3</sup>/g and a pore diameter of 5.3 nm. The mesopores should have arisen from the interspace of the accumulating nanoparticles. This was proved by the TEM images discussed in the latter paragraph. The specific surface area, pore volume, and pore diameter of the CeO<sub>2</sub>-Cu nanopowder obtained by hydrothermally treating the Cu(NO<sub>3</sub>)<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> mixed colloid were 215 m<sup>2</sup>/g, 0.45 cm<sup>3</sup>/g, and 6.6 nm, respectively, as shown in Table I. Noticeably, the specific surface area and pore volume of CeO<sub>2</sub>-Cu are much higher than those of the pure CeO<sub>2</sub> sample. Conclusively, the CeO<sub>2</sub> and Cu-doped CeO<sub>2</sub> nanopowders obtained have high BET surfaces, pore volumes, and pore diameters, which favor the transportation of the reactive molecules in them.

Figure 1 shows the XRD patterns of the as-synthesized CeO<sub>2</sub>- (a) and 5 mol% Cu-doped CeO<sub>2</sub> (b) nanocrystals by the hydrothermal method. Noticeably, all peaks in Fig. 1(a) can be indexed to a pure cubic phase [space group: *Fm3m* (225)] of CeO<sub>2</sub> according to the JCPDS file No 810792. The lattice parameter of the calcined products is calculated according to the equation  $1/d^2 = (h^2 + k^2 + l^2)/a^2$  based on the crystal plane of (111), and the calculated lattice constant is  $a = 0.547$  nm, which matches well with the literature value of  $a = 0.541$  nm. The average diameter of ceria nanocrystals, evaluated by means of the Scherrer formula, is about 4 nm. The XRD pattern of the Cu-doped ceria sample is very similar to that of CeO<sub>2</sub> nanocrystals. No diffraction peaks due to crystalline CuO or Cu(OH)<sub>2</sub> were observed. This demonstrates that Cu compounds exist as highly dispersed or amorphous surface species or its amount is low. Moreover, the diffraction peaks of the Cu-doped ceria are evidently sharper than those of CeO<sub>2</sub> nanocrystals, which should be due to the doping of Cu. In the previous papers, it was found that the starting Ce source (cerium (III) nitrate, cerium (IV) sulfate, and cerium (IV) ammonium sulfate) has a considerable influence on the crystallinity of the crystallite size of CeO<sub>2</sub> particles.<sup>8</sup> In this study, it is interesting to note that the doping of the impurity atom can also affect the resultant product and its crystallinity.

As shown in Fig. 2, representative transmission electron microscope (TEM) images reveal the particle size and morphology of the as-synthesized CeO<sub>2</sub>- and Cu-doped CeO<sub>2</sub> nanocrystals. Figure 2(a) shows that the as-synthesized CeO<sub>2</sub> nanocrystals have a uniform morphology of “quasi” zero-dimensional particles ranging from 4 to 5 nm, whereas the purple precipitate of Ce (III) compounds obtained comprised large agglomerated particles before the hydrothermal treatment. This reveals that the hydrothermal treatment transformed the large particles of Ce (III) compounds into a nanometer-scale cerium (IV) oxide. The HRTEM image of the CeO<sub>2</sub> sample in the inset shows that there are ordered crystal-lattice fringe patterns with different tropisms, which suggests that every CeO<sub>2</sub> nanoparticle possesses a good crystalline structure. The calculated interference fringe spacing is about 0.31 nm, which is consistent with the interplanar distance of the (111) plane in the cubic fluorite structure.

Nanocrystalline ceria has been prepared using H<sub>2</sub>O<sub>2</sub> as the oxidizer using a two-step precipitation process, followed by the hydrothermal treatment.<sup>23</sup> Here, we prepared ceria nanocrystals directly by the hydrothermal treatment of Ce(OH)<sub>3</sub> in a strongly basic solution without using H<sub>2</sub>O<sub>2</sub> as the oxidizer. The doping of Cu into ceria made the nanoparticle morphology of ceria more irregular, and the size of Cu-doped ceria nanocrystals seemed to show no change (Fig. 2(b)). The TEM micrograph of the CeO<sub>2</sub> shows good agreement with the crystalline size determined by XRD. Furthermore, EDS analysis of the sample Cu-doped CeO<sub>2</sub> nanopowder identified Cu and Ce with an atom ratio of nearly 9.2:1, which is close to the designed atom ratio of

**Fig. 2.** Representative TEM images of the as-synthesized ceria (a) and Cu-doped ceria nanocrystals (b). The inset in (a) is the high-resolution TEM image of the ceria nanocrystals.

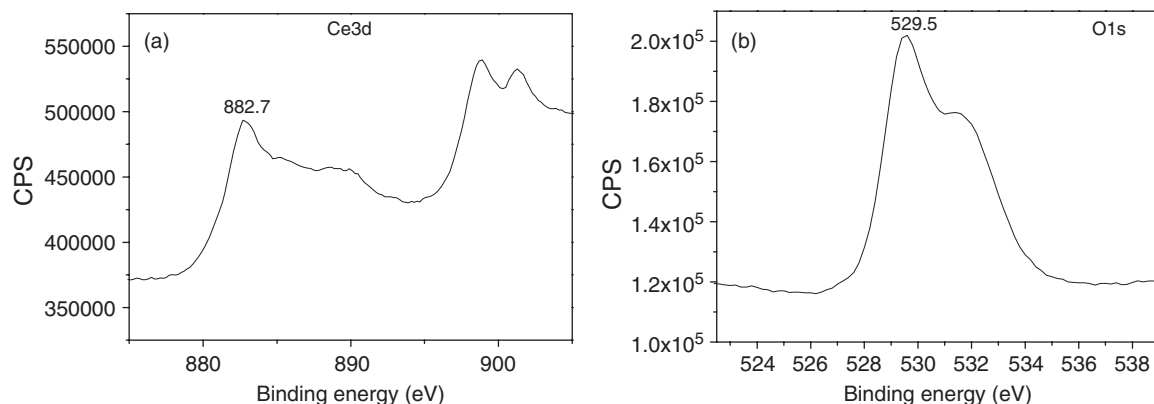


Fig. 3. Ce3d (a) and O1s (b) core level spectra observed for CeO<sub>2</sub> nanocrystals.

9:1, and no other elements were detected, except the carbon peaks from the sample grid.

It is well known that the Ce (III) oxidation state is unstable compared with the Ce (IV) oxidation state in an alkaline solution and in the presence of air. From the Ce3d core-level peak in the XPS spectra shown in Fig. 3(a), it can be seen that cerium exists in a Ce(IV) oxidation state (882.8 eV), without any impurity of the Ce (III) oxidation state. At the same time, oxygen exists in an O<sup>2-</sup> (529.5 eV) state shown in Fig. 3(b). Hence, the XPS-detected binding energies of Ce3d and O1s are in agreement with the standard CeO<sub>2</sub>.<sup>17</sup>

#### IV. Conclusions

Ceria- or Cu-doped ceria nanocrystals with a uniform size of about 4–5 nm have been successfully synthesized by the hydrothermal treatment of colloidal precursors Ce(OH)<sub>3</sub>- or Cu-doped Ce(OH)<sub>3</sub> in a strongly basic solution at 180°C for 24 h. The formation of nanocrystals involves transformation of Ce (III) into Ce (IV) under the hydrothermal conditions. Hydrothermal treatment transformed the large particles of Ce compounds precipitate into nanometer-scale ceria. The as-synthesized ceria- and Cu-doped ceria nanopowders possess high specific surface areas, pore volumes, and pore sizes, which can be used in many potential applications. The technique used here is a simple and low-cost method for the large-scale production of ceria- and Cu-doped nanocrystals as well as ceria nanomaterials doped with other elements (Zr, Tb, Pr, Er, Co, etc.). The application study is in progress.

#### References

- G. Balducci, M. S. Islam, J. Kaspar, P. Fornasiero, and M. Graziani, "Reduction Process in CeO<sub>2</sub>-MO and CeO<sub>2</sub>-M<sub>2</sub>O<sub>3</sub> Mixed Oxides: A Computer Simulation Study," *Chem. Mater.*, **15**, 3781–5 (2003).
- G. Balducci, J. Kaspar, P. Fornasiero, M. Graziani, and M. S. Islam, "Surface and Reduction Energetics of the CeO<sub>2</sub>-ZrO<sub>2</sub> Catalysts," *J. Phys. Chem. B*, **102**, 557–61 (1998).
- S. Bernal, G. Blanco, M. A. Cauqui, M. P. Corchado, C. Larese, J. M. Pintado, and J. M. Rodriguez-Izquierdo, "Cerium-Terbium Mixed Oxides as Alternative Components for Three-Way Catalysts: A Comparative study of Pt/CeTbO<sub>x</sub> and Pt/CeO<sub>2</sub> Model Systems," *Catal. Today*, **53**, 607–12 (1999).
- P. L. Chen and I. W. Chen, "Reactive Cerium(IV) Oxide Powders by the Homogeneous Precipitation Method," *J. Am. Ceram. Soc.*, **76**, 1577–83 (1993).
- Y. J. Wang, J. M. Ma, M. F. Luo, P. Fang, and M. He, "Preparation of High-Surface Area Nano-CeO<sub>2</sub> by Template-Assisted Precipitation Method," *J. Rare Earths*, **25**, 58–62 (2007).
- P. L. Chen and I. W. Chen, "Sintering of Fine Oxide Powders .1. Microstructural Evolution," *J. Am. Ceram. Soc.*, **79**, 3129–41 (1996).
- W. P. Hsu, L. Ronquist, and E. Matijevic, "Preparation and Properties of Monodispersed Colloidal Particles of Lanthanide Compounds .2. Cerium(IV)," *Langmuir*, **4**, 31–7 (1988).
- M. Hirano and E. Kato, "Hydrothermal Synthesis of Cerium (IV) Oxide," *J. Am. Ceram. Soc.*, **79**, 777–80 (1996).
- M. Hirano and E. Kato, "Hydrothermal Synthesis of Nanocrystalline Cerium (IV) Oxide Powders," *J. Am. Ceram. Soc.*, **82**, 786–8 (1999).
- C. H. Lu and H. C. Wang, "Formation and Microstructural Variation of Cerium Carbonate Hydroxide Prepared by the Hydrothermal Process," *Mater. Sci. Eng. B-Solid State Mater. Adv. Technol.*, **90**, 138–41 (2002).
- Y. X. Li, X. Z. Zhou, Y. Wang, and X. Z. You, "Preparation of Nano-Sized CeO<sub>2</sub> by Mechanochemical Reaction of Cerium Carbonate with Sodium Hydroxide," *Mater. Lett.*, **58**, 245–9 (2004).
- M. Hirano, Y. Fukuda, H. Iwata, Y. Hotta, and M. Inagaki, "Preparation and Spherical Agglomeration of Crystalline Cerium (IV) Oxide Nanoparticles by Thermal Hydrolysis," *J. Am. Ceram. Soc.*, **83**, 1287–9 (2000).
- P. Bera, K. R. Priolkar, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro, and N. P. Lalla, "Structural Investigation of Combustion Synthesized Cu/CeO<sub>2</sub> Catalysts by EXAFS and Other Physical Techniques: Formation of a Ce<sub>1-x</sub>Cu<sub>x</sub>O<sub>2</sub>-Delta Solid Solution," *Chem. Mater.*, **14**, 3591–601 (2002).
- M. Jobbagy, F. Marino, B. Schobrod, G. Baronetti, and M. Laborde, "Synthesis of Copper-Promoted CeO<sub>2</sub> Catalysts," *Chem. Mater.*, **18**, 1945–50 (2006).
- M. F. Luo, J. M. Ma, J. Q. Lu, Y. P. Song, and Y. J. Wang, "High-Surface Area CuO-CeO<sub>2</sub> Catalysts Prepared by a Surfactant-Templated Method for Low-Temperature CO Oxidation," *J. Catal.*, **246**, 52–9 (2007).
- W. Q. Han, L. J. Wu, and Y. M. Zhu, "Formation and Oxidation State of CeO<sub>2-x</sub> Nanotubes," *J. Am. Chem. Soc.*, **127**, 12814–5 (2005).
- P. X. Huang, F. Wu, B. L. Zhu, X. P. Gao, H. Y. Zhu, T. Y. Yan, W. P. Huang, S. H. Wu, and D. Y. Song, "CeO<sub>2</sub> Nanorods and Gold Nanocrystals Supported on CeO<sub>2</sub> Nanorods as Catalyst," *J. Phys. Chem. B*, **109**, 19169–74 (2005).
- S. Maensiri, C. Masingboon, P. Laokul, W. Jareonboon, V. Promarak, P. L. Anderson, and S. Seraphin, "Egg White Synthesis and Photoluminescence of Platelike Clusters of CeO<sub>2</sub> Nanoparticles," *Cryst. Growth Des.*, **7**, 950–5 (2007).
- Z. L. Wang and X. D. Feng, "Polyhedral Shapes of CeO<sub>2</sub> Nanoparticles," *J. Phys. Chem. B*, **107**, 13563–6 (2003).
- F. Zhang, S. W. Chan, J. E. Spanier, E. Apak, Q. Jin, R. D. Robinson, and I. P. Herman, "Cerium Oxide Nanoparticles: Size-Selective Formation and Structure Analysis," *Appl. Phys. Lett.*, **80**, 127–9 (2002).
- F. Zhang, Q. Jin, and S. W. Chan, "Cerium Nanoparticles: Size, Size Distribution, and Shape," *J. Appl. Phys.*, **95**, 4319–26 (2004).
- X. D. Zhou, W. Huebner, and H. U. Anderson, "Processing of Nanometer-Scale CeO<sub>2</sub> Particles," *Chem. Mater.*, **15**, 378–82 (2003).
- B. Djuricic and S. Pickering, "Nanostructured Cerium Oxide: Preparation and Properties of Weakly-Agglomerated Powders," *J. Eur. Ceram. Soc.*, **19**, 1925–34 (1999).