Formation of highly dispersed cerium oxide with cubic structure prepared by alkoxide-surfactant system

Y. MURATA, M. ADACHI*
Institute of Advanced Energy, Kyoto University, Uji, Kyoto 611-0011, Japan
E-mail: adachi@iae.kyoto-u.ac.jp

Nanostructures, such as nanocrystals and nanowires, represent key building blocks for nanoscale science and technology. They are needed to implement the "bottom-up" approach to nanoscale fabrication, whereby well-defined nanostructures with unique physical properties are assembled into optoelectronic [1] and nanoelectronic [2] devices and other functional materials [3]. Colloidal nanocrystals are promising candidates in these fields, due to their ease of fabrication and processibility. Even more applications and new functional materials might emerge if nanocrystals could be synthesized in shapes of higher complexity than the ones produced by current method (spheres, rods, discs) [4–6]. The building blocks are central to the success of this approach, and thus the more adept researchers are at controlling, for example, the size, morphology, and composition of nanocrystals through synthesis, the greater the potential for developing new nanotechnologies.

Among various rare earth compounds, cerium oxide (CeO_2)-based materials have been extensively studied and employed in various applications [7–9]. Recently, nanocrystalline CeO_2 materials benefit not only these applications, but they also possess some other unique properties, such as the Raman-allowed modes in shifting and broadening [10], and the blue shift in ultraviolet absorption spectra [11]. Various aqueous-solution-based methods for synthesizing nanocrystalline CeO_2 powders have been investigated [12, 13]. However, one main disadvantage of aqueous synthesis is the hard agglomeration of fine particles, which has imposed a major challenge to realization of the full potential of nanocrystalline powders, especially CeO_2 particles. Furthermore, although studies on the control of particle size and mono-dispersed particles for CeO_2 have so far been reported, control of the particle morphology has not yet been achieved.

In this paper, we report the successful synthesis of mono-dispersed nanoparticles of cubic shape cerium oxide by using a surfactant-assisted process in an aqueous solution system, resulting in control of their size and morphology, as characterized using high-resolution transmission electron microscopy (HRTEM). The prepared CeO_2 nanoparticles were well crystallized near room temperature, i.e., 353 K. Also, we found a clear potential to control the characteristic length and shape of the 1D, 2D, or 3D, CeO_2-materials by assembling cubic CeO_2 as a building block. In fact, we synthesized the sheet-like and rod-like structures by using the prepared cubic CeO_2 nanoparticles as a starting material.

The samples were synthesized by a kind of sol-gel method in the aqueous phase. The preparation of the cubic cerium oxide particles was achieved by mixing cerium tri-isopropoxide (CTIP, $Ce(OC_3H_7)_3$) and Laurylamine hydrochloride (LAHC) surfactant solution. In a typical synthesis process, LAHC was dissolved in distilled water. CTIP (0.5 mol/kg) solution in 2-propanol was mixed with the same moles of acetylacetone (ACA) and immediately added to 0.1 M LAHC aqueous solution of pH 4.2. The mole ratio of CTIP to LAHC was 4. When the reaction mixture was stirred for 1 hr at room temperature, a colloidal suspension was formed. The temperature was then changed to 353 K. After 1 week at 353 K, the solution became a purple precipitate with a colorless transparent liquid layer. The particles were separated by centrifugation. After washing with 2-propanol and successive centrifugation, the CeO_2 powders were dried by both freeze-drying and vacuum drying. The obtained powder was calcined in air at 673 K for 4 hrs.

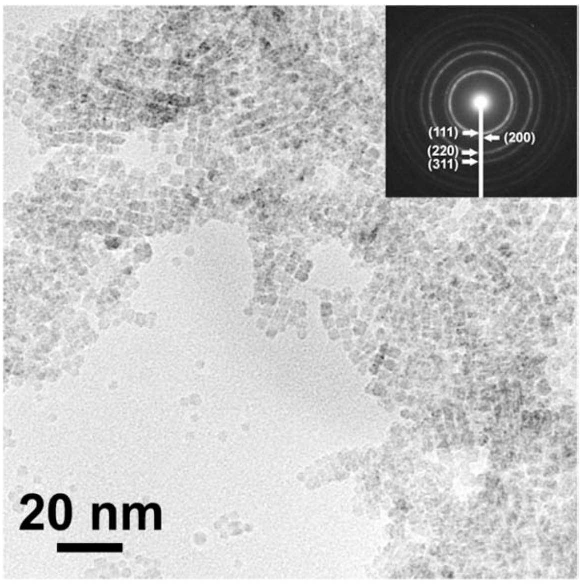

Figure 1 Low-magnification TEM images of the freeze-dried CeO_2 nanoparticles prepared at 353 K for 1 week. Inset: SAED pattern of CeO_2 nanoparticles with cubic structure shown in TEM.

---

*Author to whom all correspondence should be addressed.

0022–2461

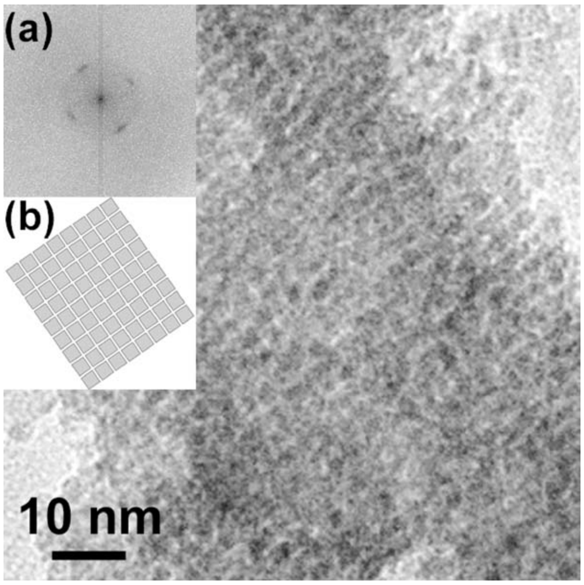

Figure 2 TEM image of CeO_2 nanocrystals self-assembled into a superlattice-like arrangement with dimensions of the order of nanoscale, Inset a: the FFT pattern confirms the orientational order of the superlattice-like structure. Inset b: the model structure demonstrates the superlattice-like assembled CeO_2 nanoparticles.

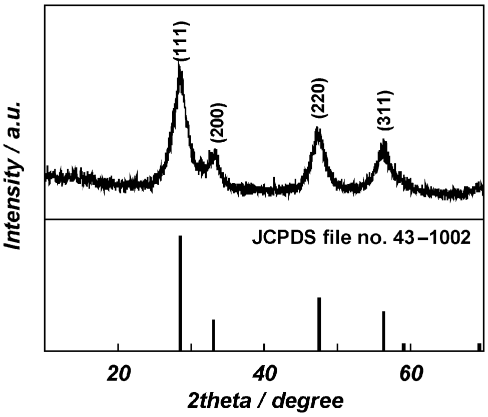

Figure 3 XRD pattern of the freeze-dried CeO_2 nanoparticles shown in Fig. 1.

Fig. 1 shows low magnification TEM (Jeol JEM-200CX operated at 200 kV) images of the freeze-dried CeO_2 nanoparticles with cubic structure prepared at 353 K for 1 week. It is evident from this figure that the particle shape was square, and the particle size was calculated to be 2.7–3.8 nm. Furthermore, it seems that the particles were aligned. TEM images of Fig. 1 clearly showed the mono-dispersed CeO_2 nanoparticles. Inset shows the selected area electron diffraction (SAED) pattern and Debye-Sherrer rings of the nanoparticles. They can be consistently indexed as those of cerium oxide with the cubic fluorite structure. The high-resolution TEM (HRTEM) images and fast Fourier transfer (FFT) pattern of the same products are carried out. The HRTEM image of CeO_2 cubic nanoparticles shows the single crystalline structure, because the lattice images are observed for many particles. The main lattice spacing of the crystalline structure was calculated to be 3.11 Å by FFT analysis. This lattice spacing corresponds to the (111) planes of CeO_2 with cubic phase, which coincides with SAED analysis.

Fig. 2 shows a TEM image obtained from the freeze-dried CeO_2 nanoparticles. The particles were seen to be organized in an ordered structure (2D or 3D superlattice-like structure). Fig. 2 shows an array of cubic nanocrystals with a mean interparticle (center-to-center) distance of 2.9 nm, determined from direct imaging and FFT pattern. We think that this assembly with ordered structure is formed to minimize the total surface energy, which is attained by association of cubic CeO_2 with face-to face-structure.

Fig. 3 shows the X-ray diffraction (XRD, Rigaku RAD-IIC using Cu K_α radiation at 35 kV, 20 mA) patterns of freeze-dried CeO_2 nanoparticles. All of the peaks can be indexed to a pure cubic phase [space group: $Fm3m$ (225)] of fluorite CeO_2 with lattice constants $a = 5.411$ Å (JCPDS file no. 43-1002), corresponding to the results of SAED analysis. XRD patterns of the freeze-dried CeO_2 nanoparticles show broad peaks, which confirmed the formation of small size nanoparticles. The particle size obtained from the Scherrer equation using X-ray line-broadening of the (111) peak is 3.6 nm, which agrees with the TEM results.

We also prepared rod-like CeO_2 structures by calcination at 673 K. Low magnification TEM images of the rod-like CeO_2 with diameters of 20–50 nm and lengths of 100–200 nm are shown in Fig. 4a, although

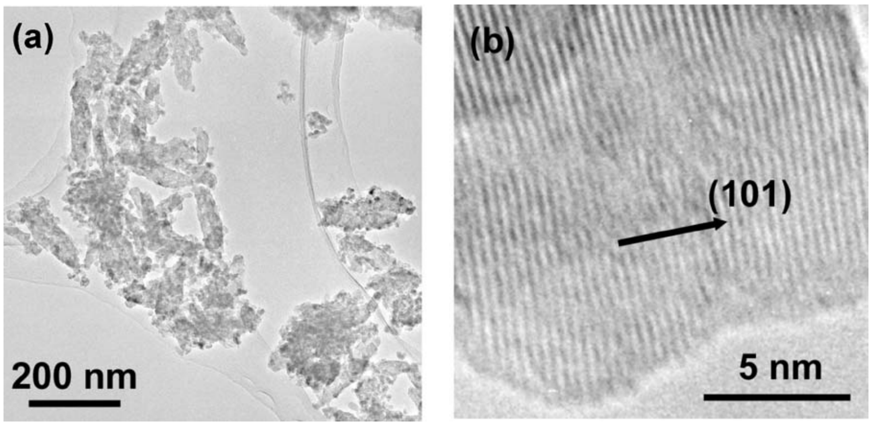

Figure 4 (a) TEM images of CeO_2 calcined at 673 K for 4 hrs. Original CeO_2 particles before calcination were prepared by the same method described for Fig. 1. (b) HRTEM image of rod-like CeO_2 with clear lattice image of (111) planes ($d = 3.11$ Å).

the majority of CeO_2 samples were assembled into the aggregates. The HRTEM image in Fig. 4b with the clear lattice images of spacing $d_{111} = 3.11$ Å show that the principal axis of the crystal growth of CeO_2 was aligned along the rod axis.

In our systems using LAHC and CTIP modified with ACA, the resulting suspensions of CeO_2 nanoparticles were exceptionally mono-disperse without aggregate, showing the high power of LAHC as a colloidal stabilizer through adsorption on the surface of CeO_2 nanoparticles. Since the adsorption of LAHC takes place to a specific crystal face, anisotropic structures such as cubes would be formed.

In summary, we have reported the selective synthesis of cubic CeO_2 nanoparticles by an alkoxide-primary amine surfactant method in a solution system at the near room temperature of 353 K. The prepared CeO_2 cubic nanoparticles had diameters of 2.7–3.8 nm, characteristics of a mono-dispersed and highly crystalline structure, and the CeO_2 calcined at 673 K using freeze-dried CeO_2 and formed a rod-like structure with diameters of 20–50 nm and lengths of 100–200 nm.

Acknowledgments

The authors are thankful to Professor S. Isoda (the Institute for Chemical Research, Kyoto University) for his assistance with TEM experiments. We also express our thanks to Hokko Chemical Industry, Co., Ltd., for the donation of cerium alkoxides.

References

1. V. L. COLVIN, M. C. SCHLAMP and A. P. ALIVISATOS, *Nature* **370** (1994) 354.
2. M. S. FUHRER *et al*., *Science* **288** (2000) 494.
3. C. A. MORRIS, M. L. ANDERSON, R. M. STROUD, C. I. MERZBACHER and D. R. ROLISON, *ibid.* **284** (1999) 622.
4. C. B. MURRAY, D. J. NORRIS and M. G. BAWENDI, *J. Amer. Chem. Soc.* **115** (1993) 8706.
5. Y. Y. YU, S. CHANG, C. J. LEE and C. R. C. WANG, *J. Phys. Chem.* B **101** (1997) 6661.
6. X. G. PENG *et al*., *Nature* **404** (2000) 59.
7. T. MASUI, M. YAMAMOTO, T. SAKATA, H. MORI and G. ADACHI, *J. Mater. Chem.* **10** (2000) 353.
8. H. INABA and H. TAGAWA, *Solid State Ion.* **83** (1996) 1.
9. E. BEKYAROVA, P. FORNASIERO, J. KASPAR and M. GRAZIANI, *Catal. Today* **45** (1998) 179.
10. W. H. WEBER, K. C. HASS and J. R. MCBRIDE, *Phys. Rev.* B **50** (1993) 13297.
11. S. TSUNEKAWA, T. FUKUDA and A. KASUYA, *J. Appl. Phys.* **87** (2000) 1318.
12. J.-G. LI, T. IKEGAMI, J.-H. LEE and T. MORI, *Acta Mater.* **49** (2001) 419.
13. T. MASUI, H. HIRAI, N. IMANAKA and G. ADACHI, *J. Mater. Sci. Lett.* **21** (2002) 489.

Received 24 February
and accepted 3 June 2004