

Direct synthesis and structure characterization of ultrafine CeO₂ nanoparticles

Chenguo Hu^{1,2,4}, Zuwei Zhang¹, Hong Liu^{2,3}, Puxian Gao² and Zhong Lin Wang^{2,4}

¹ Department of Applied Physics, Chongqing University, Chongqing 400044, People's Republic of China

² School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

³ State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

E-mail: hucg@cqu.edu.cn and zhong.wang@mse.gatech.edu

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Abstract

A new method to directly synthesize single-crystalline CeO₂ nanoparticles has been developed. The advantages of the method are rapid synthesis, at normal atmosphere, 100% productive ratio and low cost, with a great potential for scale-up. X-ray diffraction (XRD) spectra showed unusual peak width versus particle size, compared with Scherrer equation predictions. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), electron diffraction and ultraviolet (UV) absorption were used to examine the particle size and microstructure to find out the cause. As a result, ultrafine particles with a size less than 6 nm were found to be self-assembled into a 'coherent interface', so that a large group of particles behave like a large single particle in XRD.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Cerium oxide has been attracting great interest because of its effective technological applications, such as in solid-state electrolytes for electrochemical devices [1, 2], catalysts for three-way automobile exhaust systems [3, 4], abrasives for chemical-mechanical planarization [5], sunscreens for ultraviolet absorbents [6], the adsorption and reaction of formaldehyde [7], oxygen storage capacity [8], hybrid solar cells [9], H₂S removal [10] and luminescent materials for violet/blue fluorescence [11]. Present interest lies in the fabrication of nanometre-sized cerium oxide and in the exploration of the corresponding size-induced property changes, such as lattice expansion [12], phase transformation [13], and the blue-shift of absorption spectra [14].

Crystalline ceria nanoparticles have been synthesized by means of a variety of methods, including room-

temperature solution precipitation [15], sonochemical synthesis [16], hydrothermal crystallization [17], microemulsion [18], mechanochemical processing [19], thermal decomposition [20], spray pyrolysis [5, 21], sol-gel method [22], thermal hydrolysis [23], and solvothermal synthesis [24]. These techniques rely mainly on high pressure, or salt-solvent mediated high temperature, or surface capping agent, and the sizes of ceria particles are relatively large. Therefore, seeking a simple approach for low-cost, lower-temperature, large-scale, controlled growth of ceria nanostructures at atmospheric pressure is essential.

We have developed an approach for the synthesis of ultrafine single-crystal ceria nanoparticles that has the advantages of being a simple process, easy to scale-up and of low cost. The result gives a demonstration that the composite-hydroxide-mediated (CHM) approach [25, 26] not only can synthesize complex oxide nanostructures, but also can produce single oxide nanostructures at 165 °C under normal atmosphere

⁴ Authors to whom any correspondence should be addressed.

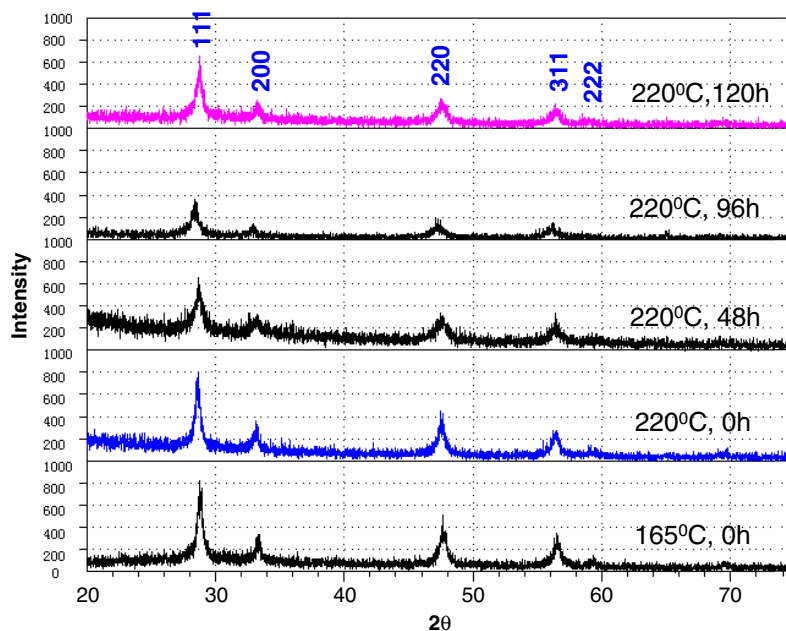


Figure 1. XRD spectra of the CeO₂ nanoparticles.

pressure. The resulting particles were characterized by HRTEM, electronic diffraction and UV–vis spectra. Unusual XRD peak width versus particle size against Scherrer equation was found as the result of perfect assembly of nanoparticles into a ‘coherent interface’.

2. Experimental details

Ultrafine CeO₂ particles were synthesized by the CHM approach [25, 26]. An amount of 20 g of mixed hydroxides (NaOH:KOH = 51.5:48.5) was placed in a 25 ml covered Teflon vessel. The vessel was put in a furnace, which was preheated to 165–220 °C. After the hydroxides became totally molten, 0.1 g Ce(NO₃)₃ was added. After reacting for 0–120 h, the vessel was taken out and cooled down to room temperature. The value 0 h means that the vessel was not put back into the furnace after adding the cerium source material, and the reaction happened instantly, accompanied by a white colour gas coming out of the vessel. The solid product was dissolved in deionized water. The product was filtered and washed in deionized water to remove the hydroxide on the surface of the particles.

The products were characterized on a Philips x-ray diffractometer. SEM images of the samples were obtained in a field emission scanning electron microscopy (FE-SEM LEO 1530). TEM images and electron diffraction pictures were recorded on high-resolution transmission electron microscope (Hitachi HF-2000). UV–vis spectrum was recorded using a UV–vis spectrophotometer (W6-Z-8).

3. Results and discussion

The productive ratio is defined as the ratio of the weight of CeO₂ produced to the weight of the theoretical calculated value from the source material. In order to find the optimization productive ratio and investigate the size change under different

conditions, we have systematically done experiments at temperatures of 165, 200, 220 °C and with growth times of 0, 1, 12, 24, 48, 72, 96, 120 h, respectively. We find that the productive ratio is 100% and is independent of growth time and temperature if we neglect the small loss during the washing process.

Figure 1 shows the XRD patterns of the as-synthesized ceria nanoparticles. All peaks in the XRD spectra were perfectly indexed as the pure cubic phase ($Fm\bar{3}m$, JCPDS-34-0394) of CeO₂ with lattice constant $a = 5.411 \text{ \AA}$. Here, we notice that the XRD patterns in the 2θ range from 25° to 60° show that samples prepared at higher temperatures or for longer time exhibit broadened peaks with a little shift toward smaller angles, except those for samples synthesized at 220 °C for 120 h (we will discuss this later). Based on the Scherrer equation, the crystallite size of a sample is inversely proportional to the full-width-half-maximum (FWHM), indicating that a broader peak represents smaller crystallite size. But some authors’ work [15, 28] has reported that the particle size might be smaller for samples grown at a lower temperature or for less time.

To examine the real particle size, the samples were systematically analysed by SEM, TEM and HRTEM. A few typical images chosen from a large number of SEM and TEM images are displayed in figures 2 and 3. Figure 2 shows the SEM and TEM images of the as-synthesized samples. Figure 2(a) shows the TEM image of the sample synthesized at 165 °C for a very short time and at the lowest temperature, displaying a particle size of 1–3 nm and strong agglomeration. Groups of ultrafine particles assemble into bigger particles with size up to 200 nm, illustrated by the SEM image of inset figure 2(a). The sample synthesized at 190 °C for 48 h, i.e., at a higher temperature and for a longer time, exhibits particles of size 3–6 nm with a polygonal shape; the particles tend to share common faces in order to maximize the packing density, as is shown in figure 2(b). And still groups of particles

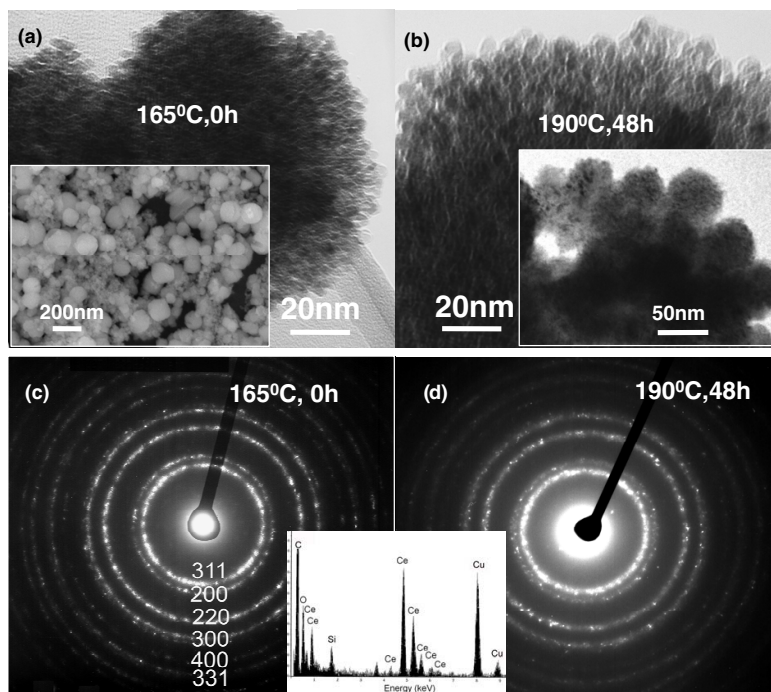


Figure 2. Typical SEM and TEM characterization of the CeO₂ nanoparticles. TEM images (a) and SEM image inset (a) for ceria synthesized at 165 °C for 0 h. TEM image (b) and inset (b) for ceria synthesized at 190 °C for 48 h. The electron diffraction pattern for ceria synthesized at (c) 165 °C for 0 h and (d) 190 °C for 48 h. The EDS of as-produced CeO₂ nanoparticles is shown as an inset between (c) and (d).

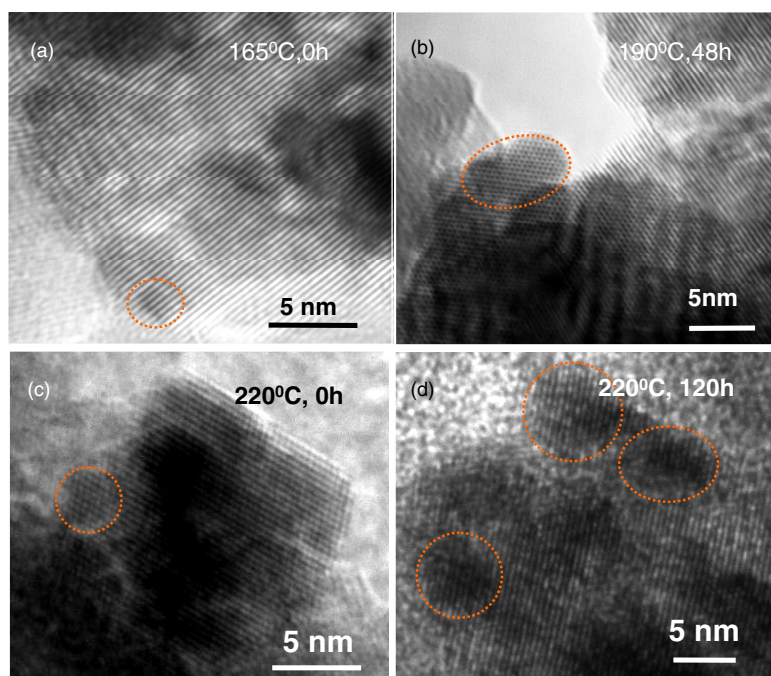


Figure 3. Typical HRTEM images of CeO₂ particles synthesized under different conditions of growth temperature and time.

assemble into bigger particles with size up to 50 nm (inset figure 2(b)). Figures 2(c), (d) show the electron diffraction patterns of these two samples, indicating the typical CeO₂ structure with CaF₂ lattice; the pattern rings for the sample synthesized at 165 °C for a very short time is narrower in comparison to those from the sample synthesized at 190 °C for

48 h, which agrees with the XRD results in figure 1. The EDS showed correct composition of the ceria nanoparticles (inset between figures 2(c) and (d)). The element Si comes from the TEM grid.

Figure 3 shows typical high-resolution TEM images to further show the details of the nanoparticles. Figures 3(a)–(d)

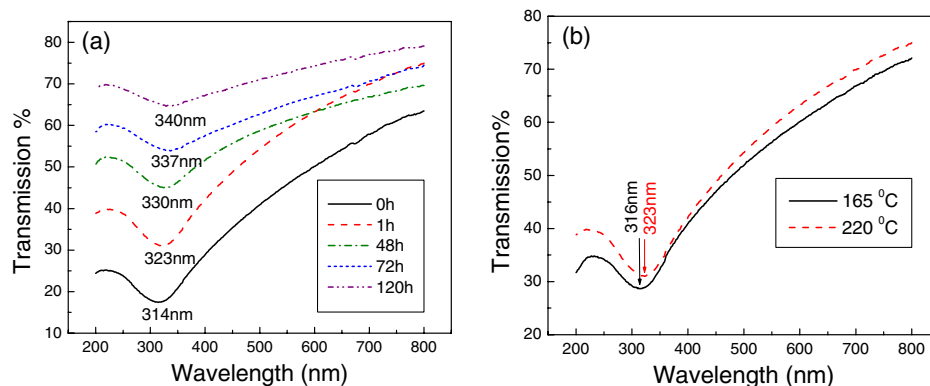


Figure 4. (a) UV-vis transmission spectra of CeO₂ synthesized at 220 °C for 0, 1, 48, 72 and 120 h and (b) at 165 °C, 220 °C for 1 h. The concentration of CeO₂ is 0.05 g l⁻¹.

show that the particle sizes for samples synthesized at 165 °C for 0 h, 190 °C for 48 h, 220 °C for 0 h, and 220 °C for 120 h are 2–3 nm, 5–7 nm, 2–4 nm and 6–8 nm, respectively. The strong assembly of the nanoparticles can be observed especially from figures 2(a)–(c). The ordered lattice over a relatively large area is the result of ultrafine particles with face-to-face contact and coherent interfacial matching [27]. The particles synthesized by the CHM method have a clean surface and there is no passivation. Thus, the lattices from the particles tend to align when they are in contact. The shape of the particles is polygonal, which is expected because the synthesis temperature is low and there is not enough energy for the particle to achieve an equilibrium shape [27], as is usually apparent in spray pyrolysis under high temperature [5]. The irregularly shape and the ultrafine particle size favours the formation of larger spherical particles to further reduce the surface energy.

UV-vis spectroscopy experiments were carried out by dispersing ceria particles in ethanol to further study the particle size. Figure 4(a) shows the UV-vis transmission spectra of CeO₂ synthesized at 220 °C for 0, 1, 48, 72 and 120 h at a concentration of 0.05 g l⁻¹, illustrating a strong UV absorption peak and a peak blue-shift (from 340 to 314 nm) with reduction of the growth time. This indicates that the particle size is smaller for short time growth [28]. The intensity of the absorption peak decreases on increasing the particle size, meaning that particles with smaller particle size exhibit better UV absorption behaviour. The smaller particle size obtained at lower temperature is demonstrated by a blue-shift in figure 4(b). These results also agree with the TEM observations in figures 2 and 3.

Figure 5 shows that the particle size changes with growth time at a temperature of 165 and 220 °C, indicating the rapid growth of particle size in the first 1 h. After 1 h, the growth speed slows down and the size increases almost linearly from 24 to 120 h. Table 1 presents the detailed information of UV transmission, particle size and peak blue-shift for the samples grown at 220 °C for different growth times.

From the comprehensive analysis of XRD spectrum, SEM and TEM image analysis and UV-vis spectrum, the unusual XRD peak width versus particle size compared with Scherrer equation predictions can be explained. Agglomeration of nanoparticles is a very common phenomenon that occurs

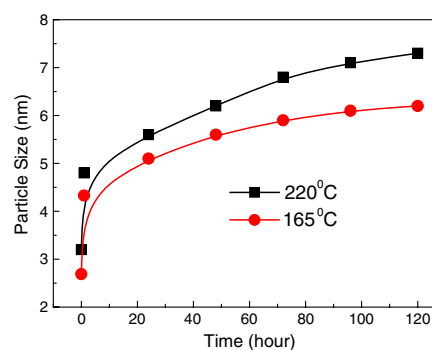


Figure 5. The CeO₂ particle size plots versus growth time.

Table 1. Growth time, UV transmission peak wavelength and intensity for CeO₂ synthesized at 220 °C and a CeO₂ concentration of 0.05 g l⁻¹.

Time (h)	Wavelength (nm)	Particle size (nm)	Transmission (%)
0	314	~3.2	17.4
1	323	~4.8	31.0
48	331	~6.2	45.0
72	337	~6.8	53.9
120	339	~7.3	64.7

because the nanoparticles tend to decrease the exposed surface in order to lower the surface energy, and the smaller particle size results in stronger agglomeration. Ceria nanoparticles have a special property which causes agglomeration by minimizing the interface energy with the formation of a lattice-matched ‘coherent interface’ [27], especially for the smaller particles of size less than 6 nm. The coherent interface results in an ordered lattice array, which causes the unusual XRD peak width versus particle size against Scherrer equation. But when the particle size becomes bigger than 6–7 nm, the XRD peak width becomes normal, as is shown in figure 1 for the sample grown at 220 °C for 120 h, due to the bigger particle size having better dispersion, which is demonstrated by the high-resolution image in figure 3(d). However, monodispersed nanoparticles in ethanol are prevented from agglomerating, displaying the normal quantum size effect of a UV absorption peak blue-shift.

4. Conclusions

Ultrafine ceria nanoparticles have been successfully synthesized by a composite-hydroxide-mediated approach, which can be further expanded to the preparation of new types of single oxide nanostructure. The ceria particle size increases with increasing growth temperature or time. The ceria particles with size less than 6 nm display a very strong agglomeration to minimize the interface energy by the formation of a lattice-matched 'coherent interface'. Such a coherent interface causes an unusual XRD peak width versus crystallite size against the Scherrer equation. The advantages of the method, rapid synthesis, in a normal atmosphere, with 100% productive ratio and at low cost, give a potential avenue for further practical scale-up of the production process and applications.

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