

Cerium oxide nanoparticles: Size-selective formation and structure analysis

Feng Zhang, Siu-Wai Chan,^{a)} Jonathan E. Spanier, Ebru Apak, Qiang Jin, Richard D. Robinson, and Irving P. Herman

Department of Applied Physics and Applied Mathematics, and Materials Research Science and Engineering Center, Columbia University, New York, New York 10027

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Nanoparticles of cerium oxide with a narrow size distribution ($\pm 15\%$) are prepared by mixing cerium nitrate solution with an ammonium reagent. High-resolution transmission electron microscopy (TEM) indicates that over 99% of the synthesized particles are single crystals. TEM and photon absorption are used to monitor particle size. The lattice parameter increases up to 0.45% as the particle size decreases to 6 nm, as observed with x-ray diffraction. Raman spectra also suggest the particle-size effect and concomitant lattice expansion. The lattice expansion can be explained by increased concentrations of point defects with decreasing particle size. © 2002 American Institute of Physics. [DOI: 10.1063/1.1430502]

Cerium oxide has been widely investigated because of its multiple applications, such as a catalyst, an electrolyte material of solid oxide fuel cells, a material of high refractive index, and an insulating layer on silicon substrates.^{1–4} Ultrafine CeO₂ powder has been prepared and used to decrease the sintering temperature from 1500 °C to 1200 °C.⁵ The electrical conductivity of multidispersed nanoceria prepared by a vacuum technique has been investigated.⁶ Most of these preparations do not yield a significant amount of nanoparticles with narrow size distribution. The difficulties involved in obtaining a significant quantity of monodispersed ceria nanoparticles have prevented the investigation of the size-dependent structural properties of these particles. The preparation method reported here produces large quantities of ceria nanoparticles with a relatively narrow size distribution.

The change in lattice constant with decreasing nanoparticle size is an important issue that is not fully understood.⁷ Tsunekawa *et al.* reported lattice expansions with decreasing particle size in three sets of nanosized CeO₂ particles.⁸ The results were from conventional electron diffraction performed in a transmission electron microscope (TEM). Usually TEM diffraction patterns can not provide the accuracy required of lattice parameter measurements, which need to be better than 0.5%. More definitive measurements of this changing lattice constant are presented here using x-ray diffraction.

In this letter, we prepare ceria nano-particles of narrow size distribution by mixing equal volumes of solutions of 0.0375 M Ce(NO₃)₃ and 0.5 M hexamethylenetetramine at room temperature.⁹ By controlling the reaction time, batches of particles with sizes in the range of 3–12 nm are obtained (Fig. 1). Larger particles are made by sintering at 400 °C–800 °C for 30 min. By measuring over 100 with TEM, the full width at half maximum (FWHM) of the size distribution peak of each batch is found to be less than $\pm 15\%$ of the median size. By checking lattice images of

more than 50 of the synthesized ceria nanoparticles, we find all particles are single crystals with few stacking faults and twin boundaries, suggesting that the CeO₂ particles are near perfect single crystals. In particles shown in Fig. 2, sets of {111} planes are imaged from octahedral particles with the electron beam parallel to their <110> edges. Particle size is also monitored by ultraviolet absorption in solution sampled during growth (Fig. 3).¹⁰ There is good agreement of particle size given in Fig. 1 with that obtained using the band gaps in Fig. 3 when a bulk ceria gap of 3.15 eV is used along with electron and hole effective masses of $\sim 0.42 m_e$ for the confinement energy.

Ceria, of cubic fluorite structure, gives isolated peaks in x-ray diffraction. By plotting the lattice parameter calculated from each (*hkl*) reflection against $\cos^2 \theta$, we obtain the lattice parameter with an accuracy of 0.005%.¹¹ All the x-ray diffraction experiments are performed using a Scintag X₂ diffractometer using the Cu *K* α line with scan rate of 0.025°/step and 5 s/step. Five peaks are selected with 2θ ranging from 80° to 140°. A comparison of x-ray spectra from nanosized and micron-sized ceria shows a peak shift towards lower angles and peak broadening in nanoparticle ceria (see Fig. 4). Particle sizes (*d*) are also determined from x-ray results using the Scherrer equation, *d*

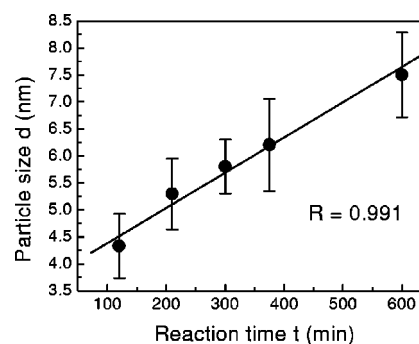


FIG. 1. In the time range shown, the average particle size as measured by TEM increases linearly with reaction time. Longer reaction times and sintering produce even larger particles. *R* is the linear regression factor.

^{a)} Author to whom all correspondence should be addressed; electronic mail: sc174@columbia.edu

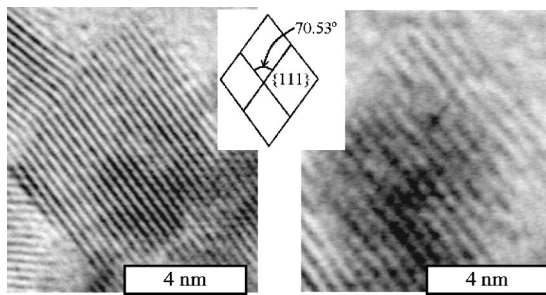


FIG. 2. High-resolution TEM images of octahedral nanoparticles showing sets of $\{111\}$ planes and surfaces. The beam direction is $\langle 110 \rangle$.

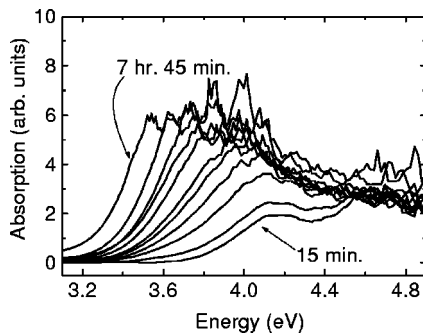


FIG. 3. Absorption at different stage of synthesis, showing a monotonic decrease in bandgap with time due to particle growth.

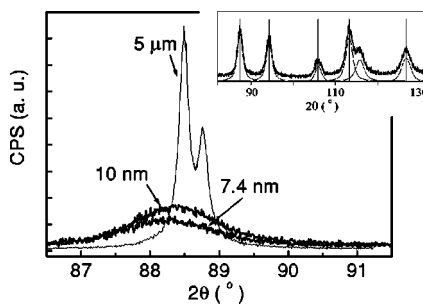


FIG. 4. X-ray spectra showing peak shift and peak broadening of 7.4 and 10 nm CeO_2 nanoparticles, compared with micron size particles (~ 5 micron). The small figure in the upper right-hand side corner shows the linewidth and lineshape fit of an x-ray diffraction pattern of 10 nm particles.

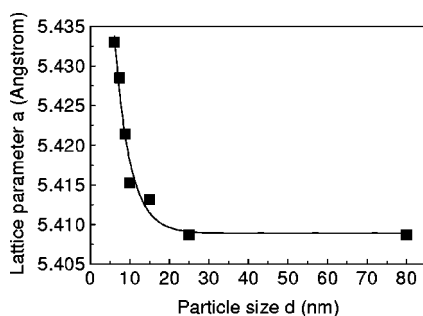


FIG. 5. Lattice parameter increases with decreasing particle size when the particle size is smaller than 20 nm.

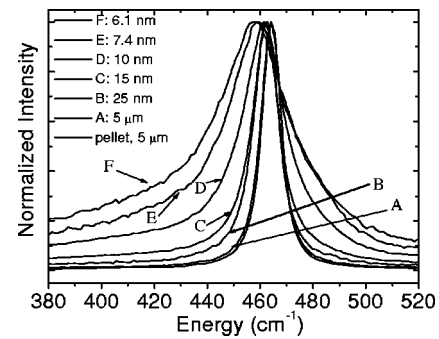


FIG. 6. Raman spectra of 464 cm^{-1} peaks, showing peak shifts to lower energy and peak asymmetric broadening with decreasing particle size.

$=0.941\lambda/B \cos \theta_B$. Accordingly, λ is the wavelength, B is the FWHM of the Bragg peak corrected using the corresponding peak in micron-sized powder, and θ_B is the Bragg angle. The particle sizes obtained from x-ray diffraction agree with the TEM results. The peak profiles are fitted with the pseudo-Voigt function.¹² The results, which are checked with Celref software,¹³ are shown in Fig. 5. Compared with micron-size CeO_2 particles (Alfa, ~ 5 micron), the lattice parameter of 6.1 nm particles increases from 5.4087 \AA (bulk) to 5.4330 \AA , i.e., by 0.45%. From high-resolution TEM results, this lattice constant change is not caused by defects such as disclinations in multiple-twinned particles or volume expansion in high angle boundaries.

Unpolarized Raman scattering is collected in the back-scattering configuration at room temperature with a 488 nm Ar-ion laser line. The peak at 464 cm^{-1} shifts to lower energy and broadens with decreasing particle size (Fig. 6). The lattice expansion with decreasing particles size largely explains this systematic change of the Raman peak, which concurs with the x-ray results. A quantitative analysis of the contributions of phonon confinement and decay, lattice strain, size dispersion, and the presence of vacancies on the Raman lineshape and width is presented elsewhere.¹⁴

The reason for lattice expansion in small particles ($d < 20 \text{ nm}$) is considered. Assuming electrostatic charge neutrality, we need two Ce^{3+} ions (given the previous x-ray photoemission spectroscopy detection of Ce^{3+} ions in ceria nanoparticles)⁸ on the two original Ce^{4+} sites for each oxygen vacancy created. Assuming that the lattice expansion is from the increased oxygen vacancies and Ce^{3+} ions with decreasing particle size, we use Ref. 15 for the increase of the CeO_2 lattice parameter per cation concentration with increasing trivalent cation radius. With the Ce^{3+} radius of 0.1143 nm for 6 nm particles, the corresponding concentrations of oxygen vacancies ($V_{\text{O}}^{\cdot\cdot}$) $y=0.047(\text{CeO}_{2-y})$ and $[\text{Ce}^{3+}]/([\text{Ce}^{4+}]+[\text{Ce}^{3+}])=0.094$ are calculated for the lattice parameter of 5.4330 \AA . Quantitative measurements of $V_{\text{O}}^{\cdot\cdot}$, Ce^{4+} , and/or Ce^{3+} concentrations will determine if there are other factors, such as surface stress and other factors affect the lattice expansion.⁷ A detailed study of point defect concentrations with different oxygenation processes will be presented elsewhere.

Ceria has been used as a solid electrolyte in fuel cells. The larger lattice parameter in nanocrystalline ceria implies the migration enthalpy of an oxygen vacancy is smaller, resulting in a higher ionic conductivity and more efficient fuel

cells.¹ The systematic increase in lattice parameter with decreasing particle size provides specific control of the surface oxygen spacing and will impact ceria catalysis of the water-gas shift and three-way auto exhaust clean-up reactions.³

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