Synthesis and Characterization of CeO2 Nanoparticles

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ABSTRACT

Nanoceria was produced by an aqueous precipitation technique in the presence of an organic stabilizer. The stable suspensions were diafiltered to remove reaction byproducts. Particles were characterized by transmission electron microscopy (TEM) with images used to size the particles and selected-area electron diffraction used to determine the lattice structure and the lattice constant. For all particles studied the electron diffraction data was consistent with that of CeO_2, not Ce_2O_3 as predicted by some researchers for very small particles sizes. At particle diameters ~1 nm the lattice expansion approached 7%. In agreement with earlier workers, we interpret this effect as due to the formation of substantial amounts of Ce^{3+} with corresponding oxygen vacancies, but within the fluorite lattice structure of CeO_2.

INTRODUCTION

Nanocrystalline CeO_2 (nanoceria) has many real and potential applications. It is an important component in three-way automotive catalysts and is used in solid oxide fuel cells. Its reactivity is connected to its redox chemistry involving the facile Ce^{4+}/Ce^{3+} electrochemistry. This allows nanoceria to store oxygen under oxidizing conditions (Ce^{4+}) and to release oxygen under reducing conditions (O vacancies are created, leading to the formation of Ce^{3+}).

Many techniques for synthesis have been used to produce nanoceria, such as chemical precipitation, hydrothermal, alchothermal, and thermal evaporation. Most wet methods produce an unstable suspension of the nanoparticles, leading to agglomeration. For some potential applications it would be desirable to produce a stable suspension. We have devised such a process based on aqueous precipitation in the presence of an organic stabilizer in which particles with diameter 1 to 4 nm are stable. Reaction byproducts can be removed by diafiltration, after which the particles can be shifted into a nonaqueous solvent by dialysis and further drying over a molecular sieve.

Of primary concern in the present study is the composition of our particles at very small sizes. Because of the ease of O removal and addition, the formula for ceria is often written as CeO_{2-x}, where x ranges from 0 to 0.5 depending on conditions of preparation and treatment of the nanoparticles. Earlier work by Tsunekawa and coworkers suggested that x = 0.5 for particles of ~1.5 nm diameter and smaller, and that the lattice was that of cubic form of Ce_2O_3, the fully reduced form of ceria.[1] A value of x = 0.5 was later confirmed by Wu and coworkers for particles ~3 nm diameter, but their electron diffraction data was consistent with the fluorite lattice expected for CeO_2.[2]

In the present work we have studied particles as small as 1.1 nm mean diameter and have found no evidence of a cubic Ce_2O_3 lattice. Remarkably, at this size the electron diffraction data indicate that the lattice is that of CeO_2. Because of the relatively large increase in the lattice constant at this small size, the particles are characterized by substantial amounts of Ce^{3+} and corresponding O vacancies.

EXPERIMENTAL

Aqueous solutions of organic stabilizer and $Ce(NO_3)_3 \cdot H_2O$ were added to a water-jacketed reaction vessel. Next, an H_2O_2 solution was added and the vessel was mixed with a high-speed shearing mixer. Aqueous NH_4OH was added under high-speed mixing, after which a prop stirrer was used. The reactor temperature was raised to 70 C over 25 min, and then held at 70 C for 70 min. The reaction vessel was cooled to room temperature and then diafiltered to an ionic conductivity of 3 mS/cm^2 or less.

Particle formation proceeds through a $Ce(OH)_3$ intermediate phase, followed by oxidation to CeO_2 by H_2O_2, probably in the form of OH radicals. For 1.1 nm particles a stabilizer combination of EDTA and lactic acid was used, whereas 2 nm particles were stabilized by methoxyethoxyethoxy acetic acid. The largest particles studied (11.8 nm) were prepared by the method of Chen and Chang.[3] In this case no stabilizer was used and the particles were not diafiltered.

Specimens for TEM examination were prepared from the diafiltered aqueous suspension by a suitable dilution in 0.02 M solution of an organic stabilizer. A 10 microliter drop was placed on a carbon-film-covered copper grid and allowed to air dry. Images and selected-area diffraction patterns were obtained in either a JEOL 2000FX or 100CX TEM. Image magnification was calibrated using phase-contrast images of asbestos fibers.

Particle sizing was done with Image J. First the images were histogram equalized to improve their contrast. Then they were thresholded to give a binary image with the threshold adjusted to give the same particle size as in the original image. Next, areas were determined for 100 to 200 particles and from these the number-averaged diameter was calculated, assuming spherical morphology. For electron diffraction the camera length was calibrated using a TlCl microcrystal standard. The radii of diffraction rings were determined using the radial profile plug-in in Image J.

RESULTS

Figure 1 shows the images and selected-area diffraction patterns for four different nanoparticle suspensions. The mean number-averaged diameter and lattice constant obtained from the electron diffraction data are given in Table 1. The diffraction pattern for all nanoparticles is consistent with that of the fluorite lattice structure of CeO_2, and not with the cubic structure expected for Ce_2O_3.

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Table 1. Mean diameter and lattice constant.

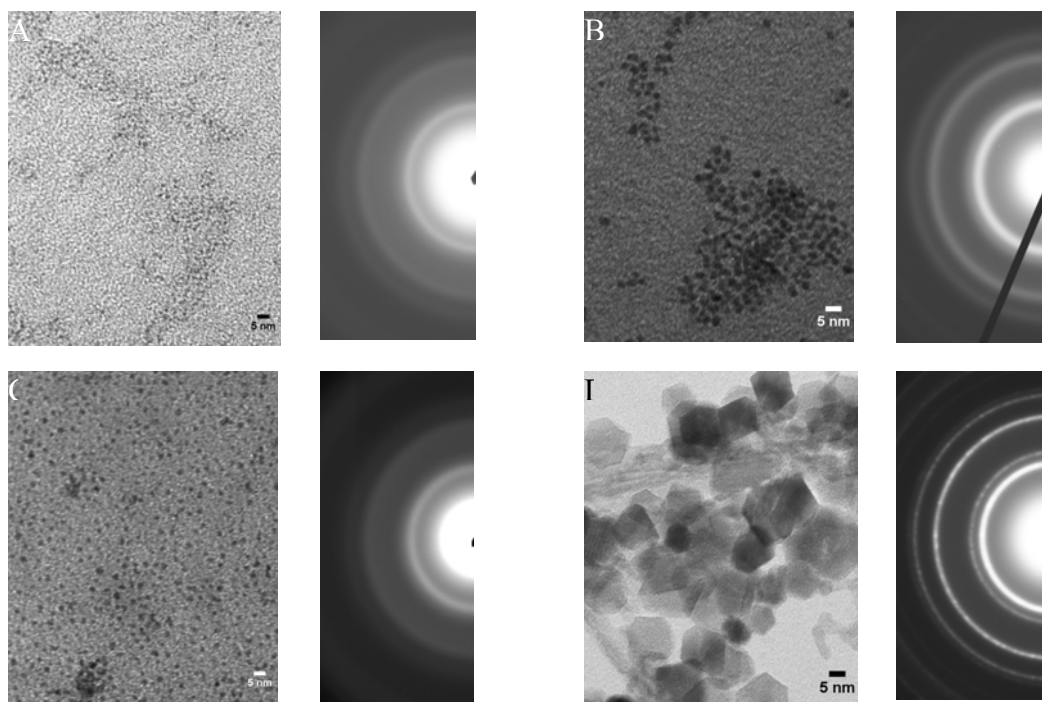| Mean diameter, nm	Lattice constant, nm
1.1 ± 0.3	0.578
2 ± 0.5	0.555
2 ± 0.5	0.555
11.8 ± 1.2	0.547
bulk	0.541

Fig. 1. TEM images and electron diffraction patterns for four nanoparticle preparations. A, 1.1 nm diameter; B, 2 nm diameter; C, 2 nm diameter (showing reproducibility); D, 11.8 nm diameter. All scale bars are 5 nm.

A plot of lattice constant vs particle diameter and the degree of lattice expansion vs particle diameter are shown in Fig. 2. The expansion of the lattice plotted in Fig. 2A follows the empirical equation

$$a = a_{bulk} + 0.036 / D$$

where a is the lattice constant of the nanoparticle suspension, a_{bulk} is the lattice constant of bulk CeO_2, and D is the particle mean diameter. Figure 2B shows that the lattice expansion approaches 7% at approximately 1 nm diameter, yet Fig. 1A shows that the fluorite lattice persists even at this small size.
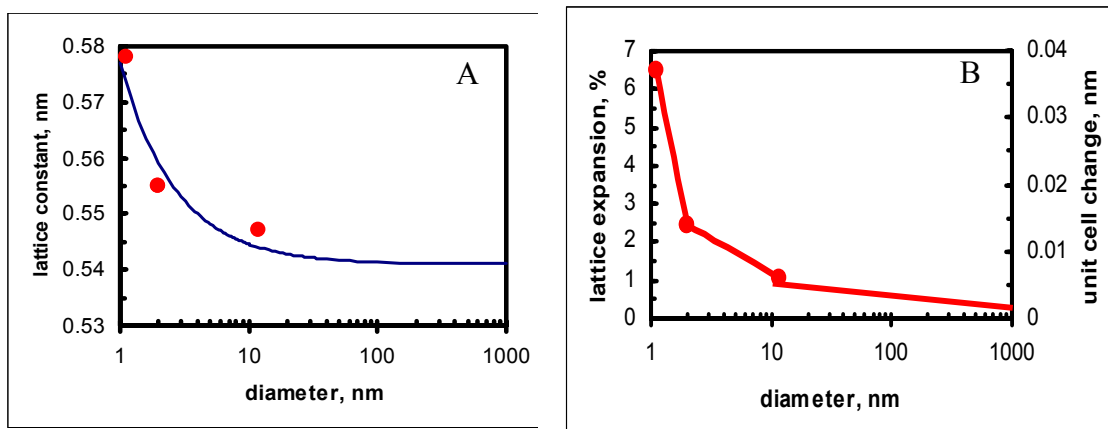
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Fig. 2. A, Lattice constant vs particle mean diameter. Curve is defined by the equation given in the text. B, Lattice expansion vs particle mean diameter.

DISCUSSION

Our results extend those of Wu and coworkers to smaller particle sizes. Wu and coworkers studied particles as small as 3 nm diameter, finding no evidence for the cubic form of ceria, Ce_2O_3.[2] But the work of Tsunekawa suggests that at this size we should not expect to see Ce_2O_3; rather, it should be observed at ~1.5 nm and smaller. We have now extended the size range down to ~1 nm, but still find no evidence of the cubic form of Ce_2O_3. Because of our smaller particle size compared to all known previous work, our lattice expansion of almost 7% is the highest seen for nanoceria.

Using a simple cubic lattice model for our particles, at ~1 nm the particle consists of eight unit cells in which ~80% of the cerium ions are at the surface of the particle. In agreement with many earlier studies, we suggest that the vast majority of these surface ions are Ce^{3+} and there is a corresponding large number of oxygen vacancies (one for each pair of Ce^{3+} formed). The larger radius of Ce^{3+} vs Ce^{4+} would explain the larger lattice constant observed at small sizes. Likewise, our lattice constant data are approximately consistent with an empirical equation, and this equation is consistent with similar versions found in the literature.

References

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