

# Synthesis of CeO<sub>2</sub> nanoparticles by salt-assisted ultrasonic aerosol decomposition

B. Xia, I. W. Lenggoro and K. Okuyama\*

Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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**Well-crystallized nanosized CeO<sub>2</sub> single crystals (20–120 nm) were prepared by modifying the aerosol decomposition technique by adding salts to a precursor solution, while the conventional method is only capable of producing submicron to micron sized polycrystalline particles.**

Ceria (CeO<sub>2</sub>) is a cubic fluorite-type oxide. CeO<sub>2</sub> and CeO<sub>2</sub>-based (e.g. Mg<sup>2+</sup>, La<sup>3+</sup>, Gd<sup>3+</sup>, Zr<sup>4+</sup> doped) materials, in both powder and film form, have a number of important applications in gas sensors, solid oxide fuel cells, catalysts and abrasives.<sup>1,2</sup> For example, rare earth-doped ceria represents an attractive electrolyte candidate for low-temperature operating (e.g. 500 °C) solid oxide fuel cells due to its high oxygen ion conductivity.<sup>1</sup> Solution-based techniques such as precipitation, hydrothermal, sol-gel and micro-emulsion techniques have been widely used to prepare CeO<sub>2</sub>.<sup>3–5</sup> In addition, CeO<sub>2</sub> materials produced by solid-state reaction, mechano-chemical methods, chemical vapor deposition (CVD) and sputtering have also been reported.<sup>6–8</sup> However, these methods are multi-step and time-consuming processes (e.g. the solution-based techniques) or it can be difficult to control the product composition (e.g. the CVD processes). Here we report a novel technique for synthesizing well-crystallized CeO<sub>2</sub> and CeO<sub>2</sub>-based nanoparticles in a simple, rapid and consecutive process.

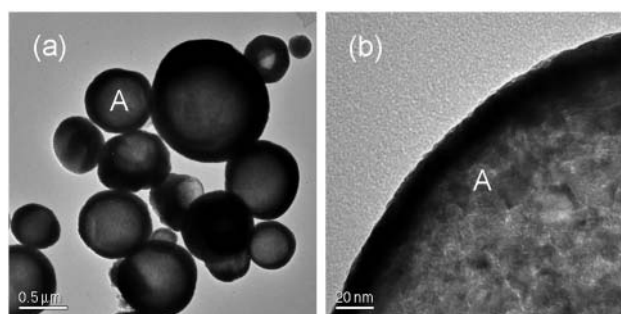
Aerosol decomposition (AD), also known as spray pyrolysis, is a liquid-to-particle conversion process and has been successfully used to prepare a variety of powdered materials<sup>9,10</sup> including CeO<sub>2</sub>.<sup>11,12</sup> This process is simple, consecutive and easily controllable. On the other hand, however, it typically produces submicron to micron sized particles because it is difficult to efficiently generate very fine droplets for nanoparticles.

This work is involved in the synthesis of nanometer sized CeO<sub>2</sub> and CeO<sub>2</sub>-based particles, which have been reported to have improved properties.<sup>3,4</sup> In this study, the currently available technique, or the conventional method, was modified simply by adding inert inorganic salts to the precursor solution before the aerosol decomposition, followed by washing the product to remove the salts. This modified process is referred to as salt-assisted aerosol decomposition (SAD) technique in comparison to conventional aerosol decomposition (CAD). In order to show the availability of this method, cerium nitrate was dissolved in distilled water to form a 0.2 mol L<sup>-1</sup> precursor solution. In the case of rare-earth (RE; La<sup>3+</sup> and Gd<sup>3+</sup>) doping, the dopant nitrate (RE : Ce = 1 : 4, atomic ratio) was added along with the cerium nitrate. In the SAD process, a mixture of potassium and sodium nitrates with a eutectic composition (54 : 46, atomic ratio) with a total concentration of 0.5–2.0 M was added to the precursor solution, while in the CAD process only the precursor was added. The solution was misted by an ultrasonic transducer (1.7 MHz) into droplets

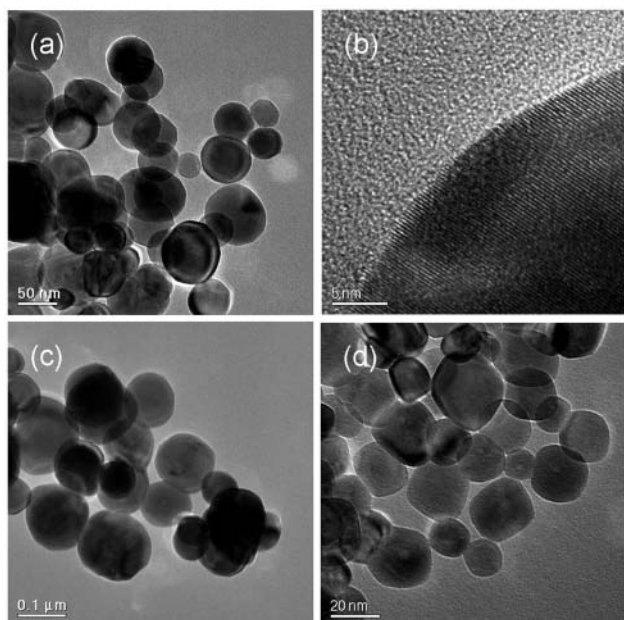
with a mean size of 4.6 μm (of a geometric standard deviation, σ<sub>g</sub>, 1.38–1.97 depending on the operating conditions), which were then carried by air into a hot tubular reactor where they were rapidly heated and decomposed to form particles. The total heating time in the reactor was less than five seconds. CeO<sub>2</sub> nanoparticles were obtained by washing the product in water to remove the salts or their derivatives, which are recyclable. The experimental setup and details can be found elsewhere.<sup>9,10</sup> In order to compare the SAD and the CAD processes, two sets of experiments were carried out under the same operating conditions using the same experimental apparatus, one with the salts in the precursor solution and the second without the salts.

Fig. 1 shows the transmission electron microscopic (TEM) images of the CeO<sub>2</sub> particles, which were synthesized by the CAD method at 800 °C. The particles (Fig. 1a) are solid and nearly spherical with a mean particle size of 0.74 μm, which consist of nanosized crystallites (Fig. 1b) with mean size of 13.8 nm determined by the X-ray diffraction (XRD) technique. These nanosized crystallites are virtually inseparable due to sintering. The CeO<sub>2</sub> particles obtained at other temperatures (400–1200 °C) have similar morphologies. Obviously, this process is not capable of producing nanometer sized CeO<sub>2</sub> particles, unless the solution concentration is extremely low. The above characteristics are also typical for other CAD CeO<sub>2</sub> particles.<sup>11,12</sup>

Fig. 2a and b show SAD particles that were synthesized under the same conditions as the CAD particles shown in Fig. 1, but with the addition of the eutectic salts to the precursor solution prior to the aerosol decomposition. Important differences between the CAD and the SAD products are indicated below. First, the SAD product (Fig. 2a) is composed of isolated nanoparticles (mean size 51 nm) while the CAD product consists of submicron to micron sized particles (mean size 0.74 μm) containing sintered nano-crystallites.



**Fig. 1** Submicron to micron CeO<sub>2</sub> particles synthesized by the CAD method at 800 °C: (a) lower magnification image; (b) higher magnification image of the particle marked A, comprising sintered nano-crystallites.

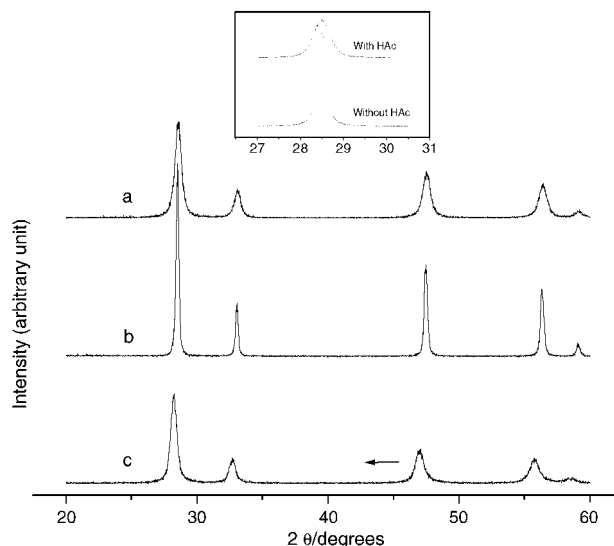


**Fig. 2** Nanometer sized  $\text{CeO}_2$  particles synthesized by the SAD method at (a) 800 °C, and (b) a typical high resolution TEM image of sample (a), showing the crystal lattice of a particle; (c) 900 °C, and (d) 800 °C with addition of acetic acid to the solution prior to aerosol decomposition.

Powder XRD patterns of the CAD and the SAD products, shown in Fig. 3a and b, illustrate the well-defined  $\text{CeO}_2$  cubic phase. Second, the SAD product has a much higher crystallinity than the CAD product, as shown from the sharp peaks in Fig. 3b. The crystallite size of the SAD 800 °C sample is 54.4 nm, as shown in Table 1. This is much larger than the corresponding CAD sample (13.8 nm) and even than the CAD 1000 °C sample (29.9 nm); it is also bigger than the  $\text{CeO}_2$  crystallites (about 40 nm) that were heated at 800 °C for 2 hours,<sup>8</sup> while the SAD product in this work was heated for only a few seconds. Third, the SAD  $\text{CeO}_2$  particles are single crystals while the CAD  $\text{CeO}_2$  particles are polycrystalline (as shown in Fig. 1b). The single crystals are evidenced by the agreement between the particle sizes and the crystallite ones at all synthesis temperatures, as shown in Table 1. The typical crystal lattice image shown in Fig. 2b confirms the presence of single-crystalline particles. In addition to the above-mentioned differences, it is also noteworthy that the geometric standard deviation ( $\sigma_g$ ) of the CAD particles is determined as 1.63, a typical polydispersity of aerosol particles produced by ultrasonic aerosol decomposition, while it is only 1.25 for the corresponding SAD particles. Clearly, the particle size distribution of the SAD product has been remarkably narrowed in comparison to the CAD product.

Although further study is needed to understand the details of the SAD process, some preliminary explanations can be made regarding this different particle formation process. Since an oxide can dissolve in some molten salts,<sup>13</sup>  $\text{CeO}_2$  can participate in dissolution and precipitation in the liquid-state salt media, which can greatly facilitate mass transfer and thus material formation and crystallization processes.<sup>14</sup> A crystallite grows by depleting its adjacent crystallites and is then isolated from others (within a submicron or micron particle) due to the energy-favorable interaction of the oxide surface with the salts.<sup>15</sup> These processes are absent in the CAD procedure where the solid-state reactions and diffusion proceed very slowly. The  $\text{CeO}_2$  nanoparticles are released upon removing the salts by washing.

As is shown in Table 1, the CAD  $\text{CeO}_2$  particle sizes change slightly with synthesis temperature, because it is well understood that the CAD particle size is primarily determined by the



**Fig. 3** Powder X-ray diffraction (XRD) patterns of products synthesized at (a) CAD, 800 °C ( $\text{CeO}_2$ ); (b) SAD, 800 °C ( $\text{CeO}_2$ ); (c) SAD 800 °C by  $\text{La}^{3+}$  doping ( $\text{La}:\text{Ce}=1:4$ , atomic). The inset shows that the addition of HAc to the precursor solution causes a decrease in crystallite size. The SAD pattern (b) has much sharper peaks than the corresponding CAD pattern (a). The XRD patterns were recorded at room temperature using  $\text{Cu K}_\alpha$  radiation operated at 40 kV and 20 mA.

**Table 1** Comparison of particle and crystallite diameters (in nanometers) of  $\text{CeO}_2$  synthesized by the CAD and the SAD processes<sup>a</sup>

	CAD			SAD		
	800 °C	900 °C	1000 °C	800 °C	850 °C	900 °C
Particle	740	720	730	51	91	119
Crystallite	13.8	20.1	29.9	54.4	85.5	106.1

<sup>a</sup>Particle and crystallite diameters were determined by TEM imaging and XRD technique, respectively. Due to its high melting point (2600 °C),  $\text{CeO}_2$  has small crystallite size even when synthesized in the CAD process at 1000 °C.

droplet size (mainly depending on the transducer vibration frequency) and concentration of the precursor solution. In the SAD process, however, we found that many factors such as precursor(s), inert salts, additives and process parameters can be used to control particle size and morphology. As shown in Fig. 2c and Table 1, for example, the mean particle size of the SAD product increases from 51 nm (Fig. 2a) to 119 nm when the synthesis temperature is increased from 800 °C to 900 °C. Fig. 2d shows that the addition of acetic acid as an additive to the precursor solution resulted in a reduction in the final particle size from 51 nm to 21 nm. The broadened XRD peak is clearly seen in the inset of Fig. 3.

We have also used the modified technique to synthesize rare-earth doped  $\text{CeO}_2$ . Fig. 3(c) shows the powder XRD pattern of  $\text{La}^{3+}$ -doped  $\text{CeO}_2$  particles ( $\text{La}_2\text{Ce}_8\text{O}_{19}$ ). All peaks shift to smaller angles due to the substitution of the larger  $\text{La}^{3+}$  ions (radii 1.061 Å) for  $\text{Ce}^{4+}$  ions (0.92 Å) while retaining the cubic fluorite structure. Similar results were obtained from Gd doping. Doping also causes a decrease in crystallite size to 17.4 nm, as shown by the line broadening in Fig. 3(c). Due to the fine, homogeneous and well-crystallized particles with nearly spherical morphologies, the  $\text{CeO}_2$  and  $\text{CeO}_2$ -based materials synthesized by using the SAD technique are expected to have excellent sinterability to be used as raw materials for solid oxygen fuel cells and other applications. By using a larger experimental apparatus in our lab,  $\text{CeO}_2$  nanopowders with production rates of 1–10  $\text{g h}^{-1}$  can be generated. In addition to  $\text{CeO}_2$ , we recently also succeeded in synthesizing

other multi-component nanoparticles such as (Sr,Ba)TiO<sub>3</sub>, (Cd,Zn)S, etc. by using this technique. Annealing is unnecessary for these well-crystallized SAD products.

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