

Synthesis of nano-sized ceria powders by two-emulsion method using sodium hydroxide

Joon-Sung Lee, Jin-Seok Lee, Sung-Churl Choi*

Department of Ceramic Engineering, Hanyang University, Seoul 133-791, Republic of South Korea

Received 5 May 2004; received in revised form 15 September 2004; accepted 21 September 2004

Available online 20 October 2004

Abstract

In the present study, nano-sized ceria powders were prepared by the two-emulsion method in the presence of aqueous sodium hydroxide. The effect of the ceria precursor concentration and the addition of an aqueous sodium hydroxide on the crystallite size, the size distribution and the morphology of the synthesized powders were investigated. The precipitates were obtained by mixing two water-in-oil emulsions with kerosene containing cerium nitrate aqueous solution and sodium hydroxide aqueous solution. The synthesized ceria powders were characterized by XRD and TEM. The synthesized ceria powders had nearly spherical shape and a uniform crystallite size in a range of 10 to 20 nm depending on the concentration of precursor solution and an addition amount of mineralizer.

© 2004 Elsevier B.V. All rights reserved.

Keywords: CeO₂; Powders-chemical preparation; Chemical mechanical planarization (CMP); Two-emulsion synthesis

1. Introduction

Cerium oxide (CeO₂) is a useful material that is widely used as an electrolyte for solid oxide fuel cells (SOFC) [1,2], abrasive materials for chemical mechanical planarization (CMP) [3], ultraviolet absorbent, oxygen pumps and automotive exhaust promoter. Especially, cerium oxide powders for chemical mechanical planarization in semiconductor devices manufacturing process are required to be nano-sized with physical properties such as spherical shape and a narrow size distribution in order to reduce scratch of wafer [4,5]. Uniform and spherical nanocrystalline powders as starting material possess considerable potential for improving the properties of existing ceramic compositions in final products.

Nano-sized ceria powders have been recently reported that it was prepared by various techniques, including hydrothermal treatment [6,7], hydrolysis of alkoxide solution (sol–gel method) [8], chemical precipitation [9],

mechanochemical processing [10] and gas-phase reaction [11]. Spherical ceramic particles can be successfully prepared by wet chemical methods (e.g. sol–gel method, spray hydrolysis process, and emulsion technique), but the starting materials such as metal alkoxides used in sol–gel and spray hydrolysis processes are expensive. Compared to other methods, the emulsion method has several advantages in producing particles with a spherical shape and narrow size distribution [12,13]. In addition, the emulsion technique can reduce the cost of producing spherical powders of high purity, and those that have a lower aggregation than the other starting materials. However, the synthesis of rare earth compounds such as ceria has been rarely reported by the emulsion method. Masui et al. [14] studied the fabrication of the nano-sized cerium oxide particles using reversed micelles by the two-emulsion method with ammonium hydroxide as a mineralizer. However, ammonium hydroxide is difficult to handle during precipitation because of its strong smell. Sodium hydroxide, a highly reactive metal hydroxide material, has been used as substitute for ammonium hydroxide as a mineralizer [15].

An emulsion is generally defined as a thermodynamically stable system composed of two immiscible liquids and a

* Corresponding author. Tel.: +82 2 2290 0505; fax: +82 2 2291 6767.

E-mail address: choi0505@hanyang.ac.kr (S.-C. Choi).

surfactant [13]. There are other factors that affect the stability of an emulsion and further affect the morphology and size distribution of produced particles. These factors include type and amount of surfactant and co-surfactant, the concentration of precursor solution, the kind of oil phase, and the water-to-oil ratio. The concentration of cerium salt as precursor and the amount of sodium hydroxide as mineralizer are practically important factors in controlling the physical properties of the synthesized powder. Surfactant is added to a mixture of oil and water in the reverse emulsion to reduce the interfacial tension between the water and oil phases [16]. A water-in-oil emulsion can be obtained by using a surfactant with a hydrophile–lipophile balance (HLB) value in the range of 3 to 7. In water-in-oil emulsions, the aqueous phase is dispersed as nano-size water droplets covered with a monolayer film of surfactant and co-surfactant molecules in a continuous nonpolar organic solvent such as hydrocarbon. Not only water but also aqueous solutions of metal salts or ammonium hydroxide can be soluble in the reversed micelles. These aqueous droplets encapsulated with surfactant molecules can continuously exchange their components such as cerium ion and mineralizer with one another when they collide. Therefore, if two water-in-oil emulsions (one dissolves reactants A and another dissolves reactants B) are mixed, a reaction between them takes place during collisions of the water droplets in the emulsions. For the emulsion method, the particles with uniform small size and narrow size distribution can be obtained because the reaction field is limited to the fine reverse micelles.

In the present study, we studied the synthesis of the nano-sized ceria powders by the emulsion method in the presence of an aqueous sodium hydroxide and characterized the effects of the ceria precursor concentration and the addition of an aqueous sodium hydroxide on the crystallite size, the size distribution and morphology of the synthesized powders.

2. Experimental procedures

The preparation of ceria powder by the two-emulsion method using sodium hydroxide as a precipitating agent is schematically illustrated in Fig. 1. Two solutions were prepared by mixing 500 ml kerosene (Kanto Chemical, Japan) as the oil phase and Span 80 (Yakuri Pure Chemicals, Japan) as a surfactant in a 1000-ml beaker by an agitator at room temperature. Span 80 has HLB value of 4.3 and is known to be a suitable surfactant for forming a water-in-oil emulsion. Isopropyl alcohol (IPA, Samchun Pure Chemical, Korea) as a co-surfactant was added into the two solutions. Distilled water was used for all experiments. After the surfactant and co-surfactant were completely dissolved in the oil phase, two aqueous solutions of equal volume were added into the each beakers separately; one containing cerium nitrate hexahydrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Kanto Chem-

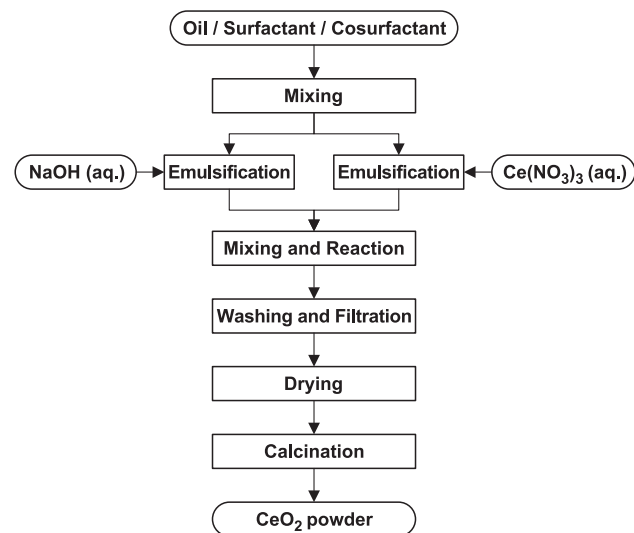


Fig. 1. Experimental flow chart of the synthesis of the ceria powder by the two-emulsion method.

ical, Japan] and the other, sodium hydroxide (NaOH, Yakuri Pure Chemicals, Japan). Then, the two aqueous solutions were emulsified with oil phase to be made into an emulsion by an agitator for about 1 h. Then, the two emulsions were mixed for 4 h and the ceria precursor and sodium hydroxide could react. The resultant slurry was washed and filtrated with isopropyl alcohol three times at least. Washing and filtration by distilled water were performed on them in order to remove the residual surfactant and ions physically adsorbed on the surface of the precipitates. The ceria precipitates were dried between 70 and 80 °C for 24 h. The light-yellow ceria powders were obtained by calcination at 700 °C for 10 min. The concentration of cerium nitrate precursor was varied from 1 to 4 M. The content of sodium hydroxide was changed 8 to 12 of the molar ratio of sodium hydroxide to cerium ion under the same procedure conditions.

Phase identification of the calcined ceria powders was performed in X-ray diffractometry (XRD, Rigaku, D/max-2C, Japan) using $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns of ceria powders were obtained in the 2θ range between 20 and 80° with a step of 0.01° and a scan speed of 2°/min. The crystallite size of the ceria powders was calculated from the line broadening of the (111) diffraction line according to the Scherrer equation.

$$D = 0.9\lambda / \beta \cos\theta$$

where D is the crystallite size (in angstroms), λ the wavelength of $\text{CuK}\alpha 1$ radiation, and β the corrected half-width of the diffraction peak. The size and morphology of the calcined ceria powders were examined by transmission electron microscopy (TEM, JEM-2010, JEOL, Japan). Samples of the calcined ceria powder were prepared by

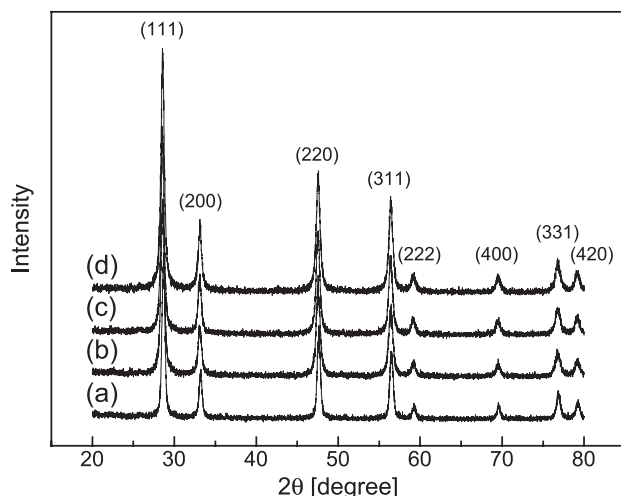


Fig. 2. X-ray diffraction patterns of ceria powders calcined at 700 °C for 10 min. These powders were prepared from various concentrations of cerium nitrate aqueous solution (a) 1, (b) 2, (c) 3 and (d) 4 M.

dipping carbon-coated copper grids into a dilute ethyl alcohol suspension of the ceria powder. The grids were then dried at room temperature or at 80–85 °C.

3. Results and discussion

Fig. 2 shows the XRD patterns of the calcined powders at a different molar fraction of cerium nitrate aqueous solution. It was found that the synthesized ceria powders were identified with the cubic fluorite structure. The width of the peaks was broad because of their fine particle size. The average crystallite size was calculated by the Scherrer equation from the (111) XRD lines. Their size slightly increased from 17 to 20 nm as the concentration of aqueous cerium precursor was increased and increasing of concentration of cerium precursor accelerates grain growth rate than nucleation rate [17].

Fig. 3 shows the transmission electron micrographs of the ceria powder prepared by the emulsion method. It reveals that the shape of the synthesized particles was nearly spherical and the size of the particles ranged from 10 and 20 nm, which agreed with the results of XRD analysis. The particles prepared from the 2 M cerium nitrate aqueous solution with a sodium hydroxide to cerium ion molar ratio of 8 had a relatively uniform and spherical shape and a narrow particle size distribution (Fig. 3(a)). As the concentration of the cerium nitrate aqueous solution was increased to 3 M, the particle size became slightly larger than that of the 2 M cerium nitrate aqueous solution (Fig. 3(b)). At the constant molar fraction of 2 M cerium nitrate aqueous solution, the particle size and particle size distribution of the 12 molar ratio sodium hydroxide to cerium ion was slightly larger and wider (Fig. 3(c)), compared to the 8 molar ratio sodium hydroxide to cerium ion. The particle diameters of each sample using linear intercept method were estimated to be 16.9 ± 0.4 nm (Fig. 3(a)), 18.1 ± 0.6 nm (Fig. 3(b)), and 17.6 ± 1.2 nm (Fig. 3(c)), respectively. There is a slight difference between the mean diameters from TEM micrographs and crystallite sizes from XRD peaks, which belongs to the range of the standard deviation.

It was evident from these figures that the particle size was very small, and that the size of the synthesized particle with sodium hydroxide as a mineralizer decreased as the cerium nitrate concentration was decreased from 4 to 1 M. This suggests that sodium hydroxide promoted the formation of particles with a uniform size distribution due to the fast reaction rate and homogeneous precipitation. This result indicated that sodium hydroxide as a mineralizer could enhance the control of the size, size distribution and the morphology of the ceria particles.

Table 1 summarizes the crystallite size and mean particle size of the cerium oxide particles synthesized by using two reverse emulsions with different concentrations of cerium nitrate aqueous solution and different amounts of sodium hydroxide. The reverse emulsions were stable and the

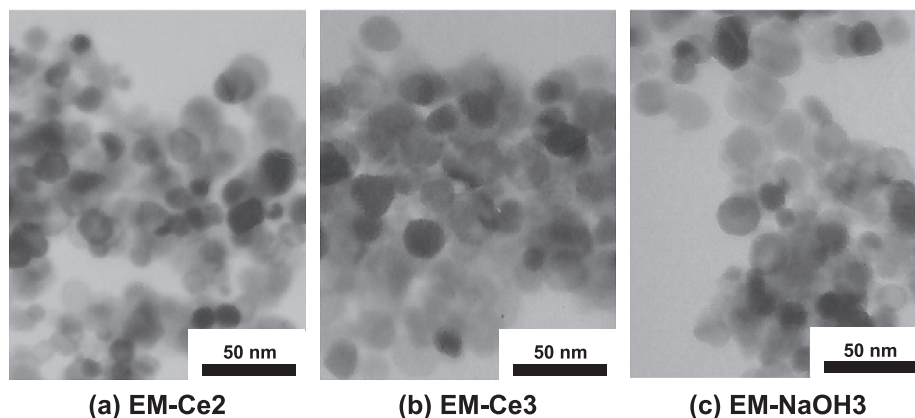


Fig. 3. Transmission electron micrographs of ceria powders synthesized by the two-emulsion method with NaOH. These powders were prepared from (a) 2 M of the cerium nitrate aqueous solution at a molar ratio NaOH to cerium ion of 8:1, (b) 3 M cerium nitrate aqueous solution at a molar ratio NaOH to cerium ion of 8:1 and (c) 2 M cerium nitrate aqueous solution at a molar ratio NaOH to cerium ion of 12:1.

Table 1

The crystallite size and mean particle size of ceria powders synthesized by the two-emulsion method

Concentration of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ aq. [M]	Mole ratio of NaOH/cerium ion	Crystallite size by XRD [nm]	Particle size by TEM [nm]
1	8	17.394	10–20
2	8	17.048	10–20
3	8	18.092	15–25
4	8	19.936	15–25
2	12	17.332	10–30

produced ceria powders had nearly spherical morphology at all concentrations of aqueous cerium precursor in the present investigation. When the molar ratio of sodium hydroxide to cerium ion is 12, the particles size was slightly larger than when compared to the molar ratio of sodium hydroxide to cerium ion of 8. Difference in particles diameters derived from different molar ratio of sodium hydroxide to cerium ion is not larger than the relative uncertainty, which can be caused by the iterative measurement conducted. This indicated that the particle size and shape of the product depend less on the molar ratio of sodium hydroxide to cerium ion than the concentration of cerium nitrate aqueous solution. However, the molar ratio of sodium hydroxide to cerium ion was one of the important factors for controlling size and size distribution of powders.

The particle size of ceria powders is mainly related to the droplet size of emulsion and the reaction between cerium salt and the mineralizer. As the concentration of cerium nitrate solution increases, the particle size became larger and the particle size distribution became broader. In contrast, at low concentrations of cerium nitrate aqueous solution, the size distribution was very narrow and the mean size was very small. Thus, particle sizes ranging from a few nanometers to several tens of nanometers could be controlled by the concentration of cerium nitrate solution. Also, change in the molar ratio of sodium hydroxide to cerium nitrate solution from 12:1 to 8:1 enabled the synthesized particles to have finer size and narrower size distribution. In the emulsion method, the final particle size of the cerium oxide particles is restricted because the chemical reaction of cerium nitrate solution with sodium hydroxide aqueous solution takes place inside the water droplets within the reversed micelles. Once the particles became a critical size in the water droplets, the surfactant molecules adsorbed on the particles surface to protect them against further particle growth. Therefore, the two-emulsion method is very available to prepare nano-sized powders with spherical shape and narrow size distribution.

4. Conclusions

The nano-sized ceria powders with spherical morphology are successfully prepared by the two-emulsion method, which is caused by the reaction between two emulsion solutions containing cerium nitrate and sodium hydroxide. From the results of XRD analysis and TEM observations in this study, the synthesized ceria powders had an average particle size of less than 20 nm and a narrow particle size distribution. A comparison of the experimental results at different concentrations of cerium nitrate precursor indicates that the particle size synthesized in 2 M cerium precursor solution became smaller than that synthesized in the precursor solution of other molar fraction. The particle size and size distribution of particle with 8 molar ratio sodium hydroxide to cerium ion were slightly smaller and narrower than the synthesized particles with 12 molar ratio sodium hydroxide to cerium ion. Therefore, the concentration of precursor solution (cerium nitrate aqueous solution) and a mineralizer (sodium hydroxide) strongly affected on physical properties such as size, shape and size distribution of particles.

References

- [1] H. Inaba, H. Tagawa, *Solid State Ionics* 83 (1996) 1–16.
- [2] H.L. Tuller, A.S. Nowick, *J. Electrochem. Soc.* 122 (2) (1975) 255–259.
- [3] T. Hoshino, Y. Kurata, Y. Terasaki, K. Susa, *J. Non-Cryst. Solids* 283 (2001) 129–136.
- [4] W.M. Sigmund, N.S. Bell, L. Bergstrom, *J. Am. Ceram. Soc.* 83 (7) (2000) 1557–1574.
- [5] M. Jiang, N.O. Wood, R. Komanduri, *Wear* 220 (1998) 59–71.
- [6] M. Hirano, Y. Fukuda, H. Iwata, Y. Hotta, M. Inagaki, *J. Am. Ceram. Soc.* 83 (5) (2000) 1287–1289.
- [7] M. Hirano, E. Kato, *J. Am. Ceram. Soc.* 82 (3) (1999) 786–788.
- [8] S. Rossignol, F. Gerard, D. Duprez, *J. Mater. Chem.* 9 (1999) 1615–1620.
- [9] Y. Gu, G. Li, G. Meng, D. Peng, *Mater. Res. Bull.* 35 (2000) 297–304.
- [10] T. Tsuzuki, P.G. McCormick, *J. Am. Ceram. Soc.* 84 (7) (2001) 1453–1458.
- [11] W. Bai, K.L. Choy, N.H.J. Stelzer, J. Schoonman, *Solid State Ionics* 116 (1999) 225–228.
- [12] M.H. Lee, C.Y. Tai, C.H. Lu, *J. Eur. Ceram. Soc.* 19 (1999) 2593–2603.
- [13] C.Y. Tai, M.H. Lee, Y.C. Wu, *Chem. Eng. Sci.* 56 (2001) 2389–2398.
- [14] T. Masui, K. Fujiwara, K. Machida, G. Adachi, T. Sakata, H. Mori, *Chem. Mater.* 9 (1997) 2197–2204.
- [15] X. Yu, F. Li, X. Ye, X. Xin, Z. Xue, *J. Am. Ceram. Soc.* 83 (4) (2000) 964–966.
- [16] J.W. Ha, J.H. Moon, S.M. Yang, *Kor.-Australia Rhe. J.* 11 (3) (1999) 241–246.
- [17] G.D. Agli, A. Colantuono, G. Mascolo, *Solid State Ionics* 123 (1999) 87–94.