Characterization of CeO_2 Ultrafine Particles Prepared Using a Thermal Relaxation Technique

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Cerium(IV) oxide ultrafine particles were prepared in a nylon 11 matrix through a relaxative auto-dispersion (RAD) process. High-resolution electron microscope (HREM) observations revealed that the lattice parameter and mean particle size of CeO_2 ultrafine particles were 0.541 nm and 4.1 nm, respectively.

In recent years, ultrafine particles have attracted much attention since such particles often exhibit the physicochemical properties which are significantly different from those of bulk materials.[1] One problem associated with nanometer-sized metal particles is that it is difficult to handle them in air because of their high surface energy. This is the reason why many workers have interest in preparing fine metal particles incorporated in polymer films.[2-8] As a work on this line, recently Noguchi et al.[9] succeeded to develop a new process to prepare composite films which consist of a polymer and ultrafine metal particles. In this composite material, nanometer-sized metal particles are stably and uniformly dispersed in the polymer matrix. This process is called the relaxative auto-dispersion (RAD) process and has been developed for such systems as gold particles embedded in the nylon 11 matrix.[9-13] This process may also be applicable to such systems as nm-sized compound particles incorporated in the polymer matrix. In the present letter, we report on the preparation of cerium(IV) oxide fine particles by the RAD process, which possess potential applications in catalyst and UV absorbent.

Nylon 11 was used in this study as a polymer matrix, as employed in the literature.[9] The nylon 11 matrix film (thickness 150 nm) was prepared on a NaCl single crystal by vapor deposition under a vacuum condition of 1.33×10^{-7} Pa and separated from the NaCl substrate by dissolving in water. Then the nylon 11 film was collected on an amorphous collodion film on a copper grid used as a sample holder for transmission electron microscopy. Cerium metal which corresponds to 2 nm thickness in the form of thin film was then deposited on the nylon film in vacuo (1.33×10^{-9} Pa). The composite film was heated under the same vacuum condition for 10 min at 363 K (90 °C), which was a temperature between the glass transition point and the melting point of nylon 11. Through the heat treatment, the cerium metal on the nylon 11 film was dispersed into the nylon substrate layer in the form of ultrafine particles. The composite film was left in air after the heat treatment, so that the produced ultrafine particles were oxidized to be cerium oxide.

High-resolution images were obtained with a Hitachi H-9000 TEM equipped with a tilting device (±10 degrees) and operating at 300 kV (C_s=0.9 mm). Images were recorded under axial illumination at approximate Scherzer focus, with a point resolution better than 0.19 nm. The diameter of the objective aperture used was 20 μm, which was large enough to include Debye-Sherrer rings from cerium oxide. The particle size distribution was determined by measuring the maximum diameter of more than 200 particles along a fixed direction on the HREM micrographs. Image simulation was also performed for a [111] oriented model particle using the "MacHREM™" program based on the multislice method.

Figure 1 shows a high-resolution electron micrograph (HREM) of a CeO_2-nylon 11 composite after the heat treatment. It is evident from this figure that fine CeO_2 particles are dispersed uniformly and isolated individually in the nylon 11 matrix. As shown in Figure 2, the particle size distribution which is obtained by measuring the maximum diameter of the particles on the HREM micrograph exhibits a fairly narrow peak. The particle sizes distributed between 2 and 8 nm, and the mean particle size was evaluated to be 4.1 nm. Information on the lattice parameter and crystal structure of the particles was obtained from the

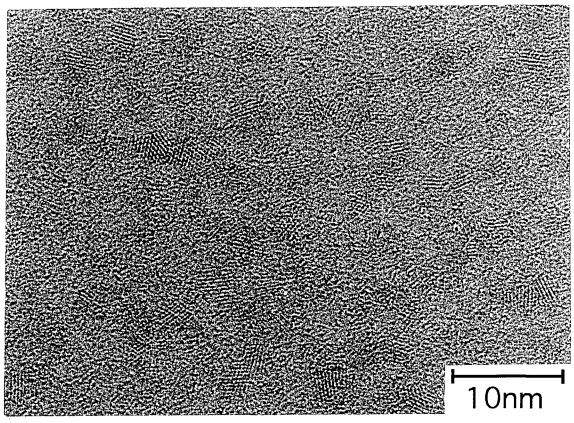


Figure 1. High-resolution electron micrograph of CeO_2 ultrafine particles in nylon 11 matrix after heating at 363 K for 10 min.

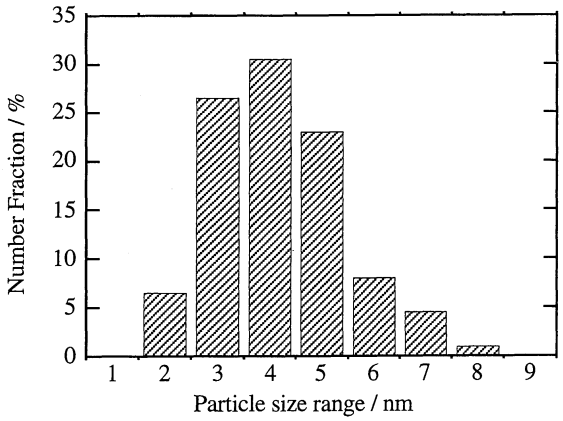


Figure 2. Particle size distribution of CeO_2 ultrafine particles in nylon 11 matrix measured from HREM micrographs.

selected-area electron diffraction patterns. Figure 3 shows an example of the diffraction patterns and the Debye-Sherrer rings can be consistently indexed as those of cerium(IV) oxide with the cubic fluorite structure. The lattice constant calculated from the radius of Debye-Sherrer rings was 0.541 nm. this value is in good agreement with that given in the literature.[14] A typical HREM image of a CeO_2 particle is shown in Figure 4 (a), whereas a simulated image of a [111] oriented particle, with a crystal thickness of 6.2 nm and defocus of 50 nm, is illustrated in Figure 4 (b).The agreement between the two images is fairly good. All these facts indicate that the ceria particles are those of cerium(IV) oxide with the CaF_2 structure.

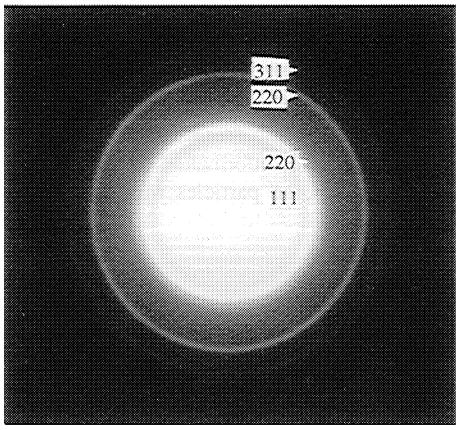
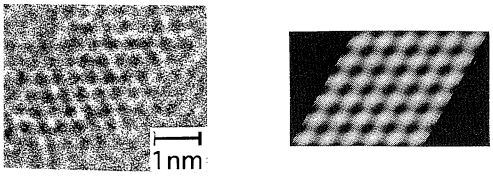


Figure 3. Electron diffraction pattern of CeO_2 ultrafine particles in nylon 11 matrix.



(a) (b)

Figure 4. Experimental and simulation images of a CeO_2 particle in [111] orientation : (a) experimental image, (b) simulated image.

Mechanism of the RAD process taking place here to form the ultrafine particles is proposed according to the previous works.[12,13] Since the polymer films formed by means of vapor deposition consist of thermodynamically metastable structure, the nylon 11 film of relatively low molecular weight changes into much stable structure during heat treatment. In this stage where the film is relaxed and stabilized through the heat treatment, the upper cerium metal deposited on the surface of nylon 11 film is dispersed into the film matrix in the form of ultrafine metal particles.

However, rare earth metals are generally liable to be oxidized by air. Therefore, the cerium metal particles produced were partially changed to cerium oxide by oxidation with the residue of oxygen or water in the vacuum chamber. Moreover, when the samples were taken out of it after the heat treatment, they were completely oxidized by air. In fact, using copper as the upper metal layer, copper(I) oxide was reported to produce as ultrafine particles.[12]

The present study can thus be summarized as follows.

(1) Cerium(IV) oxide ultrafine particles were prepared by the RAD process using the nylon 11 matrix.

(2) The average size of ceria particles was evaluated to be 4.1 nm by high-resolution TEM.

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References and Notes

1 R. P. Andres, R. S. Averback, W. L. Brown, L. E. Brus, W. A. Goddard, III, A. Kaldor, S. G. Louie, M.Moscovits, P. S. Peercy, S. J. Riley, R. W. Siegel, F. Spaepen, and Y. Wang, *J. Mater. Res.*, **4**, 704 (1989).

2 E. Kay and M. Hecq, *J. App. Phys.*, **55**, 370 (1984).

3 R. A. Roy, R. Messier, and S. V. Krishnaswamy, *Thin Solid Films*, **109**, 27 (1983).

4 Y. Asano, *Thin Solid Films*, **105**, 1 (1983).

5 L. Martinu, H. Biederman, and J. Zemek, *Vacuum*, **35**, 171 (1985).

6 K. Kashiwagi, Y. Yoshida, and Y. Murayama, *J. Vac. Sci. Technol. A*, **5**, 1828 (1987).

7 L. Martinu, *Thin Solid Films*, **140**, 307 (1986).

8 J. Perrin, B. Despax, and E. Kay, *Phys. Rev. B.*, **32**, 719 (1985)

9 T. Noguchi, K. Gotoh, Y. Yamaguchi, and S. Deki, *J. Mater. Sci. Lett.*, **10**, 477 (1991).

10 T. Noguchi, K. Goto, Y. Yamaguchi, and S. Deki, *J. Mater. Sci. Lett.*, **11**, 648 (1992).

11 T. Noguchi, S. Murakami, K. Gotoh, Y. Yamaguchi, and S.Deki, *J. Mater. Sci. Lett.*, **11**, 797 (1992).

12 Y. Yamaguchi, T. Noguchi, K. Gotoh, and S. Deki, *Sen-i Gakkaishi*, **49**, 124 (1993).

13 K. Gotoh, T. Noguchi, S. Murakami, Y. Yamaguchi, and S. Deki, *Koubunshi Ronbunshu*, **50**, 437 (1993).

14 The file of X-ray powder diffraction standards by the American Society for the Testing and Materials. Inorganic compounds : CeO_2, 34-394.