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Formation of wide bandgap cerium oxide nanoparticles by laser ablation in aqueous solution

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ABSTRACT

Cerium oxide nanoparticles were produced by laser ablation in an aqueous solution. Submicron-sized cerium oxide particles were size-reduced by pulsed-laser irradiation into those having diameters of 3.6 nm. It was found that the bandgap of the nanoparticle was larger and the Ce^{3+} concentration within it was higher than those prepared by other conventional methods. These characteristic structures are likely to originate from additional defect sites in the nanoparticles produced by laser ablation, where O^{2-} ions have a lower coordination with Ce ions, resulting in removal of O atoms and reduction of Ce^{4+} into Ce^{3+}.

1. Introduction

Synthesis of rare earth nanoparticles in a controlled manner has become an important area of material chemistry research, because the nanoparticles exhibit size- and shape-dependent chemical and physical properties. Cerium oxide, one of the most reactive rare earth oxides, is currently used as a promoter or support in three-way catalysts for automobile exhaust gases [1]. Cerium oxide is known to release a large amount of oxygen for CO oxidation while maintaining its fluorite structure due to its oxygen storage capacity (OSC) such that the lattice oxygen is reversibly transferred from cerium oxide [2]. Many researchers have prepared cerium oxide nanoparticles using various methods such as a complex thermo-decomposition method [3], combustion synthesis [4], reverse micelles route [5], and sol–gel processing [6,7]. However, these techniques are complex. Therefore, laser ablation of a solid target immersed in an aqueous solution has become an increasingly important 'top down' method for production of nanoparticles [8–11]. This method is an alternative method addressing the deficits of the conventional methods, and offers access to an unlimited nanomaterial spectrum, since nanoparticles can be generated from almost any solid material. In the present study, we examined the formation of cerium oxide nanoparticles by irradiation using a 1064-nm laser in an aqueous solution containing submicron-sized particles of cerium oxide and PVP molecules as a stabilizer.

The electrical and structural properties of cerium oxide nanoparticles strongly depend on the nanoparticle size [12]. Ce 3d X-ray photoelectron spectroscopy (XPS) of cerium oxide particles revealed that the ratio of Ce^{3+} in the nanoparticles produced by laser abaltion was larger than that in the submicron-sized particles. Moreover, the electrical and structural properties are strongly affected by the sample preparation method [13]. It is well known that defect-rich nanoparticles can be synthesized by laser ablation in a solution [14–16]. Hence, cerium oxide nanoparticles produced by laser ablation are expected to include more defects than those produced by other methods. This characteristic feature of the nanoparticle affects both the concentration of Ce^{3+} and the bandgap of it. The bandgap of the nanoparticles produced by laser ablation in a liquid in the present study was obtained from the optical absorption spectra of the nanoparticles. It was found that the bandgap was larger and the Ce^{3+} concentration was higher than for nanoparticles with the same diameter prepared by conventional methods. These characteristic properties are likely to originate from additional defect sites in the nanoparticles produced by laser ablation, where O^{2-} ions are less coordinated by Ce ions, resulting in removal of O atoms and reduction of Ce^{4+} into Ce^{3+}.

2. Experimental section

2.1. Synthesis of cerium oxide nanoparticles by laser ablation

Cerium oxide nanoparticles were produced by laser ablation of submicron-sized cerium oxide particles dispersed in an aqueous solution. Here, 100 mL of the solution was prepared in a glass vessel, which contained 0.01 g of the submicron-sized cerium oxide particles (purchased from the Nilaco Corporation, Japan) and 1.8×10^{-4} M PVP (polyvinylpyrrolidone with an average molecular

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weight of ~60 000). The particles were irradiated by the fundamental output (1064 nm) of a Quanta-ray GCR-170 Nd:YAG pulsed laser. The laser operating at 10 Hz with a pulse width of 10 ns (350 mJ/pulse) was focused by a lens having a focal length of 40 mm. A Scientech AC2501 power meter was used to monitor the laser power. Upon irradiation by the laser beam, the solution gradually turned from white to yellow as shown in Figure 1.

2.2. Characterization of cerium oxide particles and nanoparticles

Transmission electron microscopy (TEM; JEM-100S, JEOL) was carried out on samples before and after laser irradiation. Drops of a solution containing cerium oxide particles were placed on a copper grid which had been coated with collodion and sputtered to induce hydrophilicity in advance, and then dried in air. After repeating this procedure three times, the grid was washed in water to remove free PVP molecules. Size distributions of the particles were obtained by measuring the diameters of more than 300 particles viewed in the electron micrographs. In order to determine the composition of the nanoparticles and the spatial distribution of the elements, energy dispersive X-ray spectroscopy (EDX) analyses were performed along with the SEM observations. The spatial distributions of the selected chemical elements, Ce, O, N, and C, were monitored. Here, N and C were probed, because these elements are components of the PVP molecule. UV–Vis absorption spectra of the cerium oxide nanoparticles were measured using a Shimadzu UV-2450 spectrometer equipped with a quartz cell (1 cm optical path length). The spectra were measured for the samples prepared by the laser ablation for 0, 30, 60, 90, 120, 180 and 300 min. XPS measurements were carried out using a spectrometer (PHI 5000 *VersaProbe* II™ ULVAC-PHI, Inc.) with a monochromatic X-ray source of Al Kα. Here, the XPS samples were prepared by dropping the solution containing the cerium oxide particles onto a silicon wafer. The ζ potential of the cerium oxide nanoparticles in solution was measured at different pHs adjusted using buffer solutions.

3. Results

Figure 2a and b show electron micrographs of submicron-sized cerium oxide particles before laser irradiation and nanoparticles produced by laser ablation in an aqueous solution, respectively. The average diameters of the particles are 80.3 ± 46.2 and 3.6 ± 1.7 nm, respectively. Figure 2c shows the corresponding size distributions, which indicate that the submicron-sized cerium oxide particles were pulverized into nanoparticles having diameters of 3.6 nm by laser irradiation.

Figure 3 shows EDX maps for cerium oxide nanoparticles produced by laser ablation under conditions identical to those for Figure 2. Figure 3a depicts the whole image of the nanoparticles

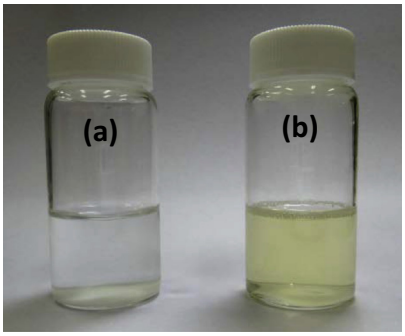

Figure 1. Appearance of solutions containing (a) cerium oxide particles before and (b) nanoparticles after laser ablation for 300 min.

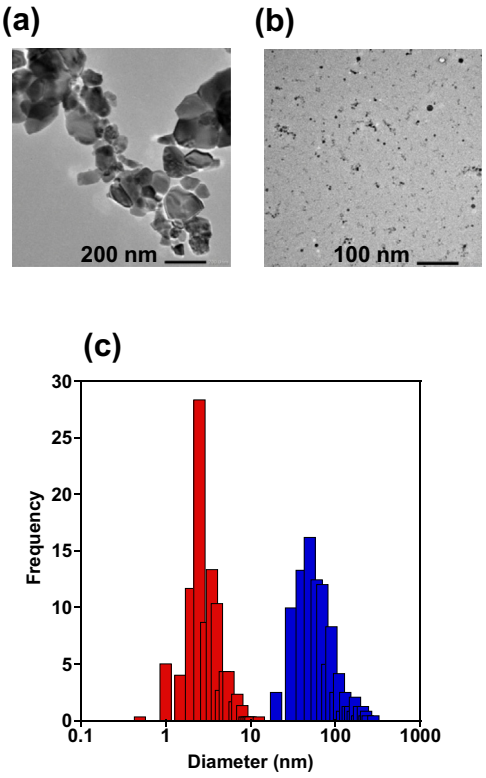

Figure 2. Panels (a and b) show electron micrographs of submicron-sized cerium oxide particles before laser irradiation and cerium oxide nanoparticles produced by 1064-nm laser ablation in an aqueous solution, respectively. Panel (c) shows the size distributions of submicron-sized cerium oxide particles (blue) and the cerium oxide nanoparticles (red).

where the EDX maps were obtained. Here, the resolution of the EDX mapping is not high enough to probe the element distribution in cerium nanoparticles as large as several nanometers. Therefore, EDX mapping was performed for the 4- and 10-nm nanoparticles located near the landmark of the nanoparticles with the diameter of 25 nm, although this is exceptionally large in the size distribution of the nanoparticles. Figure 3b–e show the results of element mapping analysis for cerium, oxygen, nitrogen, and carbon, respectively. It is clearly seen from these EDX measurements that the nanoparticle consists of Ce and O.

Figure 4a shows optical absorption spectra of cerium oxide nanoparticles produced with different laser irradiation times. The spectra exhibit a characteristic peak around 300 nm, which becomes blue-shifted with increasing laser irradiation time. Figure 4b shows the direct optical bandgap for the cerium oxide nanoparticles, which was estimated from the UV absorption data shown in Figure 4a using the conventional method [17]. The concentration of the cerium oxide nanoparticles in the solution is $C = 0.1$ g/L, which corresponds to an effective thickness $d = 137$ nm calculated by the following formula, $d = (lC/\rho)$. Here, ρ is the CeO_2 density, 0.00728 g/mm^3, and l is the present optical path length, 10 mm. By plotting $(\alpha E_{phot})^2$ vs. E_{phot}, the intersection of the extrapolated linear portions of E_{phot} to $(\alpha E_{phot})^2 = 0$ yields the bandgap, Eg, for direct transitions. Here α is the absorption coefficient given by $\alpha = OD/d$ and E_{phot} is photon energy, where OD is absorbance (optical density).

Figure 5 shows the Ce 3d XPS spectrum of the cerium oxide submicron-sized particles and the nanoparticles produced by laser ablation. The spectrum consists of a number of overlapped series of $3d_{5/2}$ and $3d_{3/2}$ peaks of the Ce 3d electron core levels [18]. In general, it is well known that 10 peaks appear for CeO_{2-x} in the Ce 3d XPS spectrum. Fitting Gaussian functions to the XPS peaks,