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Synthesis of CeO_2/TiO_2 nanoparticles by laser ablation of Ti target in cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) aqueous solution

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ABSTRACT

A new synthesis process, laser ablation in an aqueous solution of target material, was applied to synthesize nanostructured CeO_2/TiO_2 catalyst particles. Reactivity within the laser plume (plasma) can be used to synthesize CeO_2 from an aqueous solution, 2 M cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) aqueous solution, and to fabricate TiO_2 from Ti target. CeO_2/TiO_2 nanoparticles were successfully synthesized by the laser ablation of Ti target in 2 M cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) aqueous solution. Laser ablation of Ti in a liquid environment and chemical reactions of the solution within a plasma plume are discussed.

1. Introduction

Ceria (cerium dioxide, CeO_2) is a very well-known redox material for various applications. This is mainly due to its unique properties of redox ($Ce^{3+} \leftrightarrow Ce^{4+}$) [1,2]. CeO_2 has been widely applied in catalyst systems, solid state electrolytes, cosmetics materials, high temperature ceramics, gas sensors, oxygen ion conductors in solid oxide fuel cells, automobile catalytic converters, and optical materials [2–9]. It is well known that some metal ions such as Al^{3+}, Si^{4+}, Ti^{4+}, and Zr^{4+} are inserted into the ceria cubic structure to increase both the temperature stability and the ability of ceria-related catalysts to store and release oxygen [1]. CeO_2–TiO_2 oxides have also been applied in some catalytic reactions, such as CO oxidation, automobile exhaust treatment, air oxidation reactions of organics, and NO removal [10,11].

At present, a significant number of nanostructured catalytic materials have been studied due to their unique properties that are different from the bulk [12].

Increasing the number of defect sites, which are active sites for gas–solid catalysts, causes a large increase in the reaction kinetics. Especially, when the particle size is decreased below 100 nm, density of defects, which is the number density of atoms related with defects, is increased up to 50% of the atoms [1]. Thus, the nanostructures of these catalytic materials are highly important [3].

There are various fabrication methods to synthesize the nanostructured CeO_2 particles such as by sol–gel process, sonochemical synthesis, gas condensation and hydrothermal synthesis. Compared with other methods, the hydrothermal method has several advantages, which include low energy consumption, high purity and low aggregation [13]. However, hydrothermal synthesis also has drawbacks such as very complex steps with various solvents, chemicals and temperatures [14,15].

The aim of this study is to propose a new simplified approach to fabricate an ultrafine catalytic material, CeO_2–TiO_2. A unique laser technique, laser ablation in aqueous solutions, was applied to synthesize CeO_2–TiO_2 nanoparticles enabling a simplified process. The laser ablation method is a chemically simple and clean process. This process reduces byproduct formation, involves simple starting materials and uses no catalyst or heat to implement the reactions [16].

According to the previous reports on the formation of oxide particles by laser ablation in liquids, they are (1) ablation of solid targets in liquids and (2) laser induced chemical reactions in the solution. To our best knowledge, a combination of (1) and (2) has not been studied [17,18].

In this study, we synthesized ceria-based mixed oxides with titania (titanium dioxide, TiO_2) by a novel synthesis process, laser ablation of Ti target in aqueous solution of cerium, although a synthesized mechanism of CeO_2–TiO_2 nanoparticles has been discussed [1,19].

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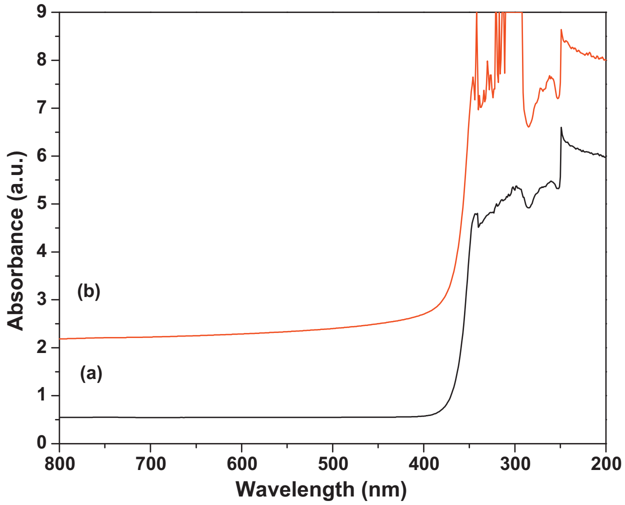

Fig. 1. UV–vis spectra of (a) 2 M cerium (III) nitrate hexahydrate aqueous solution and (b) after laser irradiation.

2. Experimental procedures

Cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, Wako Pure Chemical Industries, Ltd., Japan) was used as the raw material and was dissolved in deionized water to achieve the concentration of 2 M. Commercially used pure Ti (φ = 10, 2 mm thick, 99.99% pure) was used for a target. Nd:YAG laser was used with an output of the third harmonic (355 nm) operated at 10 Hz with a maximum output of 25 mJ/pulse and pulse duration of 7 ns. Laser irradiation was performed with 3 J/cm^2 for 5 h on Ti target immersed in 5 ml of the 2 M cerium (III) nitrate hexahydrate aqueous solution. The solution layer above the target was about 5 mm. The laser beam was irradiated through a fused silica lens ($f \approx$ 380 mm at 355 nm) at room temperature. The fabricated powders were then washed and dried in an air atmosphere. The morphologies and crystalline phase identification of the fabricated particles were characterized by transmission electron microscopy (TEM; Model JEM-2000FM, JEOL). UV–vis spectra were recorded on a V-650 spectrophotometer (JASCO).

3. Results and discussion

The results of the UV–vis absorption spectrum of the 2 M $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution before and after laser irradiation are shown in Fig. 1. The spectrum of the 2 M solution before laser irradiation exhibits a broad absorption band between 250 and 370 nm, which originate from the charge-transfer between the O_{2p} and Ce_{4f} states in O^{2-} and Ce^{4+} [20], or from OH^- and NO_3^-. Due to the synthesis of TiO_2 and CeO_2, absorbance bands in 293–320 and 340–350 nm were increased over a limit of UV–vis spectroscopy after laser ablation as shown in Fig. 1(b). It is considered that ablation of the Ti target and chemical reactions of the solution occurred during laser irradiation. A clear absorption at 293–320 nm, characteristic of rutile TiO_2 nanocrystals [21,22], and 340–350 nm, characteristic of CeO_2 nanocrystals [23], can be observed.

Fig. 2 tracks the morphological changes of CP-Ti target as a function of the laser-irradiated time from 5 min to 2 h in 2 M $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution. In the early stage of laser ablation, an ablated zone on the surface of the target was observed (Fig. 2(a)). At this stage, target material is removed and the produced nanomaterials suggest that the water and target species interact strongly to form TiO_2. A reacted product, white color in the center part of Fig. 2(a), was observed on the laser irradiated zone of the target surface. It is considered that the reaction also occurs on the target surface where the thermally excited target atoms can reactively desorbs with the aid of the hydro-molecule in aqueous solution. As the laser ablation time increased (Fig. 2(b)), the diameter of the ablated zone was increased. Ablated pool is an evidence of ablating target material.

As shown in Fig. 3(a), two kinds of particles, spherical and non-spherical, were observed. After 5 h of laser irradiation, decomposition of the particles into spherical (<30 nm) and non-spherical (<10 nm) particles, which is a typical indication of two separate particle formation mechanisms, was observed. It is expected that more than two separated physical and/or chemical origins were functioned to create two kinds of particles, spherical and non-spherical shapes, with laser irradiation [16]. It was considered that spherical nanoparicles were synthesized by explosive ejection of liquid droplets within the laser plume on the target surface. The surface displayed evidence of craters, which was confirmed by examination of the Ti target's surface after laser ablation. This dominantly corresponds to the explosive ejection of liquid droplets from the metallic target. In view of reactivity, nucleation and growth of non-spherical particles from 2 M $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution could occur with the significant reactivity of the high-temperature, high-pressure, and high-density plasma due to the absorbing the laser pulses and the plasma-induced pressure created by the shock wave. It is expected that the further growth of non-spherical particles after nucleation did not occur because of a transient progress of laser plasma plume. The particle size distribution measured from the synthesized nanoparticles by laser ablation of Ti target in cerium nitrate solution at 355 nm for 5 h (Fig. 3(d)). The distribution of particle size has a shoulder and peak around 6 nm because the number of the non-spherical particles is dominant in the fabricated particles, even if the synthesized particles are composed by two kinds of particles. Average size of the nanoparticles is 6.35 nm with a standard deviation of 2.73 nm.

In the EDX spectrum of Fig. 3(c), the peaks ascribed to Ce, Ti and O were detected from the fabricated nanoparticles. Peaks ascribed to Cu and C were also detected from carbon coated TEM grid. The composition of the synthesized nanoparticles was determined to be compounds composed with Ce, Ti and O. Ring patterns

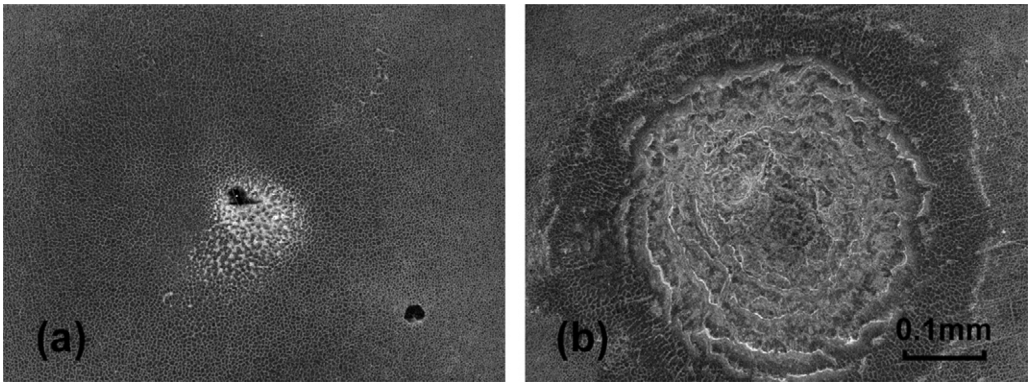

Fig. 2. SEM micrographs of CP-Ti target after laser ablation in 2 M $Ce(NO_3)_3 \cdot 6H_2O$ for (a) 5 min and (b) 2 h.

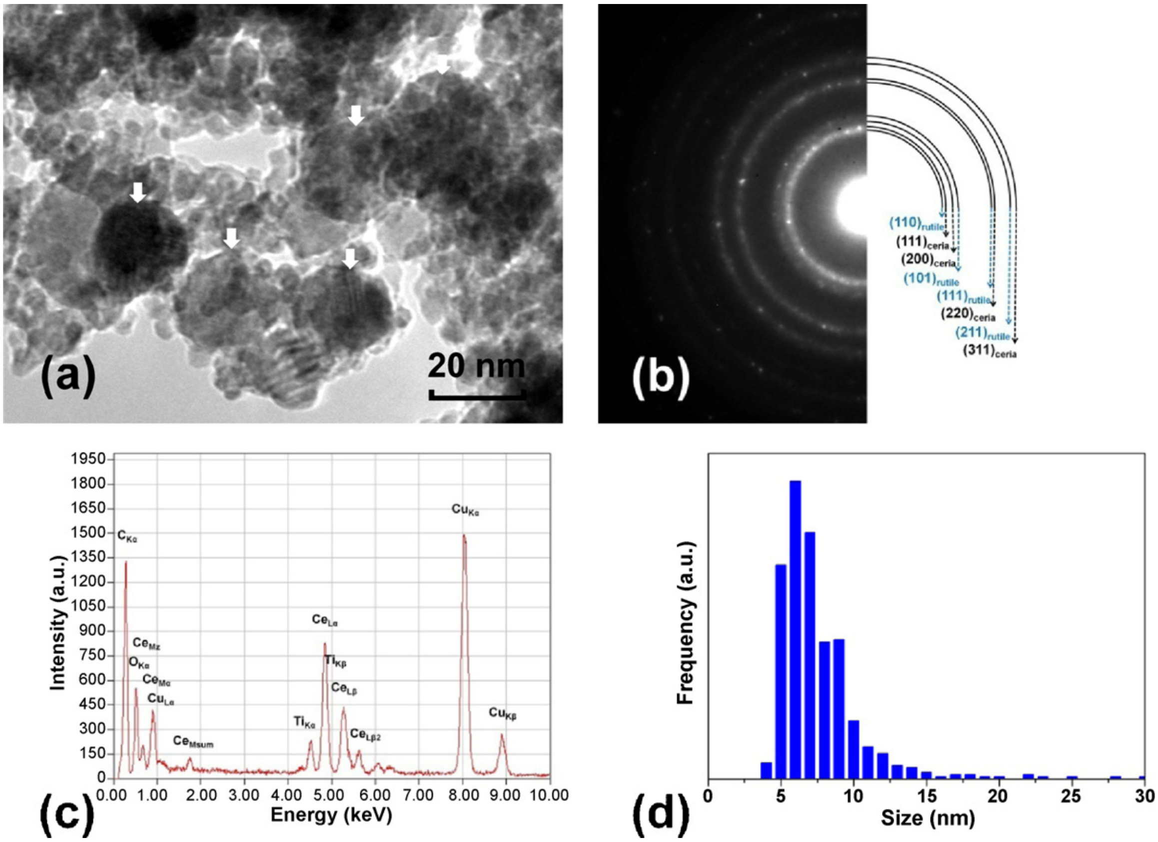

Fig. 3. TEM analysis and particle size distribution of the prepared nanoparticles by the laser ablation in 2 M $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution: (a) TEM image, (b) corresponding SAED pattern, (c) EDX image and (d) particle size distribution.

indexed according to the crystalline CeO_2 (Face-centered cubic (FCC); $a = 5.412$ Å) and TiO_2 (rutile; tetragonal, $a = 4.517$, $c = 2.940$ Å) phases were measured by SAED pattern as shown in Fig. 3(b). This suggests the presence of nanocrystalline CeO_2 and TiO_2 with random orientations.

Lattice fringes were taken to characterize the two kinds of particles, spherical and non-spherical particles, by TEM observation. The phases of both spherical and non-spherical particles were characterized with confirmation of the interplanar angle and the interplanar distance in the lattice fringes. The fringes of the spherical particle are the group of atomic planes with adjacent plane distance of 0.32 nm corresponds to the {1 1 0} plane of the rutile TiO_2 (Fig. 4(a)). The distance of the lattice fringe was well matched with the lattice plane distance of the {1 1 0} plane of the rutile calculated to be 0.319 nm. The values of lattice fringe distance, when measured for the non-spherical particles, were smaller (0.31 nm, Fig. 4(b)) than that of the spherical particles. The interplanar distance of the {1 1 1} plane of CeO_2 is calculated to be 0.312 nm. The Interplaner angle of the interplanar distances of 0.31 nm was 71° in a same grain; the interplanar angle and distance of the lattice fringe in the non-spherical shape particles correspond to {1 1 1} planes of CeO_2. From the values of measured angles and distances between the atomic planes, the spherical- and non-spherical-shaped particles were identified to be the rutile TiO_2 and the CeO_2, respectively.

TEM, EDX and SAED pattern analysis confirmed that the nanoparticles synthesized by laser ablation in the $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution is composed of CeO_2 (non-spherical particles) and TiO_2 (spherical particles). It is considered that ultra fine CeO_2–TiO_2 particles were synthesized with the chemi-

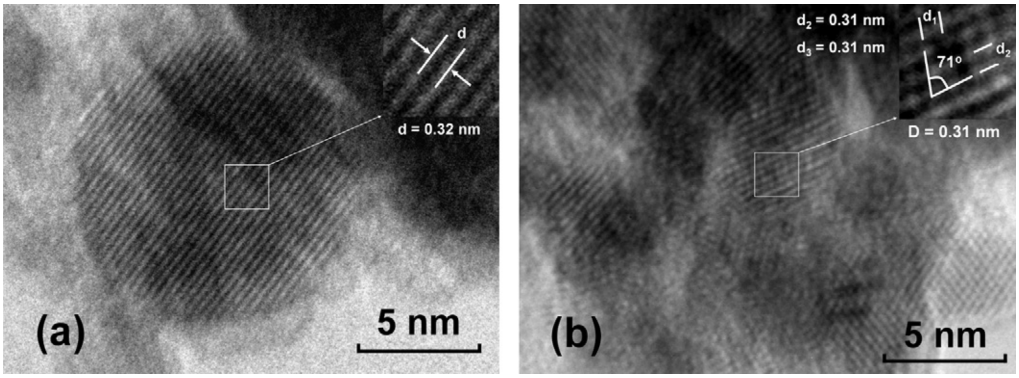

Fig. 4. TEM images of the prepared nanoparticles by the laser ablation in 2 M $Ce(NO_3)_3 \cdot 6H_2O$ aqueous solution: (a) TiO_2 and (b) CeO_2.

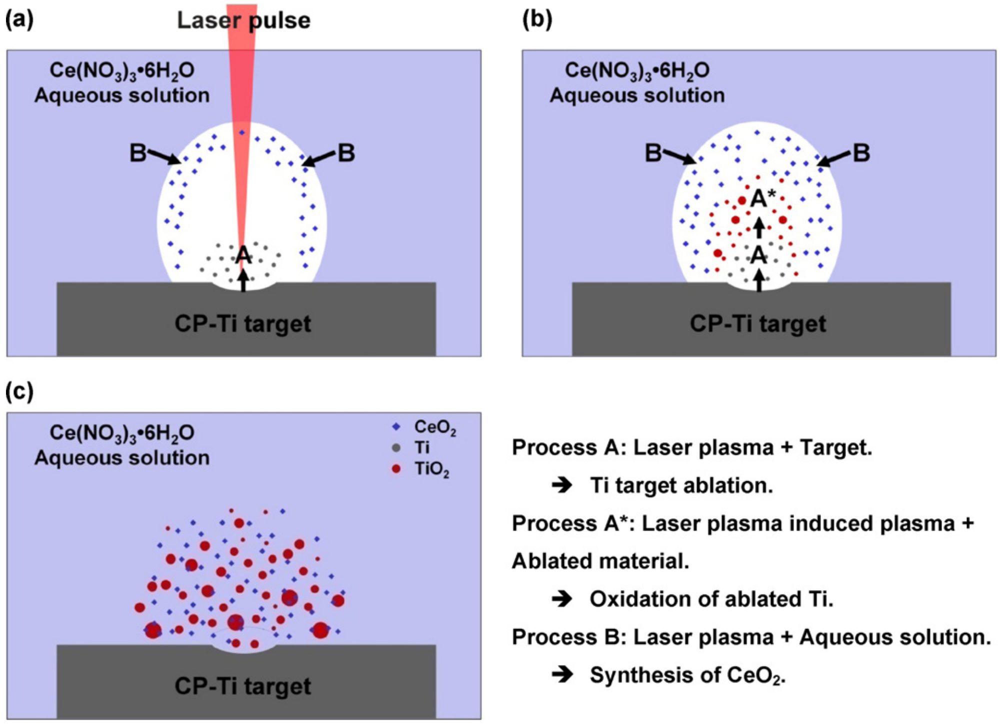

Fig. 5. Schematic diagram of laser ablation in aqueous solution process: (a) step 1: processes A and B, (b) step 2: processes A, A* and B, and (c) process 3: synthesized particles.

cal reaction between the ablated titanium species and oxygen, while the cerium species was created from the solution in the plume.

A possible formation mechanism is described below. During laser ablation on the Ti in the 2 M $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solution (Fig. 5), a plasma plume was generated on the Ti target. In the case of the reaction between the Ti target and the plasma plume, the main process is the ablation of Ti (process A). The laser-induced plasma also produces activated species from the solution. The chemical reaction between the species from the laser ablating target and the species from the liquid molecules' excitation occurs inside the laser-induced plasma (process A*). Ablated Ti is easily oxidized with the reaction between laser plasma induced plasma and ablated Ti. Rutile TiO_2 was synthesized with both Ti ablation and oxidation. The synthesis could also be attributed to aqueous oxidation, which is induced in the high-temperature and high-pressure Ti plasma on the solid -liquid interface after the interaction between pulsed laser and the metal target, to synthesis of rutile nanoparticles [24,25].

On the interface between the laser plasma plume and the aqueous solution, oxidation of cerium species also occurs because the thermodynamic state with high temperature, high pressure and high density of the laser plasma plume provides a good opportunity to the high-temperature chemical reactions between the created species and the molecules of the solution (process B). Ceria is formed due to the reaction between laser plasma and 2 M $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solution. In the solid–liquid interface, pressure ranging from several to hundreds of megabars can be obtained due to the incident laser intensity approximately from about 10^8 to 10^{15} W/cm^2 [26].

In conclusion, a new synthesis process, laser ablation in aqueous solution, is suggested to synthesize nanostructured catalyst materials composed of ceria. We believe that the new synthesis process to fabricate CeO_2–TiO_2 composites has merits due to the simple processing required. The fabrication of CeO_2/TiO_2 composite is likely to affect their multifunctional performance in catalysis and can be extended to other technological applications.

4. Summary

CeO_2/TiO_2 nanoparticles were successfully fabricated from the 2 M $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solution by the laser ablation in aqueous solution. CeO_2 with a non-spherical shape was synthesized by chemical reaction between laser plasma plume and the 2 M $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solution. The spherical-shaped TiO_2 nanoparticles were ablated from a Ti target by pulse laser ablation.

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