Synthesis of Cerium Dioxide Nanoparticles by Gas/Liquid Pulsed Discharge Plasma in a Slug Flow Reactor

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ABSTRACT: Cerium dioxide (CeO₂) nanoparticles have gained immense attention owing to their use in various applications. Current synthesis methods for CeO₂ nanoparticles including hydrothermal and chemical precipitation are time-consuming and require chemical reagents. In order to shorten the reaction time and avoid the use of organic reagents, a new method for CeO₂ nanoparticles synthesis in a slug flow system by atmospheric-pressure pulsed discharge plasma was proposed, which provided an easy, efficient, and continuous reaction at room temperature. Cerium nitrate was used as a feed solution, and starch was added as a stabilizer to separate the nucleation and growth processes of the nanoparticles to prevent their aggregation. The system was powered by a high voltage of 10.0 kV (peak-to-peak) from an ac power supply. The products were characterized by transmission electron microscopy (TEM), high-resolution TEM, energy-dispersive X-ray spectroscopy, and UV−vis spectroscopy. The results showed that when a circular capillary glass tube coil was used as the slug flow reactor, the amount of the CeO₂ nanoparticles increased compared to the case when a straight glass tube was used. The size also increased from 3.4 to 6.3 nm. The synthesis mechanism of the CeO₂ nanoparticles by gas/liquid plasma was finally elucidated.

1. INTRODUCTION

Cerium dioxide (CeO₂) nanoparticles have attracted much attention due to their inherent properties, such as catalytic ability, UV absorption ability, oxygen storage capacity, and high chemical and thermal stability.1−3 Therefore, CeO₂ materials are used in a wide range of applications in the chemical, biological, and medical fields as photocatalysts,7 antioxidants,8 anodes in solar cells,9 and sensors.10 Current methods to synthesize CeO₂ nanoparticles include hydrothermal11,12 chemical precipitation,13 solvothermal,14 and thermal hydrolysis15 methods. However, these methods are time-consuming and require chemical reagents, which are not only toxic but also increase operating costs.

Cold plasma induced by pulsed discharge is a novel technology16 and is used in various applications, such as dye treatment,17 degradation of pharmaceutical compounds,18,19 surface modification,20 and methane conversion.21 In the gas/liquid plasma system, various radical species with high reactivity are generated, such as hydroxyl radicals (OH*), hydrogen peroxide (H₂O₂), and ozone (O₃) species.22−24 Rong et al.25 reported that OH* radicals play a key role in the degradation of pharmaceutical compounds by plasma. Rahimpour et al.26 found that plasma produces O₃ and other oxidants, which are very useful in the decomposition of organic pollutants in industrial wastewater. This method did not require toxic solvents and reagents. Moreover, it was feasible to operate at room temperature and atmospheric pressure and hence showed reduced operating cost.

It is easier to initiate a discharge plasma in a gas medium than in a liquid medium.27 Discharge plasma in gas/liquid two-phase
media has been used for reactions and material processing, in which plasma is generated in the gas phase and the major reaction proceeds in the liquid phase. To produce plasma in a gas/liquid environment, bubbles are introduced from the bottom of a tank reactor.\textsuperscript{26,29} This method significantly increases the interface between the gas and liquid media. However, owing to the pressure change in the liquid, the shape and size of the bubbles change when rising in the tank, and it is difficult to produce stable plasma due to state-change bubbles, which is not beneficial for the synthesis of nanoparticles. The discharge between the electrode located above the liquid surface and the liquid itself or the electrode immersed in the liquid is used for the gas/liquid discharge system. The metal/metal ions vaporized from the electrode may be introduced into the liquid phase, resulting in the contamination of the reaction system. To solve this problem, we developed a continuous flow process using a capillary tube with a gas/liquid slug flow system, where plasma was generated in the gas phase by dielectric barrier discharge. Uniform silver nanoparticles were successfully synthesized in the system using pulsed discharge plasma.\textsuperscript{30} In the slug flow system, the feed solution and gas were alternately introduced into a capillary glass tube through a T-type junction, and the electrodes were placed outside the capillary tube. The bubbles flowed continuously in the reactor, and plasma was generated in the bubbles with high voltage. The shapes and sizes of the bubbles were uniform. The circulating flow in the liquid induced by the friction at the solid surface also accelerated the uniform reaction,\textsuperscript{31} as shown in Figure 1. It was possible to maintain a uniform interface with a high specific surface area in the system. Therefore, the slug flow system provided a uniform plasma reaction field and was effective for the synthesis of highly uniform nanoparticles. Moreover, a continuous process could be realized in the system, which improved the production rate and provided stable reaction conditions. In this study, we synthesized CeO\textsubscript{2} nanoparticles in a slug flow system using pulsed discharge plasma. The generated radicals and reaction mechanisms were investigated. Furthermore, the effects of the process factors on the synthesis of the nanoparticles were investigated.

2. MATERIALS AND METHODS

2.1. Materials. Cerium(III) nitrate (Ce(NO\textsubscript{3})\textsubscript{3}) (product no. 035-09735), starch (product no. 191-03985), and distilled water (product no. 049-16787) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Argon (purity >99.99\%) was purchased from Sogo Kariya Sanso, Inc., Nagoya, Japan. All the chemicals used in this study were used as received without further purification. The feed solution was prepared with a mixture of Ce(NO\textsubscript{3})\textsubscript{3} (1 mmol/L) and starch (0.10–0.40 wt %) aqueous solution.

2.2. Experimental Methods. Figure 2 shows the schematic of the synthesis of CeO\textsubscript{2} by atmospheric-pressure pulsed discharge plasma in a slug flow system. The slug flow system has been reported in the synthesis of silver nanoparticles\textsuperscript{30} and gold nanoparticles.\textsuperscript{32} Straight capillary tubes were used and residence time of plasma-state bubbles was approximately 10 s. However, in this study, a circular capillary glass tube coil (2.0 m × 1.8 mm i.d., G-3000, Shimadzu Co., Kyoto, Japan) was used as the slug flow reactor. Five high-voltage electrodes and 10 ground electrodes were arranged, and the distance between the adjacent electrodes was approximately 25 mm. Residence time of plasma-state bubbles was prolonged approximately 3 min. The effects of the different reactors will be discussed later. Copper (Cu) sheets with a width of 10 mm were attached to the outer surface of the glass tube as electrodes. The feed solution was introduced into the system using a high-performance liquid chromatography pump (LC-10AD, Shimadzu Co., Kyoto, Japan), and argon gas was introduced from a gas flowmeter (RK-1250, Kofloc Instruments Inc., Kyoto, Japan) into the system simultaneously through a T-type junction (SS-200-3, Swagelok). A high voltage was provided by an ac power supply (TE-HVP1510K300-NP, Tamaoki Electronics Co., Ltd., Kawaguchi, Japan). As shown in Figure 3, the voltage and current of the system were observed.
samples using a transmission electron microscope. Figure 5 shows the EDS profile and elemental maps of the CeO$_2$ nanoparticles synthesized without a stabilizer. The detected Ce and O were also detected in the elemental maps, which indicates that the cerium oxide nanoparticles are generated through plasma-induced reactions in the slug flow system.

TEM was used to examine the morphologies, growth patterns, and crystal distributions of the samples. Figure 6a shows the TEM images of the CeO$_2$ nanoparticles synthesized using 0.1 wt % starch as the stabilizer. The nanoparticles were uniform and tiny, with a mean size of approximately 6.3 nm, as determined using Nano Measurer software (Fudan Univ., Fudan, China). The size distribution of the nanoparticles was obtained by measuring more than 300 nanoparticles in several TEM images. The crystal structure of the nanoparticles was examined by obtaining their HRTEM images (Figure 6b) and selected area electron diffraction (SAED) patterns (Figure 6c). The lattice spacing of the nanoparticles was 0.31 nm, as determined from their HRTEM images. According to Verma et al., the spacing of 0.31 nm corresponds to the (111) planes of cubic CeO$_2$. Balaji et al. also attributed the fringe spacing of 0.31 nm to the (111) plane of CeO$_2$ nanoparticles. As can be observed from Figure 6c, the SAED pattern of the nanoparticles showed three rings corresponding to the (111), (220), and (311) planes of CeO$_2$ (JCPDS card no. 30-0394).

After absorbing UV–visible light, atoms and molecules undergo electronic excitation to higher-energy states. The chemical structures of atomic and molecular species can be identified from the wavelength of the light absorbed by them. Figure 7 shows the UV–vis spectra of the feed solution and products. In order to eliminate the interference of added starch, 0.1 wt % starch solution was also analyzed. All the samples except starch showed absorbance peaks at approximately 250 and 300 nm. Wang et al. reported that the absorbance peaks at around 250 and 300 nm were due to the charge transfer transition from the O$_2$ to Ce$^{4+}$ orbitals in CeO$_2$. Babitha et al. also reported similar peaks at 250 and 340 nm. The difference in the peak locations can be attributed to the difference in the particle sizes. Yin et al. reported the blue shifts of the absorption peaks with a decrease in the size of CeO$_2$ nanoparticles. The products showed higher absorbance intensity, indicating the presence of CeO$_2$ nanoparticles in them. The absorbance peak intensity of the CeO$_2$ nanoparticles increased with the addition of the stabilizer, indicating that the stabilizer addition may be beneficial for generating CeO$_2$ nanoparticles in this system investigated in this study.

3.2.2. Effects of Process Factors on the Synthesis of CeO$_2$ Nanoparticles. 3.2.2.1. Influence of the Stabilizer on the Synthesis of CeO$_2$ Nanoparticles. In the synthesis of nanoparticles, biomaterials with functional groups, including COOH, –OH, and –NH$_2$, are typically used to stabilize and cap metal ions to prevent their aggregation. In this study, starch, which is easily available, economical, and environmentally friendly, was used as the stabilizer. It is well known that starch can be used as a stabilizer for the synthesis of different nanoparticles.

As can be observed from Figure 8, the CeO$_2$ nanoparticles exhibited aggregation in the absence of the stabilizer. Initially, instantaneous and homogeneous nucleation occurred in the plasma reactor. In the absence of a stabilizer, the nanoparticle nucleation and growth processes in solutions are not adequately separated, which leads to the incorporation of the monomers into the previous stable nuclei, resulting in the generation of nonuniform nanoparticles. Therefore, in this study, we added starch as a stabilizer to the feed solution to separate the nucleation and growth processes appropriately to avoid secondary nucleation, which was conductive to the formation of uniform CeO$_2$ nanoparticles. Darroudi et al. proposed that cerium cations in aqueous solutions are attracted by the oxygen of hydroxyl groups in starch, and starch can cover

Figure 3. Voltage (black) and current (red) discharge waveforms.

Figure 4. Photographs of feed solution (left) and product solution (right): (a) room lighting; (b) Tyndall effect in solutions.
the surface of nanoparticles as a capping agent to prevent their excessive aggregation. Therefore, the diameter of the resulting nanoparticles can be controlled.

The effect of the stabilizer concentration on the formation of the CeO$_2$ nanoparticles was investigated. The concentration of starch in the feed solution was varied from 0.1 to 0.4 wt %. As shown in Figure 9, with an increase in the starch concentration from 0.1 to 0.4 wt %, the absorbance peaks of the CeO$_2$ nanoparticles showed similar shapes, and the intensity of the absorption was increased. Dao et al.$^{43}$ reported that with the content of CeO$_2$ nanoparticles increased, UV absorption intensity was enhanced and UV absorbance peak increased. This indicates that the amount of the CeO$_2$ nanoparticles

Figure 5. (a) Gray TEM image of CeO$_2$ nanoparticles with the corresponding EDS maps for (b) cerium and (c) oxygen; (d) EDS spectrum.

Figure 6. (a) TEM images, (b) HRTEM image, and (c) SAED pattern of CeO$_2$ nanoparticles synthesized with starch as the stabilizer.

Figure 7. UV–vis spectra of feed solution and solution products containing CeO$_2$ nanoparticles.

Figure 8. TEM images of CeO$_2$ nanoparticles synthesized without the stabilizer.

Figure 9. UV–vis spectra of CeO$_2$ nanoparticles synthesized with different concentrations of starch.

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formed in the solution increased with an increase in the starch concentration.

As shown in Figure 10, the mean sizes of CeO$_2$ nanoparticles obtained at the starch concentrations of 0.1, 0.2, and 0.4 wt % were 6.3, 4.9, and 5.1 nm, respectively. This indicates that the starch concentration did not significantly affect the size of the CeO$_2$ nanoparticles. Thus, higher starch concentrations may be beneficial for stabilizing and capping the CeO$_2$ nanoparticles. Yamada et al.\textsuperscript{30} also obtained high-concentration silver nanoparticles at high starch concentrations by pulsed discharge plasma, and they observed the interaction between $-\text{OH}$ functional group in the starch and silver nanoparticles through Fourier transform infrared spectroscopy.

3.2.2. Influence of the Slug Flow Reactor on the Synthesis of CeO$_2$ Nanoparticles. In our previous study,\textsuperscript{30} a straight capillary glass tube with two electrodes was used as the slug flow reactor. As shown in Figure 11a, the length of the glass tube was 0.12 m and the distance between the two copper electrodes was approximately 25 mm. CeO$_2$ nanoparticles could be synthesized by pulsed discharge plasma in the system; however, the amount of the CeO$_2$ nanoparticles generated was low. Therefore, in this study, we increased the length of the reactor tube and the number of electrodes to prolong the reaction residence time to increase the CeO$_2$ nanoparticle yield. Yamada et al.\textsuperscript{17} used a circular capillary glass tube coil as the slug flow reactor for decolorizing methylene blue and achieved high decolorization efficiency. As shown in Figure 11b, fifteen copper electrodes, including five high-voltage electrodes and 10 ground electrodes, were arranged on a circular capillary glass tube coil with a length of 2.0 m. The distance between the two adjacent electrodes was approximately 25 mm. The residence time of the plasma state bubbles increased approximately from 10 s to 3 min with the use of this assembly.

Impact ionization, which occurs in a high local electric field, is the main ionization mechanism in electric discharges.\textsuperscript{27} In this process, electrons are accelerated and ionize gas molecules or atoms to generate more electrons. The use of the circular capillary glass tube coil as the slug flow reactor increases the number of plasma production sites, and the number of energetic electrons increases with an increase in the input energy. More electrons impact the gas molecules, which leads to the generation of more reactive species, including OH$^+$, H$_2$O$_2$, and O$_3$ species.\textsuperscript{30,31} Nanoparticles are obtained after the nucleation and growth processes.\textsuperscript{30} With an increase in the number of electrodes and residence time, a large number of Ce$^{3+}$ ions get involved in the oxidation reaction to produce hydroxide complexes.\textsuperscript{12} For cold plasma, most of the coupled electrical energy is primarily channeled to the electron component to produce energetic electrons.\textsuperscript{44} Therefore, electronic temperature is much higher than room temperature.\textsuperscript{45,46} CeO$_2$ nanoparticle nuclei are generated via dehydration from the hydroxide complexes at the high local plasma temperatures.\textsuperscript{47} An increase in the nucleation frequency results in an increase in the number of the nuclei and CeO$_2$ nanoparticles formed.

Figure 12 shows the UV–vis spectra of the CeO$_2$ nanoparticle-containing solutions obtained using different slug flow reactors. The CeO$_2$ nanoparticles showed significant UV absorption peaks at approximately 250 and 300 nm. The intensity of these peaks increased when a circular capillary glass
tube coil was used as the slug flow reactor, indicating an increase in the number of the CeO2 nanoparticles formed.

The particle size distributions of the CeO2 nanoparticles synthesized in the two reactors were also analyzed. As shown in Figure 13b, the mean size of the CeO2 nanoparticles synthesized in the circular capillary glass tube was approximately 6.3 nm, and the mean size synthesized in the straight capillary tube was approximately 3.4 nm (Figure 10b). When the circular capillary glass tube coil was used as the reactor, the nucleation frequency and number of nuclei increased. The time required for the growth of the nuclei increased with an increase in the residence time, which resulted in an increase in the size of the CeO2 nanoparticles. Furthermore, the aggregation of the nuclei resulted in the generation of larger nanoparticles.

3.3. Synthesis Mechanism of the CeO2 Nanoparticles.

Figure 14 shows the synthesis mechanism of the CeO2 nanoparticles by atmospheric-pressure pulsed discharge plasma.

\[
\text{H}_2\text{O} + \text{Ar}^* \rightarrow \text{OH}^* + \text{H}^* + e^- \\
\text{OH}^* + e \rightarrow \text{OH}^- \\
\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}_2 \\
\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O} + \text{O} \\
\text{O} + \text{OH}^* \rightarrow \text{O}_2 + \text{H}^* \\
\text{O} + \text{O}_2 \rightarrow \text{O}_3
\]

Because of the generation of oxidizing radicals and molecules by plasma, the Ce3+ ions in the feed solution tended to be converted into Ce4+ ions, as shown in reaction 8. Because Ce4+ ions have low basicity and high charge, strong hydrolysis reactions tended to occur.55 The Ce4+ ions combine with H2O molecules and OH− ions in the solution to form hydroxide complexes Ce(OH)\(_x\)(H\(_2\)O)\(_{y-x}\), which served as the precursors for CeO2, as shown in reaction 9. The dehydration reaction tended to occur at high local plasma temperatures. H2O as a polar molecule attracted protons from the OH− ions, triggering the crystallization of CeO2, according to reaction 10.

\[
\text{Ce}^{3+} + \text{H}_2\text{O} \rightarrow \text{Ce(OH)}^{3+} + \text{H}^* + e^- \\
\text{Ce}^{4+} + x\text{OH}^- + y\text{H}_2\text{O} \rightarrow [\text{Ce(OH)}_x(\text{H}_2\text{O})_{y-x}]^{(4-x)+} \\
[\text{Ce(OH)}_x(\text{H}_2\text{O})_{y-x}]^{(4-x)+} + \text{H}_2\text{O} \rightarrow \text{CeO}_2 \cdot n\text{H}_2\text{O} + \text{H}_3\text{O}^+
\]

where \(x\) and \(y\) are positive integers. Instantaneous and homogeneous nucleation occurred in the slug flow system by pulsed discharge plasma. The CeO2 nanoparticles were generated after a rapid growth process at high excitation temperatures generated by plasma.33 When starch was added to the feed solution as a stabilizer, the cerium cations in the solution were attracted by the oxygen in the hydroxyl groups of starch.32 Starch was wrapped around the surface of the CeO2 nanoparticles to separate the nucleation and growth stages appropriately, which made it possible to control the diameter of the nanoparticles and generate uniform CeO2 nanoparticles.
4. CONCLUSIONS

In this study, uniform CeO$_2$ nanoparticles were synthesized in a slug flow system using atmospheric-pressure pulsed discharge plasma. In this system, radical species were produced and reacted with cerium ions (III) in the solution, resulting in an instantaneous and homogeneous nucleation and rapid growth of the nanoparticles. The effects of the process factors on the synthesis of the CeO$_2$ nanoparticles were discussed. The main findings of the study are as follows:

1. The slug flow system provided a continuous reaction field in the gas/liquid plasma environment, which was beneficial for the synthesis of uniform nanoparticles. When a circular capillary glass tube coil was used as the slug flow reactor and Ce(NO$_3$)$_3$ with 0.1 wt% starch was used as the feed solution, uniform CeO$_2$ nanoparticles with a size of approximately 6.3 nm were obtained.

2. Starch was added as a stabilizer to separate the nucleation and growth processes and prevent the aggregation of the resulting nanoparticles. With an increase in the starch concentration from 0.1 to 0.4 wt%, the amount of the CeO$_2$ nanoparticles increased and their size distribution did not change significantly.

3. The difference between the straight and circular glass tubes as the slug flow reactors was discussed. When the circular capillary glass tube coil was used as the reactor, a large number of CeO$_2$ nanoparticles with increased size distribution (from 3.4 to 6.3 nm) were formed as compared to the case when the straight glass tube was used.

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Notes
The authors declare no competing financial interest.

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