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Original Research Paper

Synthesis of CeO_2 nanocrystalline powders using DC non-transferred thermal plasma at atmospheric pressure

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ABSTRACT

Nanocrystalline CeO_2 powders were synthesized by using a DC non-transferred thermal plasma system at atmospheric pressure. $Ce(NO_3)_3{\cdot}6H_2O$ powders were employed as a raw material and a cerium nitrate solution was used as a precursor. The liquid precursor was injected into a cylindrical reactor through two different directions: the vertical and the horizontal direction. The difference of the properties of CeO_2 nanocrystalline powders according to the directions of injection were investigated by using XRD, TEM and an UV/VIS/NIR spectrometer. For the horizontal case, the cylindrical reactor acted as a cyclone providing greater tangential velocities. The higher tangential velocities increased the centrifugal forces of as-synthesized powders causing the thicker deposition layer of powders at the upper part of the reactor. The thicker deposition layer of powders was considered as the reason of the less heat treatment of powders prepared. This was confirmed by the relatively lower intensities of XRD peaks. In addition, CeO_2 nanocrystalline powders were tested as a photocatalyst using the gaseous 2-propanol decomposition. For the test, the photocatalytic activity was defined and evaluated. It appears that CeO_2 nanocrystalline powders are more suitable for the treatment of the dyes in the wastewater than the removal of the volatile organic compound (2-propanol).

1. Introduction

Cerium oxide (ceria, CeO_2) is a rare-earth oxide and has been widely applied in many fields. Typical application areas are polishing materials, catalysts, etc. [1]. Recently, few cases regarding the syntheses of ceria nanocrystalline powders have been reported, especially using the liquid-phase methods [1–5]. Unlike the liquid-phase preparation of CeO_2, a vapor-phase method was employed to synthesize CeO_2 nanocrystalline powders in this work because it has been expected that the vapor-phase method can synthesize CeO_2 nanocrystalline powders with relatively higher purity without generating wastewater streams compared with the liquid-phase methods. For the vapor-phase method, some researchers reported the syntheses of pure CeO_2 and the doped CeO_2 nano-powders using the radio frequency (RF) inductively coupled thermal plasma processing [6,7]. The RF inductively coupled thermal plasma processing has been considered to hold several advantages such as the large thermal plasma volume, and the high energy density. However, it also holds disadvantages such as the huge employment of gases, and the great use of the electricity. In other words, the RF inductively coupled thermal plasma processing is an expensive method. For example, the approximate cost of various kinds of plasma reactors has been presented by Roth J. R. According to his analysis, the cost for the inductive plasma reactors was 0.5–3.0 US dollars per watt ($/W) and that for the DC was 0.2–1.0 $/W [8]. Therefore, we tried to prepare CeO_2 nanocrystalline powders at a more economically and environmental-friendly basis using the DC non-transferred arc plasma reactor.

A liquid solution was prepared as a precursor and introduced into a cylindrical reactor through two different directions. The effects of the directions of the liquid precursor injection on the properties of ceria nanocrystalline powders synthesized were investigated in this process. Additionally, the prepared CeO_2 nanocrystalline powders were tested as a photocatalyst using the gaseous 2-propanol decomposition.

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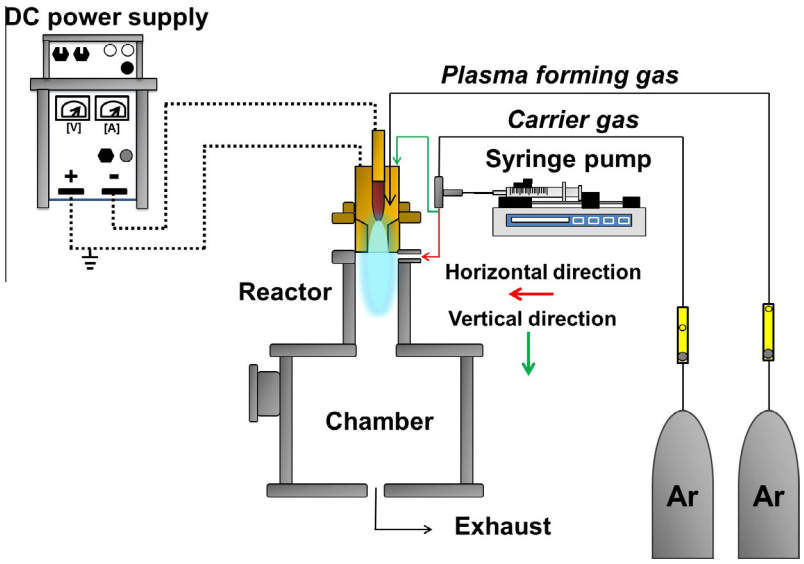

Fig. 1. Schematic diagram of the DC non-transferred thermal plasma system.

2. Experimental

2.1. Synthesis of CeO_2 nanocrystalline powders

CeO_2 nanocrystalline powders were synthesized by a DC non-transferred thermal plasma system using the cerium nitrate solution as a precursor at atmospheric pressure as shown in Fig. 1. The raw material of $Ce(NO_3)_3{\cdot}6H_2O$ powders (Alfa Aesar, stock no. 11330) was dissolved in the distilled-water to make the cerium nitrate solution and the concentration of the liquid precursor solution was 1 M. The liquid precursor solution was fed into the cylindrical reactor through a 1/8-in. Teflon tube. An argon gas was employed to carry the liquid solution at 8 L/min to the cylindrical reactor and was also used to generate and maintain the thermal plasma at the flow rate of 15 L/min. In this work, the liquid solution was injected into the cylindrical reactor through two different directions. One was the vertical injection of the liquid solution and the other was the horizontal injection as presented in Fig. 1. The aim was to investigate the effects of the directions of the precursor injection on synthesized ceria particles' properties. Generally for the DC non-transferred thermal plasma system, the horizontal injection of the precursor into the cylindrical reactor has been preferred because it is relatively easier for researchers to introduce the reactants into the cylindrical reactor.

A syringe of 10 mL was connected to the 1/8-in. Teflon tube using a tee fitting to feed the liquid solution into the cylindrical reactor. The solution inside the syringe was sent to the tee by a syringe pump (KDS-100 Model, KD Scientific Inc.) and the flow rate of the solution was 60 mL/h. The solution injected into the cylindrical reactor formed liquid droplets; it appeared that the droplets were immediately vaporized by the high temperature caused by the thermal plasma flame. For example, the temperature distribution of an argon-nitrogen thermal plasma flame is presented in the modelling result of Kim et al. the temperature of the flame at the center is about 13,000 K at 10.2 kW [9].

CeO_2 powders were collected on the inside wall of the cylindrical reactor cooled by the water. Since the water cooling provided the cold inner wall surface, the supersaturation ratio of the vapor phase of CeO_2 on the inner wall was high, resulting in the solidification of CeO_2. It is easily expected for the both injection cases because this vapor-method is the homogeneous chemical vapor deposition process. Almost all of the CeO_2 powders were collected at the upper part of the cylindrical reactor. The upper part was about 2 cm below from the top of the cylindrical reactor. The inner diameter was 4 cm. The details of the experimental conditions are given in Table 1.

Table 1
Details of the experimental conditions.

Operating parameters	Values
Total voltage (V)	30
Total current (A)	300
Input power (kW)	9
Plasma forming gas (Ar) flow rate (L/min)	15
Carrier gas (Ar) flow rate (L/min)	8

The identification of the prepared powders as CeO_2 was performed using X-ray diffraction (XRD, D/MAX 2200, Rigaku Co.) and the phase compositions of CeO_2 powders were also confirmed by the XRD. The morphologies of the powders were observed by the field emission transmission electron microscopy (FE-TEM, JEM-2100F, Jeol Co.). To estimate the band-gap energies of CeO_2 powders, an UV/VIS/NIR spectrometer (Lambda 750, PerkinElmer) was used.

2.2. Evaluation of photocatalytic activity of CeO_2 nanocrystalline powders

The photocatalytic efficiencies of the prepared CeO_2 nanocrystalline powders were estimated by monitoring the decomposition of the gaseous 2-propanol (isopropyl alcohol, IPA). An aqueous suspension containing 8.0 mg of the CeO_2 nanocrystalline powders was spread on a 2.5×2.5 cm^2 Pyrex glass in film form and subsequently dried at room temperature. The net volume of the gas-tight photocatalytic reactor was 200 mL and the photocatalytic film was located at the center of the photocatalytic reactor. The entire area of the photocatalytic film (2.5×2.5 cm^2) was irradiated by a 300 W Xe lamp through a water filter to cut-off the IR spectrum. After evacuating the photocatalytic reactor, 1.6 mL of the water-diluted IPA (IPA:H_2O = 1:9 in volume) was injected into the photocatalytic reactor. The total pressure of the photocatalytic reactor was then increased to 750 Torr by additional oxygen gas. Under these conditions, the IPA and H_2O remained in the vapor