The Synthesis, Characterization and Optical Properties of Nanocrystallined Cerium Dioxide by the Hydrothermal Method

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Nano-sized cerium dioxides (CeO₂) are prepared by the hydrothermal method, using nitric cerium. The XRD study shows that nano-sized CeO₂ has an appreciable amount of cubic phase. The nano-sized CeO₂ obtained has an average particle size in the range of 4.5–10.3 nm. TEM micrographs show well-dispersed spherical-like and cubic-like CeO₂ nanoparticles. The UV–DRS absorption spectrum for alkali-treated CeO₂ shows an absorption peak at 365–384 nm. [doi:10.2320/matertrans.M2016285]

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1. Introduction

Cerium dioxide (CeO₂) is a cheap material that has a rapidly increasing number of applications in numerous fields, because of its ability to store large amounts of oxygen, its high oxygen ionic conductivity¹⁾ and its ability to absorb large amounts of ultraviolet (UV).²⁾ CeO₂ also has widespread applications in many fields, such as its uses as the solid-state electrolyte for fuel cells,³⁾ as an abrasive for chemical-mechanical planarization,⁴⁾ in automotive exhaust catalysts,⁵⁾ gas sensors⁶⁾ and UV-shielding materials.⁷⁾ In recent years, nano-sized CeO₂ has been the subject of much study because of improvements in its redox properties, transport properties and its surface-to-volume ratio with respect to bulk materials.⁸⁾ In order to prepare CeO₂ nanocrystalline powder, various methods are used to prepare the CeO₂ nanostructures, such as combustion processing,⁹⁾ solid-state reaction,¹⁰⁾ mechano-chemical processing,¹¹⁾ solvothermal processing,¹²⁾ the sol-gel process¹³⁾ hydrothermal processing¹⁴⁾ and precipitation.¹⁵⁾ All of these processes have unique advantages for growing CeO₂ nanostructures. Hydrothermal synthesis is one of most effective and economical routes, as it allows a one-step low-temperature synthesis, results in powder with high reactivity, good crystallinity and uniform shape. The reactions, such as hydrolysis, co-precipitation, oxidation, decomposition and complexation, can be performed using the hydrothermal method.¹⁶⁾

Although CeO₂ systems have been investigated, the reaction time effect in CeO₂ nanoparticles with well-characterized size and the band gap have not been examined previously. Herein, this study synthesizes nano-sized CeO₂ using the hydrothermal method. Nano-sized CeO₂ is synthesized using nitric cerium and an ammonia reaction. This process is cheaper, simpler, allows control of shape and is suited to large-scale production. The structural and optical properties were studied using XRD, TEM and UV-Vis.

2. Experimental Procedure

This paper reports a hydrothermal route for the fabrication of CeO₂ poly-crystalline nanoparticles. Cerium nitrate hexahydrate Ce(NO₃)₃·6H₂O (99.9%, Alfa Aesar) and ammonia solution (25% NH₄OH, Junsei Chemical) were used as starting materials. Ce(NO₃)₃·6H₂O was dissolved in de-ionized water to produce a transparent solution with a concentration of 0.1 M, which was added to the ammonia solution in a fixed amount and stirred vigorously for 2 hr. The pH value was adjusted to 7 by adding nitric acid and ammonia. This solution was vigorously stirred for 4 hr until the reaction reached equilibrium. 100 ml of the mixture was then transferred to a Teflon-lined stainless-steel autoclave. A temperature of 180°C was maintained for 2, 6, 12, 24 and 48 hr, after which the solution was cooled to room temperature. After reaction, the solid products were filtered and rinsed, firstly with de-ionized water and then with alcohol. The obtained solid was dried overnight at 343 K. The nanoparticles of all CeO₂ products have a characteristic light yellow color. The crystallinity, purity, crystal morphology and size of the CeO₂ products were analyzed using powder XRD and TEM. All CeO₂ products were obtained as pure phases at high yields.

Thermogravimetric (TG, Perkin-Elmer thermogravimetric analyzer TGA-7) analysis were conducted on a 50 mg powder sample at a heating rate of 5°C/min from 25°C to 800°C in air with Al₂O₃ powders as a reference material, and the thermal behavior was examined by differential scanning calorimetric (DSC, 2920 Modulated DSC, TA Instruments) analysis in the as-prepared materials.

XRD data was collected by means of powder XRD (Rigaku D/max-IV Tokyo, Japan) using CuK_α radiation (K_α = 0.1518 nm). TEM and HR-TEM images were obtained using high-resolution field-emission transmission electron microscopy (HR-TEM 2100). Samples were generally prepared by depositing a drop of the dilute nanoparticle solution in alcohol onto carbon-coated Cu grids. A spectroscopic study of the product was performed using a UV–Vis. (JASCO, UV-760) spectrophotometer.

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3. Results and Discussion

Following the heat treatment of the CeO_2 powder in the hydrothermal reactor, the precipitation product was obtained. The nature and morphology of the product were then observed. After several washings, the product was filtered and dried. The crystalline phase and the effect on the growth of crystals in the CeO_2 nanoparticles that were synthesized using the hydrothermal method at 180°C for various times were determined.

Figure 1 shows the TGA/DSC analysis of the precursor as-prepared CeO_2 powder. The total measured weight loss from 25 to 800°C was about 7.3%. A unique endothermic peak appears at around 53°C and there is an exothermic band at around 206°C . Above 500°C , the weight loss decreases and eventually becomes negligible. In general, the weight loss associated with the structural water molecule is about 17.3%, calculated the thermal decomposition formula as follow:

In the present study, the relative lower content of adsorbed water can be explained, as the precipitate consisting of a partially hydrated form of CeO_2 , (i.e. $\text{CeO}_2 \cdot x\text{H}_2\text{O}$), for which about 7.3% weight loss occurs on decomposition of the partially hydrated quality for the unit of CeO_2 , and the precipitate consists of a mixture of phases like $\text{CeO}_2 \cdot 2\text{H}_2\text{O} + \text{CeO}_2^{17)}$. At 500°C , the weight loss rate becomes slower and continues to change slightly. The precipitation reactions can be described¹⁷⁾ as follows:

The use of ammonium hydroxide results in forming a slightly yellowish precipitate from cerium nitrate solution. The Ce^{3+} would be oxidized to Ce^{4+} in a higher pH value solution¹⁸⁾, i.e. $\text{Ce}^{3+} + \text{H}_2\text{O} \rightarrow \text{Ce}(\text{OH})^{3+} + \text{H}^+ + \text{e}^-$ with subsequent hydrolysis to $\text{Ce}(\text{OH})_4$ and precipitation. However, oxidation of $\text{Ce}(\text{OH})_3$ also occurs readily in air at room temperature to form a slightly yellow $\text{Ce}(\text{OH})_4$, which is a hydrous oxide and can also be described as $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ dehydrates progressively.

Fig. 1 The TGA/DSC curves for CeO_2 precursor from room temperature to 800°C .

Figure 2 shows the results for the CeO_2 nanoparticles that were synthesized using heat treatment at 180°C for 2, 6, 12, 24 and 48 hr. XRD was used for the analysis and all responses demonstrate that the main body is CeO_2 , with the intensity position at approximately $2\theta = 28.54, 33.07, 47.48, 56.33$ and 59.08° . The crystalline phases, (111), (200), (220), (311) and (222), conform with the literature (JCPDS Card No. 81-0792), which demonstrates that the crystals have a face-centered cubic fluorite structure. There is a slight improvement in the crystalline structure as the reaction time increases for the as-synthesized CeO_2 powders after hydrothermal treatment at a fixed temperature of 180°C for reaction times of 2, 6, 12, 24 and 48 hr. As the reaction time increases, the intensity of the diffraction peaks increases significantly, because larger crystals are formed and there is a greater degree of crystallization for longer hydrothermal reaction times. The crystallite size of the heat-treated CeO_2 , as calculated using the FWHM and Scherrer's formula for (111) XRD peaks is in the range of 4.5–10.3 nm. It is interesting that the crystallite size increases linearly at elevated temperatures between 2 and 48 hr. CeO_2 particles grow only slightly by about 4.5 nm after treatment for 2 hr, but can become as large as about 10.3 nm after 48 hr, as shown in Table 1. It is noted that the crystallite sizes that are calculated from the peak broadening are nearly the same

Fig. 2 The XRD patterns for CeO_2 that is synthesized using the hydrothermal method at 180°C for (a) 2, (b) 6, (c) 12, (d) 24 and (e) 48 hr.

Table 1 The mean crystal size and bandgap energy for CeO_2 that is synthesized using the hydrothermal method at 180°C for various durations.

Time (hr)	Mean crystallite size (nm)	Bandgap energy (eV)
2	4.5	3.70
6	6.2	3.61
12	8.1	3.52
24	9.7	3.32
48	10.3	3.20

as those measured by TEM.

Figure 3 shows the TEM images and the SAED patterns for the CeO₂ nanoparticles. Uniform poly-crystalline CeO₂ nanoparticles are obtained at different stages of a facile hydrothermal system at 180°C. As Fig. 3(a) shows, the CeO₂ particles are spherical-like and polyhedron-like in shape, with an average size in the range of 4–6 nm. Prolonging the reaction time to 12, 24 and 48 hr results in a slight increase in the size of the nanoparticles, with respective average grain sizes in the range 6–8, 8–10 and 8–11 nm. For a reaction time of up to 24 hr, the grains exhibit almost no growth and the size and morphology of each product are comparatively uniform. The morphology of these nanoparticles is polyhedron-like, with some spherical-like shapes. It has been proposed¹⁹⁾ that during the oxidation from Ce⁺³ to Ce⁺⁴ (or the conversion from Ce⁺³ to Ce⁺⁴), the formation of CeO₂ nanoparticles with different morphologies (such as spherical and polyhedron-like) depends strongly on the pH value of the solution. The pH values of those solutions were neutral, so the nanoparticles have more varied spherical, cubic and regular hexahedral morphologies.

Figure 4 shows the HR-TEM images for the CeO₂ nanoparticles. The obtained CeO₂ nanoparticles have a regular cubic shape with a mean size of 6–10 nm and some have a nano-spherical shape with a size of about 4–8 nm. These samples have a respective lattice spacing of 0.32 nm and 0.27 nm in *d*-spacing. The lattice planes with *d*-spacing of 0.32 nm correspond to the (111) planes, and *d*-spacing of 0.27 nm corresponds to the (002) planes. Those with spherical and octahedral shapes that are enclosed by eight {111} planes exhibit the highest surface density of atoms and the lowest surface energy for a face-centered cubic structured CeO₂.^{14,20)}

Figure 5 shows the UV-Vis. diffuse reflectance spectra for CeO₂ that is synthesized at 180°C for 2, 6, 12, 24 and 48 hr at

a concentration of 5 mg/100 ml. A strong UV absorption peak is noted and there is a red shift in the peak (from 365 to 384 nm) as growth time increases (2~48 hr). This demonstrates that the particle size increases as growth time is prolonged.²¹⁾ When the particle size is reduced, the band gap energy increases, so the absorption edge shifts toward a shorter wavelength and the smaller particles exhibit better UV absorption. However, the extent of agglomeration in the powders has little influence on their ability to absorb UV radiation. The UV absorption domains of 365 to 384 nm are at the long end of the UVA spectrum, with wavelengths between 340 and 400 nm. This domain of UVA radiation is responsible for early skin aging.²²⁾

The size-related band gap shift of semiconductor nanocrystals can be quantified. The direct band gap can be determined by fitting the absorption data to the direct transition equation by extrapolating the linear portions of the curves to

Fig. 4 The HR-TEM images for CeO₂ that is synthesized using the hydrothermal method at 180°C for (a) 2, (b) 12, (c) 24 and (d) 48 hr.

Fig. 3 The TEM images and the SAED patterns for CeO₂ that is synthesized using the hydrothermal method at 180°C for (a) 2, (b) 12, (c) 24 and (d) 48 hr.

Fig. 5 The absorption spectra for CeO₂ that is synthesized using the hydrothermal method at 180°C for (a) 2, (b) 6, (c) 12, (d) 24 and (e) 48 hr.

Fig. 6 A $(\alpha h\nu)^2$ versus $(h\nu)$ plot for estimating the band gap. (The Tauc band gap (E_g) was obtained from the extrapolation of the linear part of the curve at $\alpha = 0$.) (a) 2 hr, (b) 12 hr, (c) 24 hr, (d) 48 hr.

absorption equal to zero, such as

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the direct band gap, and A is a constant. The band gap value for the samples was calculated using the Tauc plot, a narrowing of the band gap value is observed as growth time decreases. The results show that CeO_2 with band gap of 3.70, 3.61, 3.52, 3.32 and 3.20 eV, for 2, 6, 12, 24 and 48 hr, respectively, as shown in the Fig. 6 and Table 1. These values are comparable to data reported previously in the literatures.^{23,24} The band gap will increase with the decrease in particle size, this means that smaller particles exhibit better UV absorption.²⁵

For spherical-like nanoparticles with an infinitely high potential energy outside the sphere, the change in the optical absorption of synthesized CeO_2 is mainly due to the CeO_2 particle size.²⁶

4. Conclusions

This study fabricates CeO_2 spherical and cubic crystallites using a facile conventional hydrothermal process that is not assisted by a surfactant via the oriented aggregation of small CeO_2 nanoparticles in the range of 4–6 nm. Prolonging the reaction time results in greater growth of the nanoparticles. The grain diameter is 8–11 nm after a reaction time of 48 hr.

The crystal grows to twice its initial size. CeO_2 appears in the form of spherical and cubic-like grains, under neutral conditions. UV-Vis. light irradiation tests on the as-obtained CeO_2 crystallites show that the UV absorption domains are from 365 to 384 nm, so they are ideal for as an ultraviolet shielding material in optics products.

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