



Isothermal crystallization kinetics and effect of crystallinity on the optical properties of nanosized CeO₂ powder

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Abstract

The isothermal crystallization kinetics and effect of crystallinity on the optical properties of cerium dioxide (CeO₂) nanopowders synthesized using a coprecipitation route at 293 K and pH 9 were investigated using X-ray diffraction, transmission electron microscopy, selected area electron diffraction, and ultraviolet–visible absorption spectrophotometry. The activation energy of CeO₂ crystallization from dried cerium dioxide precursor powders by isothermal method of 64.1 ± 3.24 kJ/mol was obtained. The average value of the growth morphology parameter (n) is 1.94, meaning that two-dimensional growth with plate-like morphology was the primary mechanism of CeO₂ crystallization from cerium dioxide precursor powders. The indirect band gap energy (E_i) of CeO₂ decreased from 3.03 eV to 2.83 eV when the crystallinity increased from 18% to 82%, and the direct band gap energy (E_d) of CeO₂ also decreased from 3.76 eV to 3.64 eV.

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1. Introduction

Recently, various synthetic routes, such as hydrothermal [1], sol–gel [2], microwave [3], microemulsion [4], reverse micelles [5], and homogeneous precipitation [6,7] have been used for synthesizing nanosized CeO₂ particles with promising control of the properties. Among those, homogeneous precipitation is one of the most promising techniques because of the advantage of a low-cost, easy-to-acquire apparatus, a simple synthesis process, and nanometric precursor particles. For the CeO₂ nanoparticles prepared, although precipitation techniques have been widely used, most studies were focused on the effects of cerium precursors, ligands, additives, and reaction media for CeO₂ nanoparticle formation.

Nanocrystalline cerium dioxide (CeO₂) powders have been the subject of numerous studies because of its many useful applications, such as solid oxide fuel cells [8], photocatalytic

oxidation of water [9], gas sensors [10], and UV absorbents and filters [11,12]. The performances in practical uses are strongly depend on the properties of morphologies, crystallinity and crystallite size of CeO₂ particles.

Moreover, Yang et al. [13] have pointed out that an activation energy of 56.42 kJ/mol was obtained for CeO₂ crystallite growth from dried cerium dioxide precursor powders synthesized by coprecipitation process. The indirect band gap energy of CeO₂ powders decreased from 3.03 eV to 2.6 eV when the crystallite size increased from 10.4 nm to 66.8 nm, and the direct band gap energy of CeO₂ powders also decreased from 3.79 eV to 3.38 eV [14]. However, the studies carried out for the crystallization kinetics and effect of crystallinity on the optical properties of nanosized CeO₂ powders were discussed in detail.

In the present study, the isothermal crystallization kinetics and effect of crystallinity on the optical properties of CeO₂ powders prepared using cerium nitrate hexahydrate as the initial material by a coprecipitation route were investigated. The characteristics of the crystallization kinetics and effect of crystallinity on the optical properties of the nanosized CeO₂ powders were determined using X-ray diffraction (XRD),

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transmission electron microscopy (TEM), selected area electron diffraction (SAED), and ultraviolet–visible (UV–vis) absorption spectrophotometry. The purposes of this investigation are (i) to evaluate the activation energy of CeO₂ crystallization from cerium dioxide precursors by the isothermal method; (ii) to study the relationship between optical properties and crystallinity of nanosized CeO₂ powders; and (iii) to observe the microstructure of CeO₂ precursor powders before and after calcination by TEM.

2. Experimental

2.1. Sample preparation

Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, purity ≥ 99.0%, supplied by Sinopharm Chemical Reagent Co., Ltd., China) was used as the initial material to prepare the cerium dioxide precursors. Polyethylene glycol (PEG, MW 600, supplied by Sinopharm Chemical Reagent Co., Ltd., China) was used as a dispersant. Ce(NO₃)₃·6H₂O was dissolved in a water-and-ethanol solution for a volume ratio of 4:1, and then the 0.1 M Ce(NO₃)₃ solution was prepared, and 1 wt% PEG was added as a dispersion agent for reducing agglomeration. The mixed solution was stirred with a magnetic stirrer at 293 K. Subsequently, NH₄OH (supplied by Sinopharm Chemical Reagent Co., Ltd., China) was slowly added to the solution to maintain a pH of 9. After precipitation, the precipitates were repeatedly rinsed with a large amount of deionized water and ethanol. Subsequently, the precursor powders were dried at 313 K in an oven. Finally, the cerium dioxide precursor powders were calcined at different temperatures and durations.

2.2. Sample characterization

The crystalline phase was identified by X-ray diffraction (XRD, Rigaku D/MAX-RB X-ray, Tokyo) with Cu K α radiation and a Ni filter operation at 40 kV, 50 mA, and a scanning rate (2 θ) of 1°/min.

The integrated intensity of maximum reflection (111) (2 θ from 27.68 to 29.48) of CeO₂ for precursors after calcination at 1273 K for 24 h were as 100%. Then the crystallinity of cerium dioxide precursors after calcination at various temperatures and different durations was determined by comparing the intensities of its maximum reflection (111) (2 θ from 27.68 to 29.48) of CeO₂.

Therefore, the crystallinity (C%) of CeO₂ precursor calcined at various temperatures for different times was calculated using the following equation:

$$C(\%) = \frac{I_A(111)}{I_S(111)} \times 100\% \quad (1)$$

where I_A and I_S are denoted the integrated intensities of CeO₂ (111) for precursors after calcination at various temperatures for different durations and the standard samples, respectively.

The ultraviolet–visible (UV–vis) (UV-3600, Shimadzu Co. Japan) diffuse reflectance spectra were performed under

ambient conditions with an integrating sphere. BaSO₄ was used as a reference, and spectra were recorded over the range of 200–600 nm.

The UV–vis absorption spectra of the cerium dioxide dried precursors before calcinations and calcined products dispersed in water were recorded for the determination of the band gap energies. The optical absorption coefficient, α , was calculated using the following equation [15,16]:

$$\alpha = \frac{2.303 \times 10^3 A \beta}{lc} \quad (2)$$

where A is the absorbance of the calcined product sample, β is the density of CeO₂ (7.172 g/cm³), l is the path length of the quartz cell (1.0 cm), and c is the concentration of the calcined product sample in the suspensions.

The morphology of the dried CeO₂ precursor powders before and after calcination was examined by transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) with SAED analysis.

3. Results and discussion

3.1. Crystalline structure of the cerium dioxide precursor powders after calcination for different durations

Fig. 1 reveals the XRD patterns of the dried CeO₂ precursor powders after calcination at 1073 K for various durations. Fig. 1(a) shows the XRD pattern of the CeO₂ precursor powders before calcined. It reveals that the reflection peaks of (111), (200), (220), and (311) of CeO₂ appeared (JCPDS Card 81–0792), which corresponds to the center-facing cubic cerium oxide (CeO₂). The XRD pattern of cerium dioxide precursors after calcination at 1073 K for 5 min as shown in Fig. 1(b) revealed that the weak intensity and broad peaks were attributed to the CeO₂ powders, which still maintained the poor crystallinity and fine crystallite [17]. Fig. 1(c–e) shows the

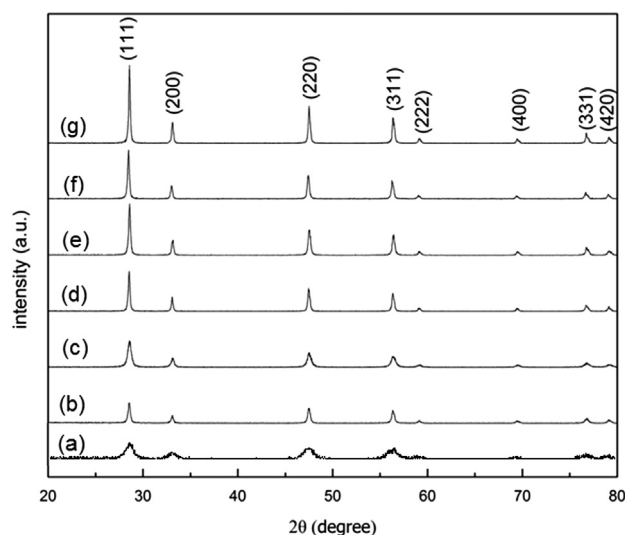


Fig. 1. XRD patterns of cerium dioxide dried precursor powders after calcination at 1073 K for various durations: (a) uncalcined, (b) 5 min, (c) 15 min, (d) 30 min, (e) 60 min, (f) 120 min and (g) 240 min.

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