



# Growth and optical properties of cerium dioxide nanocrystallites prepared by coprecipitation routes

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## Abstract

Nanosized cerium dioxide ( $\text{CeO}_2$ ) powders have been synthesized using coprecipitation methods and cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) as the starting material. The growth and optical properties of nanosized  $\text{CeO}_2$  powders were investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), nano-beam electron diffraction (NBED), high resolution TEM (HRTEM), and ultraviolet–visible (UV–vis) absorption spectrophotometry. The XRD result shows that the dried  $\text{CeO}_2$  precursor powders (both before and after calcination at various temperatures and times) contained a single crystalline phase of  $\text{CeO}_2$ . In the dried precursor powders, the crystallites of  $\text{CeO}_2$  measured 10.4 nm and 66.8 nm before and after calcination at 1273 K for 240 min, respectively. The indirect band gap energy ( $E_i$ ) of  $\text{CeO}_2$  decreased from 3.03 eV to 2.68 eV as the crystallite size increased from 10.4 nm to 66.8 nm, whereas the direct band gap energy ( $E_d$ ) of  $\text{CeO}_2$  also decreased from 3.79 eV to 3.38 eV.

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**Keywords:** C. Optical properties; D.  $\text{CeO}_2$ ; Crystallite size; Band gap energy

## 1. Introduction

Materials based on cerium dioxide ( $\text{CeO}_2$ ) are important due to their extensive use in applications, such as gas sensors [1], solid oxide fuel cells [2,3], auto exhaust emission control [4,5], catalytic wet oxidation [5], photocatalytic oxidation of water [6], glass polishing materials [7], ultraviolet (UV) absorbents and filters [8], optical, electro-optical, microelectronic and opto-electronic devices [9]. Recently, nanosized particles have attracted considerable attention because their physical and chemical properties are significantly different from those of the bulk materials [10].  $\text{CeO}_2$  nanocrystallite powders have considerable potential for use as UV absorbents and high-activity catalysts.

When using  $\text{CeO}_2$  for UV absorbents and filters applications, the crystallite size and morphology significantly influence the absorption properties. Recently, numerous routes for synthesizing nanosized  $\text{CeO}_2$  particles with promising control of properties have been reported, such as hydrothermal [11], sonochemical [12], sol–gel [13], microwave [14], microemulsion [15], reverse micelles [16], and homogeneous precipitation. Among these routes, homogeneous precipitation is one of the most promising techniques because of its low cost, easy-to-acquire apparatus, simple synthesis process, and nanometric precursor particles.

The synthesis of  $\text{CeO}_2$  rhombic microplates prepared at room temperature via ultrasonication using polyethylene glycol as a structure-directing agent has been reported by Zhang et al. [17]. The authors noted that polycrystalline  $\text{CeO}_2$  nanorods with 5–10 nm diameters and 50–150 nm lengths were obtained. In addition, Hassananzadeh-Tabrizi et al. [18] proposed that the activation energy of  $\text{CeO}_2$  nanopowder growth is 14.6 kJ/mol for the precursors obtained using the reverse precipitation synthesis process. The activation energy of 56.42 kJ/mol has been reported

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by Yang et al. for CeO<sub>2</sub> growth from precursor powders obtained via coprecipitation routes [19]. Conversely, Liu et al. [20] used a facile one-step hydrothermal process to prepare CeO<sub>2</sub> nanosheets with a (110) dominated surface that exhibits an obvious blue-shift in UV absorbance compared to bulk CeO<sub>2</sub>. Moreover, Lu et al. [21] noted that the absorption edge for octahedrons and spheres red-shifted and that the absorption edge of the octahedrons was near the visible region.

Although the precipitation technique has been widely used for CeO<sub>2</sub> nanoparticle synthesis, most studies were focused on the effects of the cerium precursors, ligands, additives, and reaction media on CeO<sub>2</sub> nanocrystallite formation. However, the growth and optical properties of nanosized CeO<sub>2</sub> crystallites have not been studied in detail. In this study, the crystallite growth and optical properties of CeO<sub>2</sub> precursor powders prepared from cerium nitrate via coprecipitation routes were investigated in detail. Characteristics of the CeO<sub>2</sub> powders were determined using X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), nano-beam electron diffraction (NBED), high resolution TEM (HRTEM) and UV–vis spectrophotometry.

The purposes of this investigation were (i) to study the growth behavior of CeO<sub>2</sub> powders of the dried precursor powders after calcination, (ii) to study the effect of crystallite size on the optical properties of CeO<sub>2</sub> powders, and (iii) to examine the TEM microstructure of uncalcined and calcined CeO<sub>2</sub> powders.

## 2. Experimental procedures

### 2.1. Sample preparation

In this study, cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, purity ≥ 99.0%, supplied by Sinopharm Chemical Reagent Co., Ltd., China) was used as the starting material. Polyethylene glycol (PEG, MW 600, supplied by Sinopharm Chemical Reagent Co., Ltd., China) was used as a dispersant. Cerium nitrate hexahydrate was dissolved in a solution of deionized water and ethanol at a volume ratio of 4:1. A concentration of Ce(NO<sub>3</sub>)<sub>3</sub> equal to 0.1 mol/L in solution was prepared, and 1 wt% PEG was added as a dispersion agent for reducing agglomeration. The mixed solution was stirred by a magnetic stirrer at 293 K. Next, NH<sub>4</sub>OH (supplied by Sinopharm Chemical Reagent Co., Ltd., China) was slowly added into the solution until a pH value of 9 was obtained. 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 dried precursor powders after calcination at various temperatures and durations.

### 2.2. Sample characterization

The crystalline phase was identified using X-ray diffraction (XRD, Rigaku D/MAX-RB X-ray, Tokyo) with Cu K $\alpha$  radiation and a Ni filter operating at 40 kV, 50 mA, and a

scanning rate (2 $\theta$ ) of 1°/min. The average crystallite size of the dried cerium oxide precursor powders after calcination at different temperatures for various durations was determined using Scherrer's equation [22] as follows:

$$D_{hkl} = \frac{0.89\lambda}{\beta \cos \theta} \quad (1)$$

where  $D_{hkl}$  denotes the average crystallite size of the CeO<sub>2</sub> powders,  $\lambda=0.15405$  nm is the X-ray wavelength of Cu K $\alpha$ ,  $\beta$  is the full-width at half maximum intensity (FWHM) of the peak, and  $\theta$  is the Bragg's angle of the peak.

The ultraviolet–visible (UV–vis) (UV-3600, Shimadzu Co., Japan) diffuse reflectance spectra were performed under ambient conditions with an integrating sphere. BaSO<sub>4</sub> was used as a reference, and spectra were recorded over the range of 200–600 nm.

The UV–vis absorption spectra of the dried cerium oxide precursor powders and the products of calcination dispersed in water were recorded for the determination of the band gap energies. The optical absorption coefficient,  $\alpha$ , was calculated using the following equation [11,23–25]:

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

where  $A$  is the absorbance of the product sample,  $\beta$  is the real density of CeO<sub>2</sub> (7.172 g/cm<sup>3</sup>),  $l$  is the path length of the quartz cell (1.0 cm), and  $c$  is the concentration of the product sample in the suspensions.

The morphology of the dried cerium oxide precursor powders before and after calcination was examined using transmission electron microscopy (TEM, JEM-2010 Electron Microscope, JEOL Co., Tokyo, Japan) operating at 200 kV. The TEM sample was prepared by dispersing the CeO<sub>2</sub> powders in an ultrasonic bath and then collecting on a copper grid. SAED and NBED examinations were also made on the TEM sample.

## 3. Results and discussion

### 3.1. The growth behavior of the cerium dioxide dried precursor powders after calcination

XRD patterns of the dried cerium dioxide precursor powders after calcination at various temperatures for 240 min are presented in Fig. 1. The XRD pattern reveals reflection peaks of (1 1 1), (2 0 0), (2 2 0), and (3 1 1) for the dried precursor powders before calcination as dried precursor powders, which correspond to cerium dioxide (CeO<sub>2</sub>). This phenomenon is attributed to crystalline CeO<sub>2</sub> in the dried cerium oxide precursor powders. However, the broad and weak intensity of the dried CeO<sub>2</sub> precursor powder peaks showed poor crystallinity and/or a composition of finer crystallites in the nanometer to submicron range [26,27]. When the calcination temperature was increased to 673 K, the XRD pattern still exhibited broad and weak peaks that were nearly unchanged. This result occurred because the CeO<sub>2</sub> powders maintained poor crystallinity and finer crystallite size when the calcination

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