

# SYNTHESIS AND CHARACTER OF CERIUM OXIDE (CeO<sub>2</sub>) NANOPARTICLES BY THE PRECIPITATION METHOD

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In this paper cerium oxide (CeO<sub>2</sub>) nanoparticles with 200-300 nm in diameter were synthesized via a precipitation method using ammonia water and oxalic acid as precipitant, respectively. The as-prepared CeO<sub>2</sub> nanoparticles were characterized by means of different techniques including X-ray, scanning electron microscopy and FT-IR. The effect of calcine temperature and precipitant on the crystal size and morphology were discussed. The results showed that the shape of CeO<sub>2</sub> nanoparticles prepared is strongly dependent on the precipitant. The average particle size as well as the crystallite size increased with increasing the calcine temperature. The structure of the nanoparticles was fluorite-type structure in the samples.

**Key words:** cerium oxide, synthesis, precipitant, nanostructures, powders

## INTRODUCTION

In the recent years, much effort has been focused primarily on the development of new synthetic routes for preparing nanostructure cerium oxide due to their potential uses in many applications, such as high-storage capacitor devices, buffer layers for conductors, fuel cells, polishing materials, UV blocks and optical devices [1].

Several methods, such as chemical vapor deposition, electrochemistry, templates, photoinduced conversion, biological synthesis, et al [2]. Among them, owing to the advantages of simple process, easy scale-up and low cost, the precipitation technique has attracted the most extensive attentions. For example, Zhou et al [3]. CeO<sub>2</sub> produced particles of about 4 nm from cerium nitrate and ammonia. Chen et al [4] synthesized of nanocrystalline cerium oxide particles by the precipitation method and the influences of reaction temperature and atmosphere on the character of cerium oxide were investigated. Although CeO<sub>2</sub> particles prepared by the precipitation technique have been extensively studied, most of the previous reports were focused on effects of cerium precursors, ligands and additives reaction media. Less information was reported on the influences of reaction temperature.

In this paper, the cerium oxide nanoparticles were successfully synthesized by a facile precipitation method and the effects of reaction temperature on the formation of CeO<sub>2</sub> particles were investigated. The properties of the materials were characterized by X-ray diffraction

(XRD) analysis, Fourier transformed infrared (FT-IR) spectra, scanning electron microscopy (SEM).

## EXPERIMENTAL

All chemicals provided by Xinxi Chemical Co.(china) were reagent grade and used without further purification.

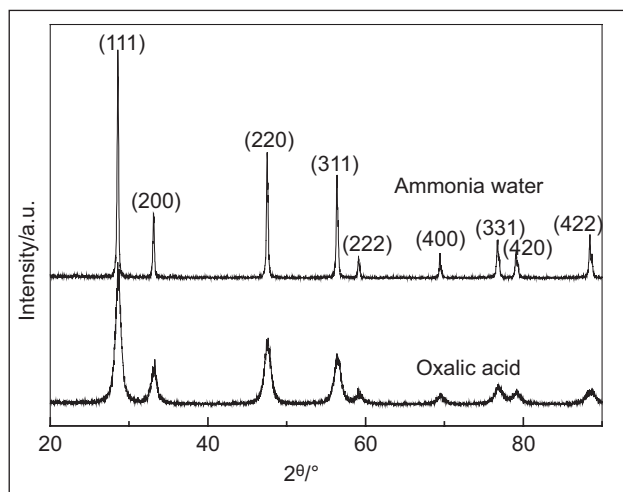
Cerium oxide nanopowder was prepared by a precipitation method using cerium sulfate, oxalic acid (ammonia water) and dispersing agent OP-10. In a typical synthesis procedure, 1 g of cerium sulfate and 0.2 g dispersing agent OP-10 were put into 100 mL distilled water to form a clear solution, which was stirred strongly at room temperature for about 0.5 h. The obtained clear solution was added drop-wise to 10 ml precipitating agent (1.4 M ammonia water or oxalic acid) under constant stirring condition for 2 h. The resultant synthesis precipitate was washed with deionized water and dried at 80 °C for 24 h. The dried precipitate (the precursor) was calcined for 2 h in a tube furnace at different temperatures.

FT-IR spectra of the specimen was recorded on a microscope FT-IR US Nicolet 380 apparatus in transmittance mode. The crystalline structure of the powders was determined by a Rigaku D/max-RB X-ray diffraction (Japan) with Cu K-radiation. The morphology of the specimen was studied by a PhilipXL-20 scanning electron microscope.

## RESULTS AND DISCUSSION

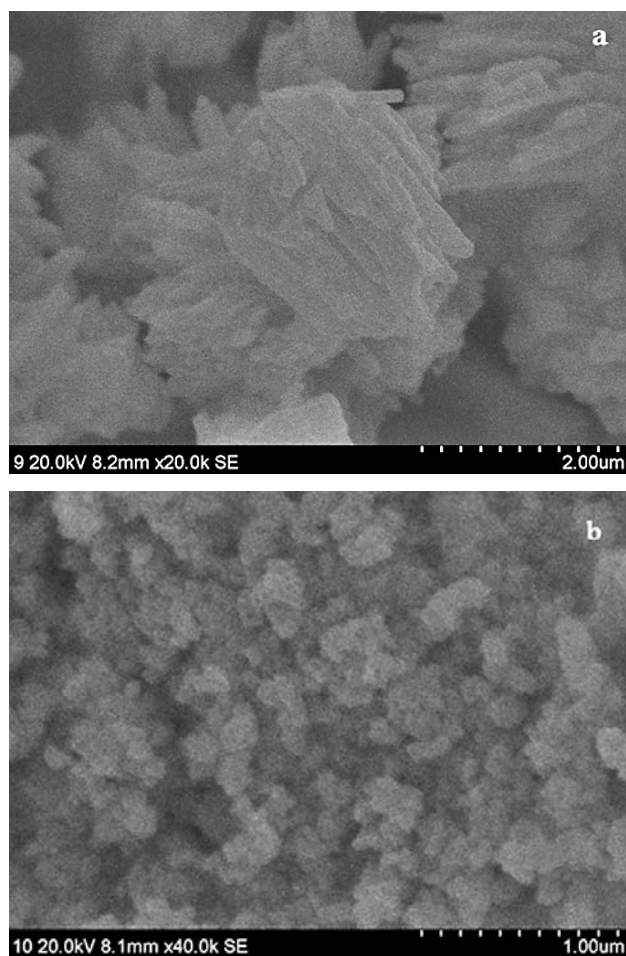
The experimental X-ray powder diffraction (XRD) pattern of the as-synthesized nanoparticles using ammonia water and oxalic acid as precipitant is shown in

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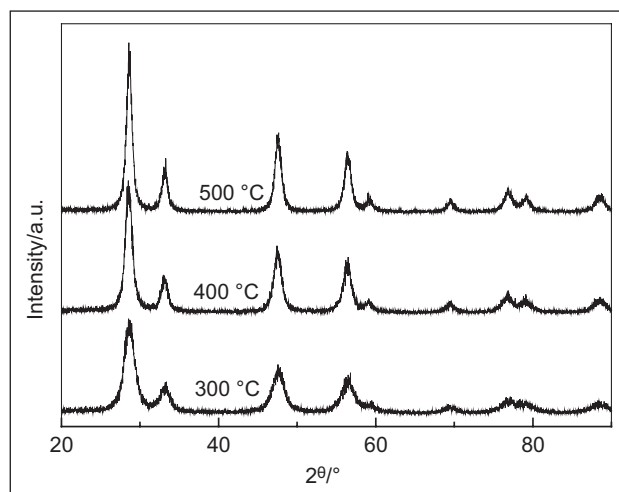


**Figure 1** XRD pattern of the  $\text{CeO}_2$  particles synthesized using different precipitant

Figure 1. The characteristic peaks are very close to the fluorite structured  $\text{CeO}_2$  crystal [5]. The characteristic peaks corresponding to the (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes are located at  $2\theta = 29.2^\circ, 33.1^\circ, 47.5^\circ, 57.6^\circ, 59.0^\circ, 64.5^\circ, 76.7^\circ, 79.2^\circ$  and  $88.4^\circ$ , respectively. No peak of any other phase was detected indicating the high purity of the product. The diffraction peaks of  $\text{CeO}_2$  particles prepared using oxalic acid as precipitant are quite broad,



**Figure 2** SEM images of the  $\text{CeO}_2$  particles synthesized using different precipitant: (a) Ammonia water (b) Oxalic acid



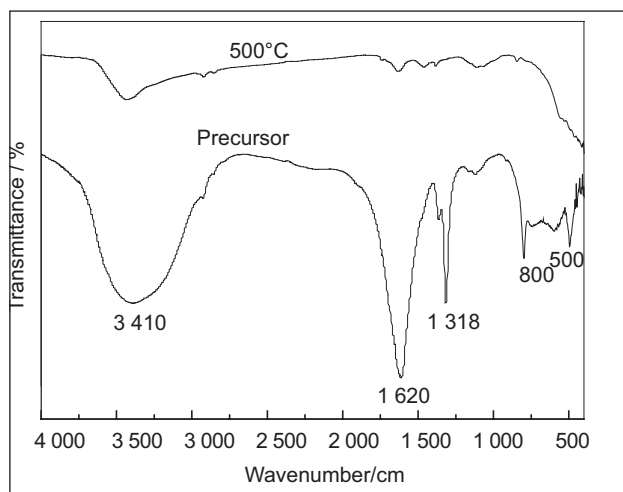
**Figure 3** XRD patterns for  $\text{CeO}_2$  particles prepared at different calcine temperatures

which indicates that the crystalline sizes of samples are very small.

Figure 2 shows the particle morphologies of  $\text{CeO}_2$  particles synthesized using different precipitant. SEM image of ceria nanopowder for the ammonia water sample is shown in Figure 2a. Large chunks of powder aggregates made up of fine particles are seen. Particles in Figure 2b display poor contrast agglomeration amongst extremely fine particles. Particles obtained by oxalic acid are about 100-300 nm in size and displays spherical shape in comparison to the nanorod shape obtained by ammonia water in Figure 2a.

Figure 3 shows the XRD patterns of  $\text{CeO}_2$  particles and the relationship between particle sizes of ceria powders and the calcining temperature. It can be seen that the intensities of diffraction peaks associated with  $\text{CeO}_2$  increased and half-peak-width became narrow as calcining temperature increased. According to the Scherrer equation, it is inferred that mean crystallite size of ceria increases gradually with the temperatures ranging from 300 to 500 °C. Moreover, these low intensities and broad peaks result most probably from destabilization of the low-temperature cubic phases, rather than from actual shrinking of crystallites [6].

FT-IR spectra of as-synthesized  $\text{CeO}_2$  precursor and nanoparticles are shown in Figure 4. The features in the IR spectra of powders dried precipitate are bands in the 1100~1700 and 3000~3800  $\text{cm}^{-1}$  regions. In addition, the band due to the stretching frequency of Ce-O can be seen below 770  $\text{cm}^{-1}$ . The band centered at 3410  $\text{cm}^{-1}$  corresponds to the -OH stretching vibration which is originated from physical absorbed  $\text{H}_2\text{O}$  or surface -OH groups. Bicarbonate-like species and monodentate carbonate species with O-C-O stretching frequencies of 1318  $\text{cm}^{-1}$ , 1620  $\text{cm}^{-1}$  and 800  $\text{cm}^{-1}$  can be also observed. The “scissor” bending of H-O-H will have a broad absorption band located at about 1630  $\text{cm}^{-1}$ , this band is observed in the spectra and partly overlapping the O-C-O stretching band [7]. The strong broad band below 700  $\text{cm}^{-1}$  is assigned to the Ce-O stretching mode.



**Figure 4** FT-IR spectra of as-synthesized CeO<sub>2</sub> precursor and nanoparticles

After calcinations, such bands originating from the residual water or carbonate species become weaker or disappear except for the bands of Ce-O stretching mode seeing clearly [8].

## CONCLUSIONS

Ceria oxide nanoparticles with 200-300 nm in diameter were successfully synthesized by a facile precipitation method in the presence of the difference precipitant. From the present results, the shape of CeO<sub>2</sub> nanoparticles prepared are strongly dependent on the precipitant.

The structure of the synthesized CeO<sub>2</sub> nanoparticles was determined by means of XRD. The structure of the nanoparticles is fluorite-type structure in all the samples.

The average particle size is increased by increasing the calcine temperature.

## Acknowledgements

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**Note:** The responsible for English language is the lecturer from Northeastern University, Liaoning, China