

Diethylene Glycol-Mediated Synthesis of Nano-Sized Ceria (CeO_2) Catalyst

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ABSTRACT

Nano-crystalline particles of CeO_2 have been synthesized by a low temperature chemical precipitation method. The precursor materials used in this research were $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, NaOH and diethylene glycol as surfactant. X-ray powder diffraction results showed that face centered cubic CeO_2 nanoparticles with crystalline size in nanometer scale were formed. Scanning electron microscopy measurement showed that by increasing the calcinations temperature the crystallite size decreases. The particle size of CeO_2 was around 20 nm as estimated by X-ray powder diffraction technique and direct high-resolution transmission electron microscopy observation. High-resolution transmission electron microscopy studies showed the size of CeO_2 particles increase from 10-90 nm by increasing the ratio of diethylene glycol surfactant. The sharp peaks in Fourier transform infrared spectrum determined the purity of CeO_2 nanoparticles and absorbance peak of ultraviolet-visible spectroscopy spectrum showed the small bandgap energy of 3.26 eV.

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INTRODUCTION

Cerium oxide (CeO_2) containing materials have been in focus of intensive research during last years due to the diversity of their applications. Cerium dioxide or ceria is an important rare earth oxide, which has multiple applications such as electrolyte materials of solid oxide fuel cells [1], ultraviolet blocking materials [2], catalysts [3], chemical mechanical polishing [4] and oxygen gas sensors [5]. It has a fluorite like cubic structure in which each cerium site is surrounded by eight oxygen sites in face-centered cubic (FCC) arrangement and each oxygen site has a tetrahedron cerium site. Recently, a variety of methods based on wet chemical routes have been extensively employed to synthesize of CeO_2 nanoparticles like precipitation [6-9], hydrothermal

[10,11], sol-gel method [12], and microemulsion method [13]. For many applications, precipitation is an attractive route to ceria NP synthesis due to the cheap salt precursors, simple operation, and ease for mass production [14, 15]. Most of the applications require the use of nonagglomerated nanoparticles, as aggregated nanoparticles lead to inhomogeneous mixing and poor sinter ability. In this article, a CeO_2 nanoparticles has been prepared via a simple precipitation route. Novelty in this article is that the samples powder is prepared without washing and purification before calcinations and high homogeneity emerged in the samples surface by increasing annealing temperature. Synthesis of CeO_2 nanoparticles is reported by $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as precursor and sodium hydroxide as precipitator in presence of diethylene glycol as surfactant. Finally

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they have been calcined different temperature at 400°C and 1000°C [13]. The objective of this research is the synthesis of CeO₂ nanoparticles by the chemical precipitation process in the presence of sodium hydroxide, which is a very simple way and low in cost since the starting materials are few and inexpensive. The surface studies and structural properties of CeO₂ have been studied by XRD, HRTEM, SEM, FTIR and UV-Vis analyses.

MATERIALS AND METHODS

The starting chemicals used were iron (III) nitrate 9-hydrate (99.9%, Merck), ethanol (99.9%, Merck) without further purification.

High purity Ce(NO₃)₃·6H₂O, sodium hydroxide, diethylene glycol were used in the preparation of CeO₂ nanoparticles. In a typical synthesis of ceria (CeO₂) nanoparticles were prepared as follows: the precursors like Ce(III) nitrate and sodium hydroxide (NaOH) were taken in 1:4 molar ratios and dissolved completely in de-ionized water. Initially, 0.02 M of Ce(NO₃)₃ (2.17 g of Ce(NO₃)₃ in 250 ml of water) and 1.5 M of sodium hydroxide were prepared. A surfactant namely diethylene glycol (50 mL) was added suitably to the sodium hydroxide solution. It has been reported that a surfactant plays a significant role in preventing agglomeration and getting finer particles [16]. Next, a Ce(NO₃)₃ solution was added drop wise into the solution of surfactant. They were mixed perfectly by a magnetic stirring apparatus (800 rpm) at room temperature for 1 hour. Here, the pH value of the solution was adjusted to be 13. The resultant yellow colored precipitate (Ce(OH)₄) was not filtered and not washed with deionized water or alcohol. After that the product was dried at 220°C

for 6 hours. Then, the calcination was carried out at 1000 °C for 4 hours. During calcination at a high temperature, the surfactant was removed and phase pure yellow colored CeO₂ was formed. The specification of the size, structure and morphological properties of the as-synthesis and annealed CeO₂ nanoparticles were done. X-ray diffractometer (XRD) was used to identify the crystalline phase and estimated the exact crystalline size. The XRD pattern were recorded with 2^θ in the range of 4-85° with type X-Pert Pro MPD, Cu-Ká: λ = 1.54 Å. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and high resolution transmission electron microscopy (HRTEM) with type Zeiss EM-900, 80 kV. The optical properties of absorption were measured by ultraviolet–visible spectrophotometer (UV–Vis) with optima SP-300 plus, and Fourier transform infrared spectroscopy (FTIR) with WQF 510. All the measurements were carried out at room temperature.

RESULTS AND DISCUSSION

X-ray diffractometer with scanning rate of 0.02 °/s was applied to record the pattern in the 2θ range of 4- 80°. Fig. 1 shows the XRD morphology of CeO₂ nanoparticles annealed at 1000 °C for 3 hours. The exhibited picks correspond to the (111), (200), (220), (311), (222), (400), (331) and (420) of a cubic fluorite structure of CeO₂ is identified using the standard data [17,16]. The mean size of the ordered CeO₂ nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B \cos \theta} \quad (1)$$

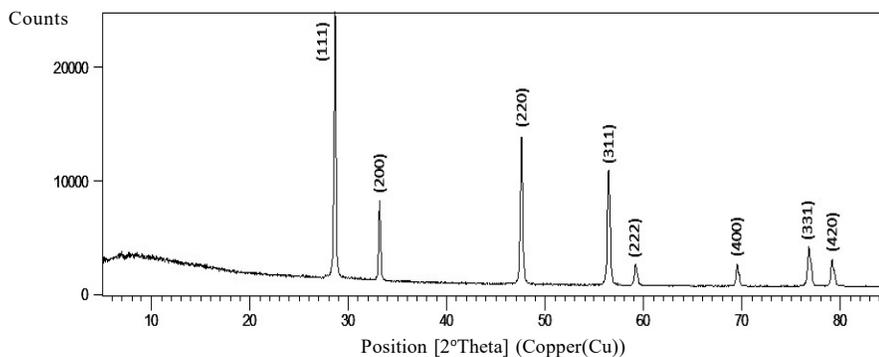


Fig. 1. XRD pattern of annealed CeO₂ nanoparticles.

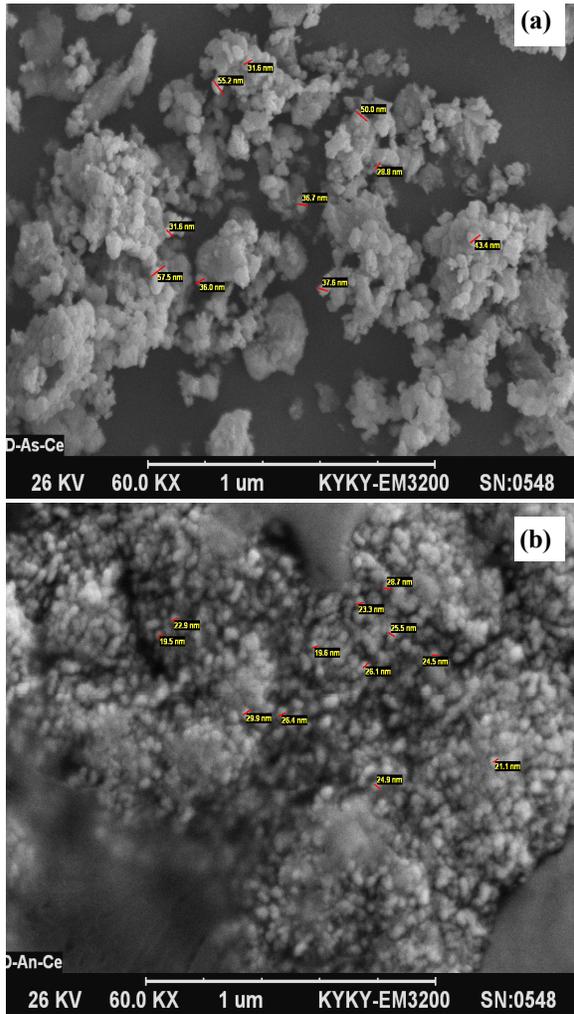


Fig. 2. SEM images of the CeO₂ nanoparticles

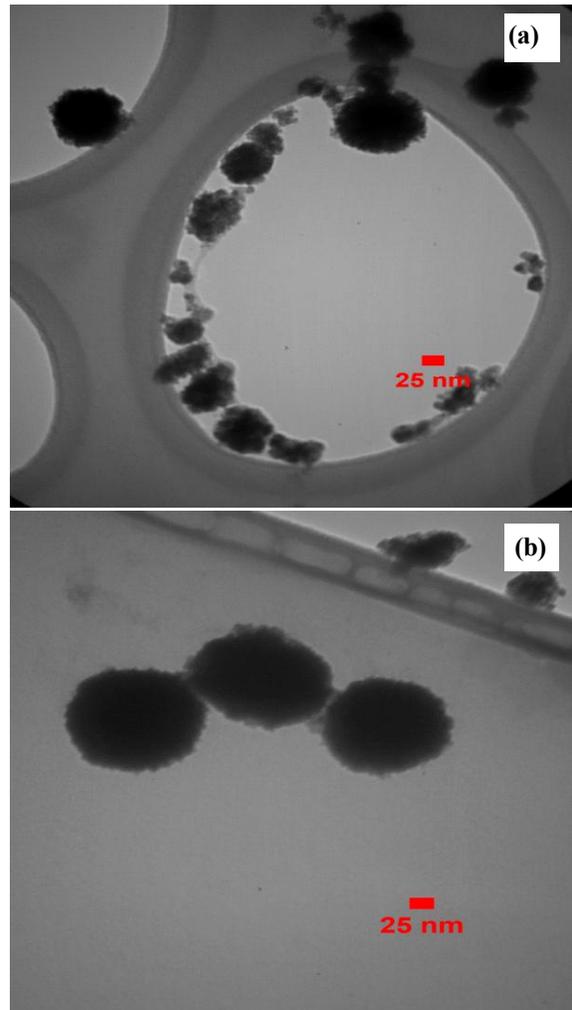


Fig. 3. TEM images of as prepared CeO₂ nanoparticles

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared CeO₂ nanoparticles was around 20 nm from this Debye-Scherrer equation. Fig. 2 show the SEM images of CeO₂ nanoparticles. Fig. 2(a) shows the as-prepared CeO₂ nanoparticles with slight agglomeration and Fig. 3(b) shows annealed sample at 400°C for 3 hours. It can be seen that the size of CeO₂ decrease with increasing annealing temperature and the uniformity of size increases with increasing temperature. The average crystallite size of annealed nanocrystals is around 20 nm.

TEM analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. TEM images of the CeO₂ nanoparticles is given in Fig. 3. CeO₂ particles are spherical in the range size of 10-90 nm with less agglomeration. It can be seen that with increasing the rate of diethylen glycol from 10 to 50 mL, the size of CeO₂ nanoparticles increase from 10 nm (Fig. 3a) to 90 nm (Fig. 3b).

According to Fig. 4, the infrared spectrum (FTIR) of the synthesized CeO₂ nanoparticles was measured in the range of 400-4000 cm⁻¹ wavenumber which identify the chemical bonds as well as functional groups in the compound. The large broad band at

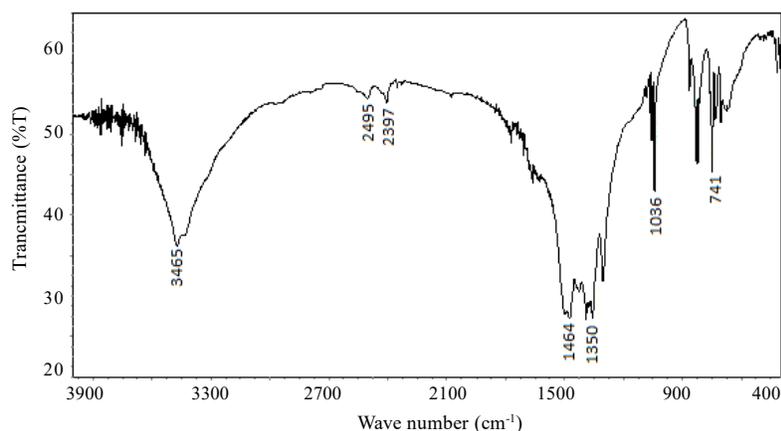


Fig. 4. FTIR spectrum of the CeO_2 nanoparticles

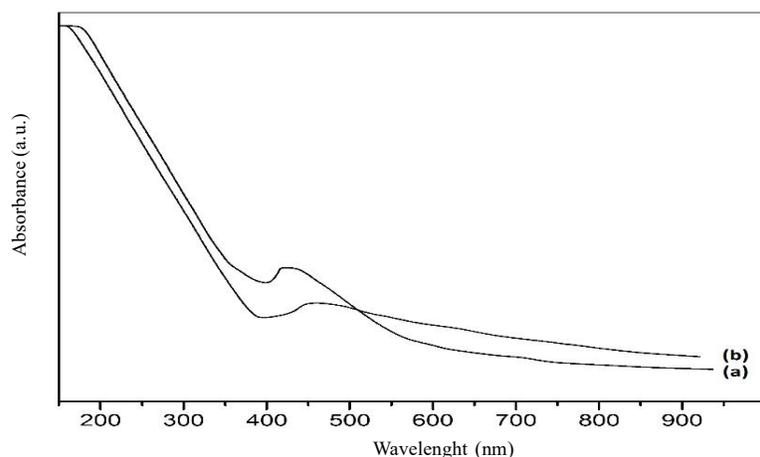


Fig. 5. UV-Vis absorption spectra of the CeO_2 (a) as-synthesized and (b) annealed sample

3465 cm^{-1} is ascribed to the O-H stretching vibration. The absorption peaks around 1464 cm^{-1} is assigned to the bending vibration of C-H stretching. The strong band below 700 cm^{-1} is assigned to the Ce-O stretching mode [19]. The broad band, corresponding to Ce-O stretching mode of CeO_2 is seen at 500 cm^{-1} [20,21]. UV-visible absorption spectral study may be assisted in understanding electronic structure of the optical band gap of the material. Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. UV-Vis absorption spectra of as-prepared and annealed CeO_2 nanoparticles are shown in Fig. 5. For as-synthesized CeO_2 nanoparticles, the strong absorption band at low wavelength near 380 nm correspond to bandgap energy of 3.26 eV (Fig. 5a) and for annealed CeO_2

nanoparticles the strong absorption band at low wavelength near 385 nm correspond to 3.22 eV (Fig. 5b). In comparison with UV visible absorption spectrum of CeO_2 nanoparticles reported in the literature [22], band/peak in the spectrum located at around $400\text{-}700\text{ nm}$ are observed to be shifted towards lower wavelength side, which clearly shows the blue shift. It indicates the absorption positions depend on the morphologies and sizes of CeO_2 . The UV absorption ability of CeO_2 is related with band gap energy. The UV-absorption edge provides a reliable estimate of the band gap of any system.

CONCLUSION

In summary, ceria nanospheres have successfully synthesized via a simple precipitation by cerium

nitrate and sodium hydroxide in presence of diethylene glycol as surfactant. The synthesis parameters were investigated in detail. It is found that the surfactant species and reaction temperature were the crucial factors determining the formation of ceria nanospheres and the size of ceria nanospheres can be controlled by adjusting the reaction temperature and surfactant. XRD spectra shows cubic fluorite structure of CeO_2 is identified using the standard data. From SEM images, it is clear that with increasing annealing temperature the size of particles decreases with less agglomeration. TEM image exhibits that the as-synthesized TEM image of spherical CeO_2 nanoparticles prepared by precipitation route with a diameter in the range of 10-90 nm. TEM measurement demonstrated that size of CeO_2 nanoparticles increase with increasing ratio of surfactant. FTIR data showed the presence of Ce-O stretching mode of CeO_2 . The Ceria nanoparticles show a strong UV-vis absorption below 400 nm with a well-defined absorption peak at 380 nm, the direct band gap is found to be 3.26 eV. The shift of the band gap absorption in the UV-vis spectrum agrees closely.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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