NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (4), P. 728–731

Investigation on the preparation and properties of nanostructured cerium oxide

G. Jayakumar, A. Albert Irudayaraj*, A. Dhayal Raj, M. Anusuya

PG & Research Department of Physics, Sacred Heart College, Tirupattur, Vellore District, Tamil Nadu, India

*gjayaphysics@gmail.com

PACS 61.46.-w **DOI 10.17586/2220-8054-2016-7-4-728-731**

Cerium oxide (CeO_2) nanoparticles were successfully synthesized by the hydrothermal method with different reaction times. The synthesized CeO_2 nanoparticles were characterized by Powder X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Vis spectroscopy and FTIR spectroscopy. The effects of the reaction time on the structure and morphology of the prepared samples were investigated using XRD and SEM. The XRD studies reveal that the ceria nanoparticles have face-centered cubic structure. The SEM images reveal that the prepared Ceria nanoparticles are an aggregated form of spherical nanoparticles and the particle size decreases with increasing reaction time. FTIR analysis confirms the presence of CeO_2 in the prepared samples. UV-Vis spectral studies show that the UV cut off wavelength decreases and the optical band gap increases with increased reaction time. Photoluminescence (PL) studies indicate that the PL emission of both the samples occurs at 683 nm, however, the emission intensity increases with longer reaction times.

Keywords: ceria nanoparticles, hydrothermal method, photoluminescence.

Received: 8 February 2016

Revised: 10 May 2016

1. Introduction

Cerium oxide (CeO_2) is a refractory material possessing cubic fluorite crystal structure [1, 2]. It is one of the most reactive rare earth metal oxides due to its oxygen storage capacity (OSC), oxygen deficiency, and electronic conductivity. It has promising applications in fuel cells, oxygen sensors and mechanical polishing. It also has utility as an ultraviolet blocking agent, luminescent material and photocatalyst. Ceria nanoparticles can be prepared by methods such as hydrothermal [3], reverse micelles, micro-emulsion [4], homogeneous precipitation [5] etc. The main objective of this research paper is studying the effect of reaction time on the structural and optical properties of nanostructured cerium oxide prepared by the hydrothermal method.

2. Experimental

2.1. Synthesis

All the reagents used in the synthesis process were of analytical grade purity and used without any further purification. In the synthesis process, 0.274 g of ammonium ceric nitrate ($(NH_4)_2Ce(NO_3)_6$) was dissolved in 5 ml distilled water and 0.499 g of Sodium hydroxide (NaOH) was dissolved in 25 ml distilled water. These two solutions were mixed and the mixture was stirred for 30 min. To the resultant precursor solution obtained, 0.1808 g of urea ($CO(NH_2)_2$) dissolved in 10 ml of distilled water, was added. The solution was transferred to a Teflon-lined autoclave which was maintained at 200°C for 24 hours. The autoclave was allowed to cool down naturally and to reach the room temperature. The final product was collected from the autoclave and washed several times with distilled water and ethanol. The product was dried at 80°C for 6 hours. The dried sample was calcined at 400°C for 2 hrs.

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2 \uparrow$$

$$NH_4^+ + OH^- \leftrightarrow NH_3 \cdot H_2O \leftrightarrow H_2O + NH_3 \uparrow$$

$$(NH_4)_2Ce(NO_3)_6 + 4NaOH \xrightarrow{200^\circ C} Ce(OH)_4 + 4NaNO_3 + 2NH_3 \uparrow + 2NO_3 + H_2 \uparrow$$

$$Ce(OH)_4 \cdot xH_2O \xrightarrow{80^\circ C} Ce(OH)_4 + xH_2O \uparrow$$

$$Ce(OH)_4 \xrightarrow{400^\circ C} CeO_2 + 2H_2O \uparrow$$

2.2. Characterizations

The XRD measurements were carried out using Rigaku X-ray diffractometer with CuKα (λ = 1.54187 Å) radiation in the range of 10 – 80 ° at room temperature. The surface morphology of the particles was studied by scanning electron microscope.The optical transmittances of the samples were studied by Varian Cary 50 UV-Visible spectrophotometer in the range 200 – 800 nm. The FTIR spectra were recorded in the range of 400 – 4000 cm^{-1} by PERKIN ELMER SPECTRUM II FTIR spectrometer. The photoluminescence spectra were obtained by PERKIN ELEMER LS45 fluorescence spectrophotometer using excitation wavelength of 343 nm.

3. Results and discussions

3.1. XRD analysis

The powder XRD patterns of CeO_2 nanoparticles prepared with different reaction times are shown in Fig. 1. The peaks are indexed using JCPDS card #34-0394. Both 12 hour and 24 hour CeO_2 samples have Face Centered Cubic structure with lattice parameters $a = b = c = 5.411$ Å and $\alpha = \beta = \gamma = 90$ °. The diffraction peaks found at 28.27, 33.09, 47.34, 53.36, 69.26 and 76.75 ° showed a broadening effect, which suggests the formation of nanosized CeO_2. The absence of impurities indicates that pure CeO_2 is synthesized by the hydrothermal method. The average crystallite sizes (D) of the CeO_2 nanoparticles prepared with different reaction times, were calculated using the Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta},$$

where λ is the wavelength of the CuKα radiation, D is the crystallite size, K is a constant and its value is taken as 0.9, θ is the diffraction angle and β is the full-width half maximum (FWHM). The average crystallite size decreased slightly from 3.9 nm to 3.6 nm as the reaction time increased from 12 to 24 hours. The decrease of crystallite size with increasing reaction time was also confirmed from SEM images.

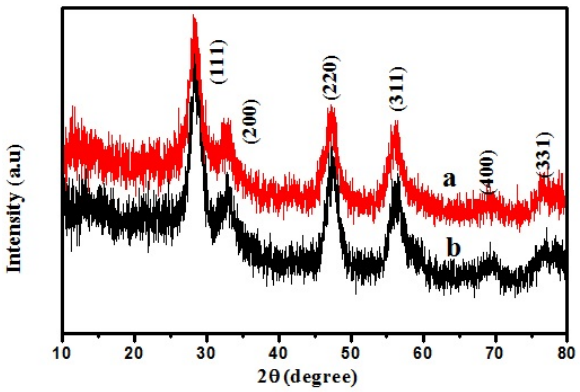

FIG. 1. XRD spectra of the CeO_2 nanoparticles prepared at (a) 24 hours and (b) 12 hours

3.2. FTIR spectra

The FTIR spectra of CeO_2 nanoparticles prepared by hydrothermal method with different reaction times are shown in Fig. 2. The band below 700 cm^{-1} is due to the Ce–O stretching vibrations [6–8].

3.3. UV-Visible spectra

The optical properties of synthesized CeO_2 were examined by UV-Visible spectrophotometer and the results are depicted in Fig. 3. The UV cutoff wavelength of the 12 hour sample was 349 nm, while the UV cutoff wavelength of the 24 hour sample was 343 nm. Additionally, the UV-Visible spectra showed no other peak related with impurities and structural defects, which confirmed that the synthesized nanoparticles are pure CeO_2. The band gap energy of 12 hour sample was 3.54 eV, whereas the band gap energy for the 24 hour sample was found to be 3.67 eV. As the reaction time increased, the band gap energy increased while the crystallite size decreased.

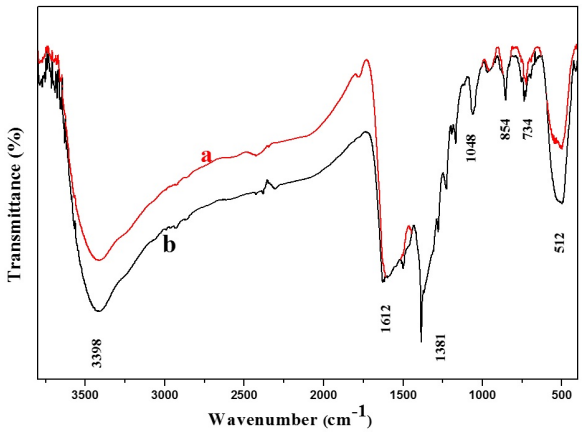

FIG. 2. FTIR spectra of the CeO_2 nanoparticles prepared at (a) 24 hours and (b) 12 hours

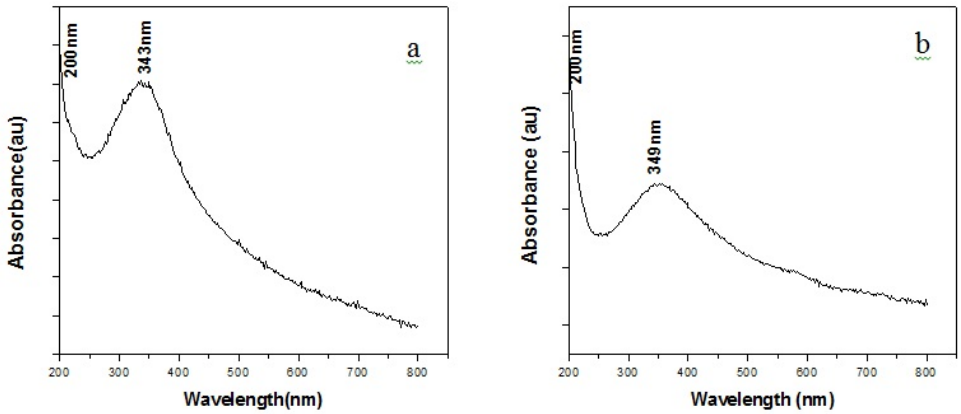

FIG. 3. UV-Vis spectra of the CeO_2 nanoparticles prepared at (a) 24 hours and (b) 12 hours

3.4. Scanning electron microscopy

The SEM images of the CeO_2 nanoparticles prepared by hydrothermal method with different reaction times are shown in Fig. 4. The CeO_2 nanoparticles prepared with 12 hours reaction time had sphere-like structure with an average particle size of 78 nm. The CeO_2 nanoparticles prepared with 24 hours reaction time also had sphere-like structure with an average particle size of 63 nm. Hence, it may be said that the change in the reaction time does not lead to any change in the shape of the CeO_2 nanoparticles, however, the change in the reaction time definitely had an effect on the particle size. The particle size decreased with additional reaction time.

3.5. Photoluminescence studies

The PL spectra of the CeO_2 nanoparticles prepared with different reaction time are shown in Fig. 5. The samples were excited by 343 nm wavelength, and the emission wavelength of these samples was obtained at approximately 683 nm. This emission peak corresponds to red-light. The emission intensity increased from 110.8 a.u to 132.6 a.u with longer reaction times.

4. Conclusions

CeO_2 nanoparticles were successfully synthesized by hydrothermal method and were analyzed by XRD, FTIR, SEM, UV-Visible spectroscopy and photoluminescence measurements. The studies indicate that the reaction time has an effect on the particle size and hence on the optical properties of CeO_2 nanoparticles. The CeO_2 nanoparticles prepared at 24 hours exhibited smaller particle size. The XRD studies revealed that they have face centered cubic structure and have the average grain size of 3.6 nm. From the SEM studies, the average particle size of CeO_2 nanoparticles prepared at 24 hours was found to be 63 nm. The UV-visible spectroscopic studies and PL studies

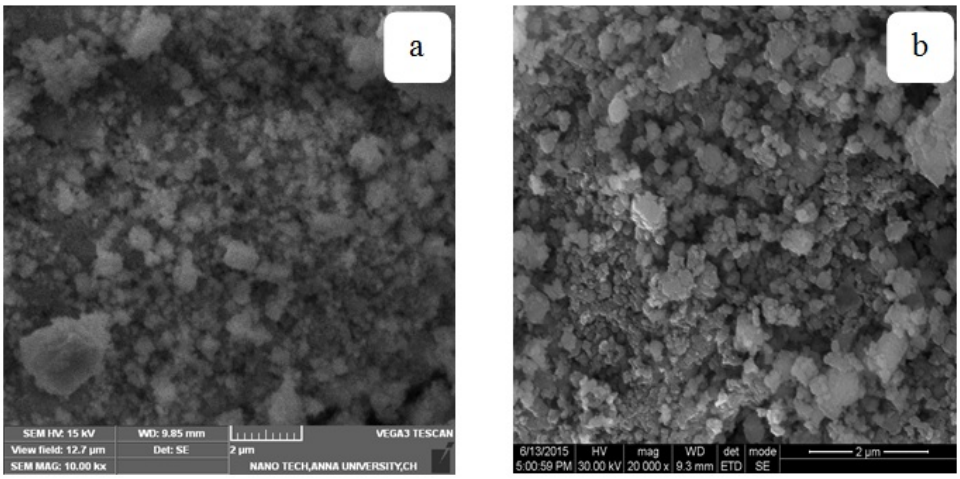

FIG. 4. SEM images of the CeO_2 nanoparticles prepared at (a) 24 hours and (b) 12 hours

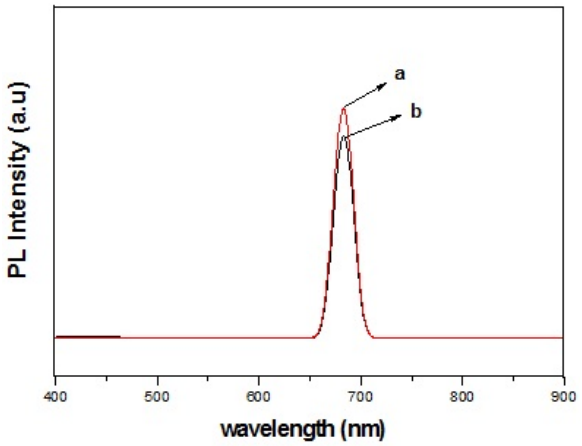

FIG. 5. PL spectra of CeO_2 nanoparticles prepared at (a) 24 hours and (b) 12 hours

reveal that the CeO_2 nanoparticles prepared at 24 hours have a lower UV cut off wavelength, wider optical transmission range and higher PL emission intensity; i.e. it has better optical properties.

References

[1] Kang H.S., Kang Y.C., Koo H.Y., Ju S.H., Kim D.Y., Hong S.K., Sohn J.R., Jung K.Y., Park S.B. Nano-sized ceria particles prepared by spray pyrolysis using polymeric precursor solution. *Journal of Materials Science and Engineering B*, 2006, **127**, P. 99–104.

[2] Jayakumar G., Albert Irudayaraj A., Dhayal Raj A., Magimai Antoni Raj D., Daniel Lawrence D. Comparative studies on Cerium Phosphate and Cerium Oxide Nanoparticles. *Journal of Chem. Tech Research*, 2015, **7**(3), P. 1385–1391.

[3] Masui T., Fujiwara K., Machida K., Adachi G. Characterization of cerium (IV) oxide ultrafine particles prepared by reversed micelles. *Journal of Chem. Mater.*, 1997, **9**, P. 2197–2204.

[4] Chen H., Chang H. Homogeneous precipitation of cerium dioxide nanoparticles in alcohol/water mixed solvents. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2004, **242**, P. 61–69.

[5] Khan S.B., Faisal, Mohammed Rahman M., Jamal A. Exploration of CeO_2 nanoparticles as a chemi-sensor and photo-catalyst for environmental applications. *Science of the total Environment*, 2011, **409**, P. 2987–2992.

[6] Wang G., Mu Q., Chen T., Wang Y. Synthesis, characterization and photoluminescence of CeO_2 nanoparticles by a facile method at room temperature. *Journal of Alloys and Compounds*, 2010, **493**, P. 202–207.

[7] Bo Liu, Bingbing Liu, Li, Zepeng Li Q, Ran Liu, Xu Zou, Wei Wu, Wen Cui, Zhao dong Liu, Dongmei Li, Bo Zou, Tian Cui, Guangtian Zou. Solvothermal synthesis of monodisperse self-assembly CeO_2 nanospheres and their enhanced blue-shifting in ultraviolet absorption. *Journal of Alloys and Compounds*, 2010, **503**, P. 519–524

[8] Kumar E., Selvarajan P., Muthuraj D. Synthesis and characterization of CeO_2 nanocrystals by solvothermal route. *Journal of Materials Research*, 2013, **16**, P. 269–276.