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The effect of microwave on the solvent free, solid state synthesis of Cerium oxide nano particles

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ABSTRACT

Cerium oxide nanoparticles have been synthesized by microwave method using cerium nitrate and ethylene glycol as precursors. The material was structurally characterized by XRD and SEM and the optical characterization was carried out using UV–visible and Photoluminescence spectro fluorimeter techniques. The X ray studies reveal the face centered cubic structures for cerium oxide nano particles. The absorption and emission spectrum shows a greater blue shift when synthesized using microwave. The purity of the sample was confirmed using XRD and EDAX.

KEYWORDS

Solvent free synthesis;
Optical properties;
Blue shift;
Luminescence.

INTRODUCTION

Cerium oxide (CeO_2) and ceria based materials have been investigated widely in recent years due to their potential applications in catalysis[1-6] and photo catalysis[7, 8], electronic, ceramic and gas sensors, solid oxide fuel cells (SOFC) and solar cells[9-13].etc., CeO_2 is a chemically stable oxide which has an outstanding capacity to store or release oxygen due to the variation in the oxidation state between +3 and +4. This varying oxidation state, make cerium to play an important role in scavenging reactive oxygen and nitrogen species which makes it a suitable candidate in nano biology and regenerative medicine[14].

Several methods have been reported to synthesize CeO_2 nanostructures with different morphologies, such as hydrothermal[15, 16] solvothermal[17, 18] microwave-assisted hydrothermal[19] microemulsion[20], chemical precipitation[21] urea–nitrate combustion[22], reverse micelle route[23] and sonochemical[24] etc.

Among these preparation methods, microwave-assisted method is a simple and economic way to prepare nanomaterials. The microwave energy is more efficient in selective heating, which is environmentally friendly, cost effective, quite fast, requires less energy and high product yield than the conventional heating. The frequency of the applied irradiation is low enough so that the dipoles have time to respond to the alternating electric field and therefore rotation. However, the frequency is not high enough for the rotation to precisely follow the field, which causes energy to be lost from the dipole by molecular friction and collision, giving rise to dielectric heating[25]. Due to the properties of internal and volumetric heating, thermal gradients during microwave processing are avoided, providing a uni-

form environment for reaction. Hence this method has been successfully applied for the preparation of a variety of nanosized inorganic materials.

The synthesis of cerium oxide nano particles reported by H. Yang *et al*.[26] using microwave from ceric ammonium nitrate and sodium hydroxide in aqueous medium V. D. Araujo *et al*.[27] reported microwave assisted hydrothermal synthesis using cerium nitrate and sodium hydroxide Hui Wang *et al*.[28] reported preparation of CeO_2 by microwave induced method using cerium ammonium nitrate, Hexa methylene tetrammine, Poly ethylene glycol, in 100ml distilled water. B. S. Shirke[29] synthesized cerium oxide nano particle using propylene glycol as a precursor in a microwave method. In all the above methods, in addition to the precursor they used other materials to maintain the pH. Hence there are lot of possibility for the contamination But in our method, we limit the use of reagents and hence the chance of contamination is less. We already reported the formation of zinc oxide and cerium oxide nano particle using conventional solid state method[30]. In this current investigation, we bring out the advantages of microwave heating over conventional heating.

EXPERIMENTAL

Cerium nitrate hexa hydrate $Ce(NO_3)_2$. 6 H_2O. A.C.S. reagent (sigma Aldrich 99% purity by weight) and the glycerol (anhydrous) were obtained from Merck. All the reagents used were of analytical grade purity and hence were used without further purification. About 4.3 g of cerium nitrate hexa hydrate was mixed with 2 drops of glycerol and kept in the microwave for 3 minutes (30seconds on and off method. The amount of glycerol (stabilizing agent) was adjusted after several trials. The substance was crumbled into yellow crystalline powder. The yellow crystalline powder was annealed at 500 æ%C for 6 hours. In the conventional method, the same amount of cerium nitrate was mixed with 2 drops of glycerol and kept in the conventional oven for 6 hours at 500 ˚C.

RESULTS AND DISCUSSION

Structural characterization

XRD studies

The x-ray diffraction pattern was studied using scifert – X –ray diffractomer with a CuKα (1.5406A˚) radiation. The diffracted intensities were recorded from 10˚ to 70˚ angle. The absence of extra peak claims the purity of the substance and also confirms the complete conversion of Cerium nitrate into CeO_2. In both the methods[30,b], the peaks are observed approximately at the same angle. All the diffraction peaks agreed well with the standard values for the face centered cubic structure of cerium oxide and matches well with the JCPDS number 81-0792.

The crystalline size of the sample was obtained from Scherrer's formula.

$$D = 0.9\lambda / \beta \cos\theta \quad eq \qquad (1)$$

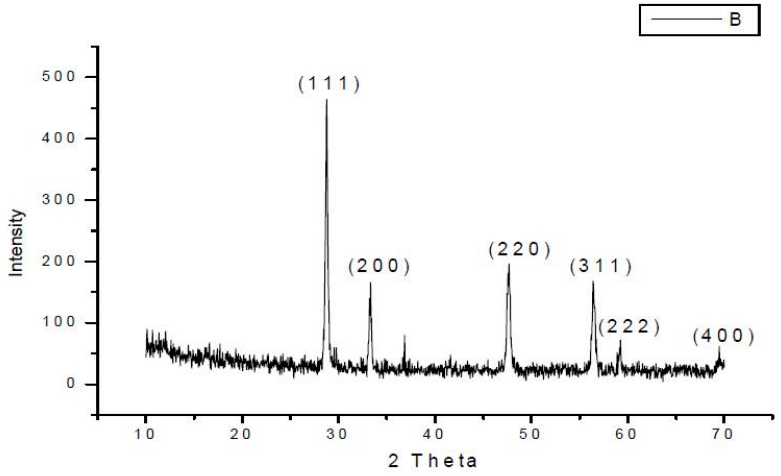

Figure 1 : XRD spectrum of cerium oxide nanoparticle synthesized using microwave

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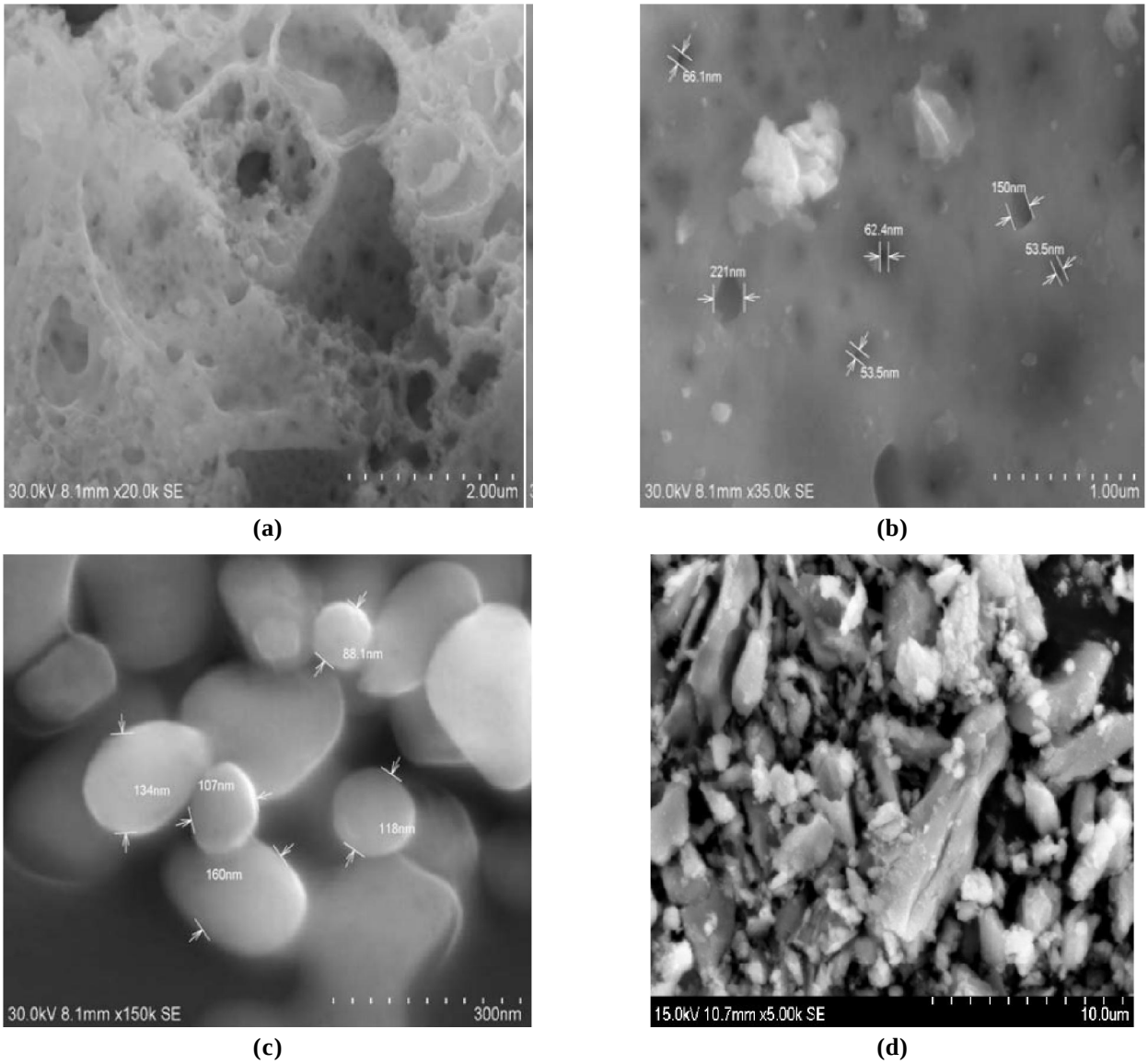

Figure 2 : SEM images of cerium oxide nanoparticles. (a) and (b) describes the porosity (c) morphology of the nanoparticle synthesized using microwave and (d) morphology of the nanoparticle synthesized using Conventional method

Where D-Crystallite size, λ- Wavelength (1.5406 A°), β-Full width at the half maximum of the peak (111) = 0.2525 θ- is the diffraction angle which is half of 2 θ = 28.74

The average crystalline size found to be around 56 nm It was found that the size decreases by microwave heating. The average particle size of the products prepared by conventional and microwave-assisted method are calculated to be ca. 59 and ca.56 nm respectively.

FESEM and EDAX analysis

The SEM image of conventional heating method show particle aggregates of irregular shapes and larger size. From the SEM image of cerium oxide nano particle synthesized using microwave, it was observed that the particles are spherical and almost of regular shape. This is due to the uniform environment provided by the microwave irradiation. A lot of pores are also found in the SEM image (Figure 2(a) and 2(b)) due to the steady evolution of gases. It is clear that, as more gases are evolved during combustion, more agglomerates were disintegrated and more heat could be carried away from the system, thereby reducing the size of the particle. The presence of voids makes the sample to act as sen-

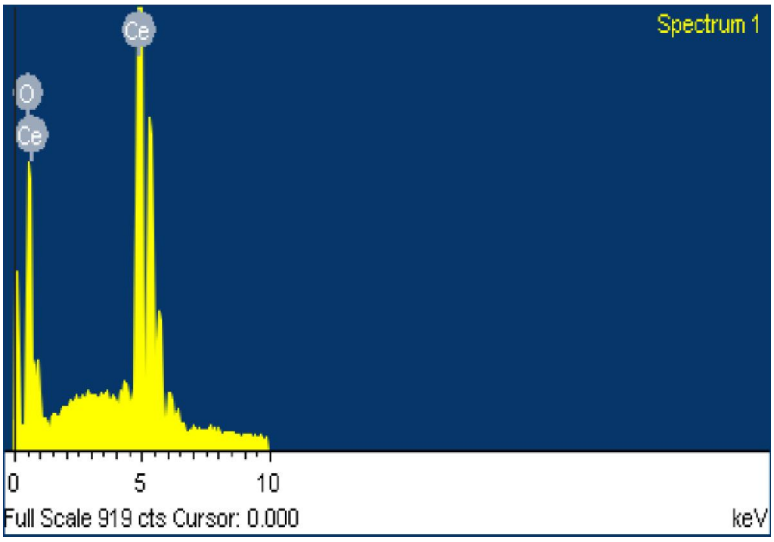

Figure 3 : EDAX spectrum of cerium oxide nano particle

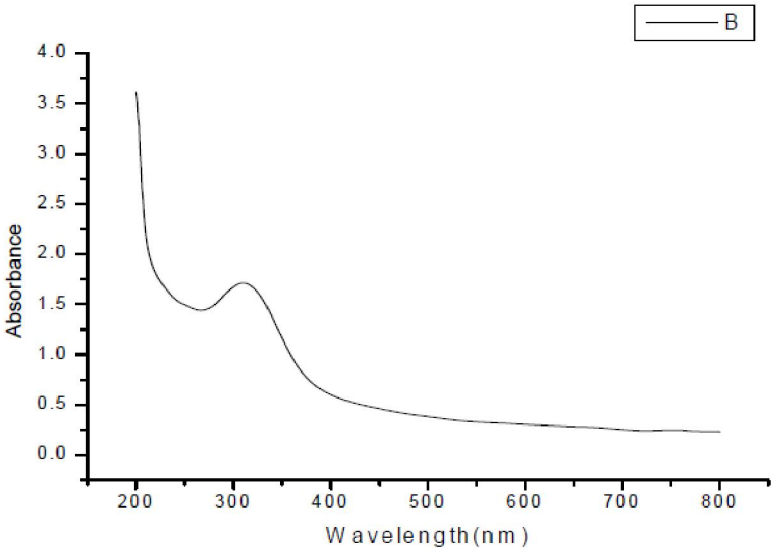

Figure 4 : Shows the absorption spectrum of cerium oxide synthesized using microwave method

sors for trapping the gaseous molecules[31].

The EDAX analysis represented in Figure 3 shows peaks only for Cerium and Oxygen which assures the purity of the sample.

Optical characterization and structural characterization

Cerium oxide nano particle synthesized using microwave method shows a strong absorption peak at 310 nm due to the charge transfer between the oxygen and cerium in CeO_2. The absorption peak shows a blue-shift (from 338 to 310nm) along with change in the mode of synthesis from conventional to microwave method. The blue shift confirms the size reduction in CeO_2 prepared using the microwave method[32]. The approximate bandgap value calculated from the λ_{max} using the formula given below.

Energy band gap = 1.2/ λ_{max} (eV) **(2)**

The band gap value calculated from the above equation is around 3.87 eV.

Luminescence spectral studies

The emission spectrum of cerium oxide nanoparticles synthesized using microwave shows peaks around 360, 410, 435 and a shoulder was observed around 460 nm. The peaks are blue shifted compared to the peaks observed for cerium oxide prepared using conventional method (378 nm, 438 nm and 484 nm). The investigation showed that the

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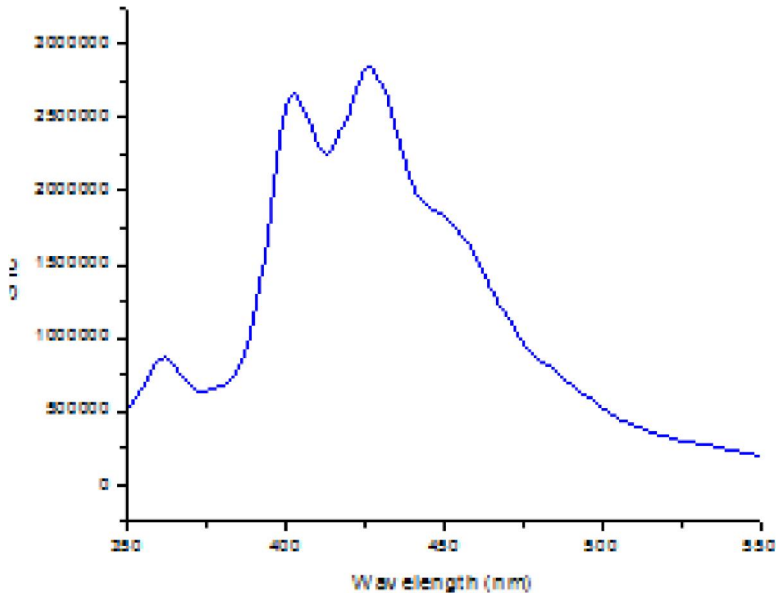

Figure 5

emission bands ranging from 400 to 500 nm for CeO_2 sample are attributed to the hopping from different defect levels of the range from Ce 4f to O 2p band[33]. In addition to this, the intensity of the peaks are very high compared to the conventional cerium oxide. This is due to the abundunt defect such as dislocations which is useful for fast oxygen transportation. The appearence of emission peak depends upon the mode of preparation and the presence of voids[34].

CONCLUSION

The CeO_2 nanoparticles were successfully synthesized by the solvent free and ecofriendly method using microwave and conventional method. The structural and optical characterization was carried out using XRD, SEM, absorption and fluorescence measurements respectively. The structural morphology changes with the method of synthesis. The shape changes from rod shape to spherical and the size reduces from 59 to 56 nm. The XRD spectrum shows the nanoparticles are crystalline pure phase CeO_2 nanoparticles with face centered cubic structure and the mean grain size was around 59 nm. The absorption shows blue shift in the absorption maximum from 338 nm to 310 nm which reflects the smaller size of the particle. The compound shows luminescence spectra with maxima at 378 nm, 438 nm and 484 nm respectively. The intensity of the peaks are high in the case of CeO_2 synthesized using microwave. The current investigation proves that the microwave method is the best method for the synthesis of the nano particles.

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