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A novel eco friendly synthesis of cerium oxide nano particles using glycerol as stabilizing agent

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ABSTRACT

Cerium oxide nano particles are synthesized by solvent free method using cerium nitrate as starting material and glycerol as organic dispersant. The material was characterized by XRD, SEM, UV - visible and fluorescence techniques. XRD analysis revealed that the cerium oxide nano particles has face centered cubic structure. The average grain size was about 59 nm. The surface morphology of the compound was carried out using SEM and the particles forms a nano tubular structure which grows up to 3 nm. The EDAX spectrum reveals the purity of the compound. The UV-spectrum shows a maximum at 338 nm which is due to the charge transfer from oxygen to cerium in cerium dioxide. The fluorescence spectrum shows three emission around 378, 438 and 484 nm.

INTRODUCTION

Cerium dioxide and ceria based materials have been investigated widely in recent years due to its potential application in electronic, ceramic, ultra precise polishing, gas sensor, catalysis, solid oxide fuel cells and so on[1-4]. Because of its excellent ionic conduction, doped cerium oxide nano particles are promising electrolyte materials for SOFC[5]. Hence the extensive research is going on in the synthesis of cerium oxide nano particles.

Many synthetic approaches such as Precipitation[6], So–gel method[7], microwave assisted hydrothermal process[8], electrochemical process[9], combustion method[10], direct sono chemical route[11] and the gas liquid co–precipitation have been used for the preparation of Cerium oxide nano particles[12]. Uekawa et al. prepared CeO_2 fine powders by forced hydrolysis at 383 K in polyethylene glycols[13]. They found that the reaction performed in polyethylene glycol solution with higher molecular weight favored the formation of mono dispersed CeO_2 powders. Verdon et al[14] adopted solvo thermal method in the preparation of sub micrometer CeO_2 particles at 150 bar. Micro emulsion is a very efficient method for preparing highly mono dispersed cerium oxide nano particles.

In all the above mentioned methods of synthesis, either a toxic solvent or expensive capping agents have been involved in the preparation of synthesis. Synthesis of zinc oxide nano particles was already reported in our earlier publication[15]. This is for the first time we are reporting the synthesis of cerium oxide nano particles of high purity through a solvent free, eco friendly and a high economic method. The absence of solvent in the synthesis avoids the contamination from the solvent and hence pure compound is obtained.

EXPERIMENTAL

All the reagents used were of analytical grade purity and hence were used without further purification. 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) was obtained from Merck.

Preparation of cerium oxide nano particles

About 4.3 g of cerium nitrate hexa hydrate was weighed and made into a paste with glycerol in a 50 ml. silica crucible. The amount of glycerol (stabilizing agent) was adjusted after several trials. The temperature of the muffle furnace was initially kept at 50°C. The temperature of the furnace was slowly raised to 200°C after the sample was kept inside the furnace. The nanoparticles formed are annealed at 800°C for 6 hours. The slight yellow crystalline powder obtained was characterized.

Characterization

The morphology of the compound was examined by scanning electron microscope (SEM) using Hitachi Su-6600. The elemental analysis were carried out using the energy dispersive X- ray analysis (EDAX) technique. The x-ray diffraction patterns was studied using scifert – X –ray diffractomer with a CuKα radiation. The diffracted intensities were recorded from 10 to 70 angle. The average grain size of the sample was estimated using Scherer equation[16].

The absorption spectra and emission spectra were recorded using Cary 100 Bio UV-Visible spectrophotometer and Fluoromax-4P spectrofluorometer respectively. For spectral analysis, the cerium oxide nano particles are dispersed in HPLC methanol with the help of a sonicator. Cerium oxide nano particles are sonicated in methanol for 10 minutes and the spectrum was recorded at room temperature.

RESULTS AND DISCUSSION

Structure and morphology characterization

The characteristic peak corresponding to the (111), (200),(220),(311),(222) and (400) are located at 2θ = 28.54, 33.07, 47.47, 56.33, 59.07, 69.40 respectively. All the diffraction peaks agreed well with the standard values for the face centered cubic structure of cerium oxide. The values matches well with the JCPDS number 81-0792.The absence of extra peak clearly tell the purity of the sample. The average crystalline size was obtained from the Scherer formula

$$D = 0.9\lambda / B\cos\theta \quad (1)$$

Where β is the full width half maximum and it is about 0.24 for the (111) plane. The λ value = 1.5406 and the 2θ = 28.54 for the (111) plane. The average grain size of the cerium oxide nanoparticle calculated is around 59 nm.

The surface morphology of the sample was examined using the SEM. Figure 2(a), (b) and (c) represent the surface morphology of the prepared cerium oxide.

The SEM image revealed that there were various sizes of particles in the prepared sample. The largest particles are composed of small crystallites and show particle aggregates of irregular shapes and larger sizes. The single nano rod grows even up to 3 μm. The energy dispersive X-ray spectrum in Figure 3 performed on the materials suggests the existence of Cerium and oxygen apart from the carbon peak. The carbon peak is due to the surface of the sample sprayed with carbon. The absence of any other extra peak clearly reveals the purity of the sample.

The EDAX spectrum in Figure 3 and the data in the TABLE 1 clearly shows that the weight percentage of cerium and oxygen is approximately 1:2.

Mechanism

Cerium nitrate on heating it becomes cerium oxide

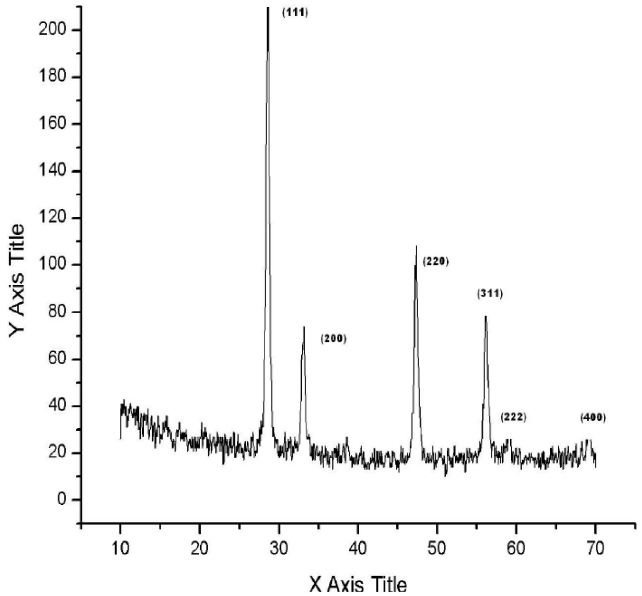

Figure 1 : Shows the typical XRD pattern of the as obtained nano particles

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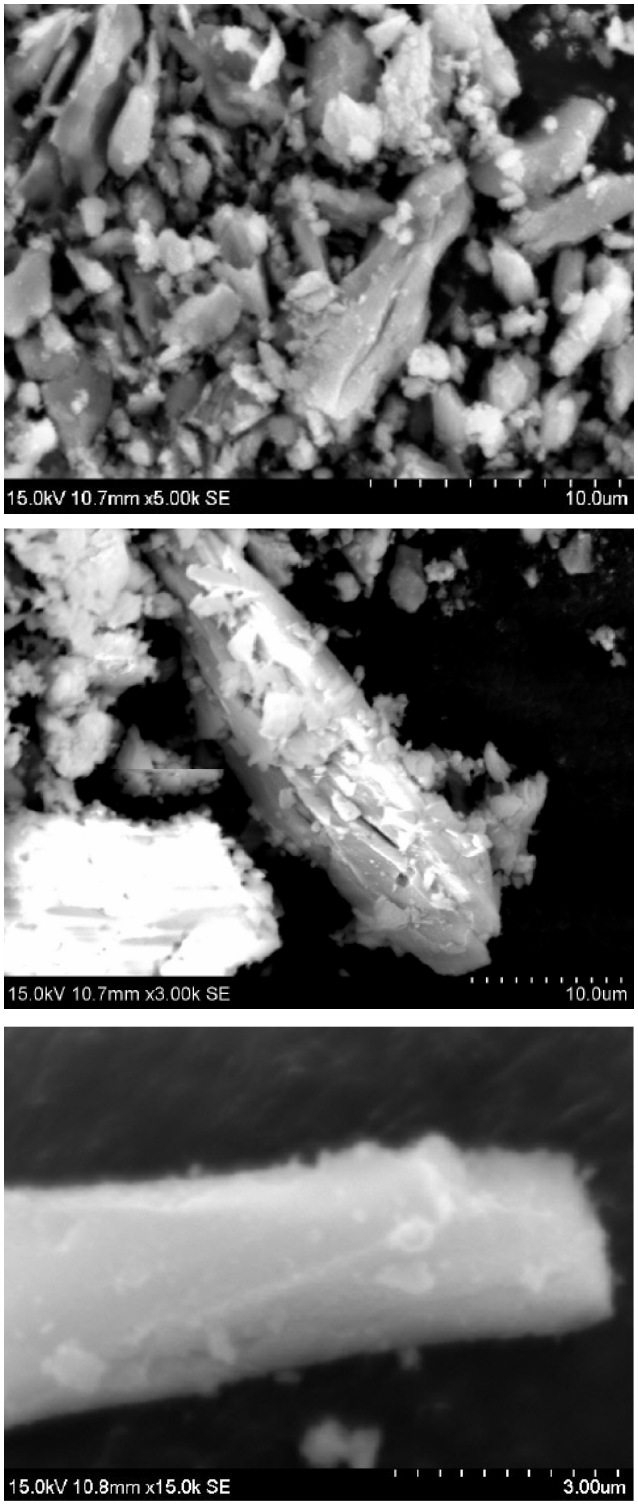

Figure 2 : A, B & C. SEM micrograph of the cerium oxide nano particles

and nitrogen dioxide. Glycerol acts as a stabilizing agent to avoid agglomeration.

$$Ce(NO_{3)})_2 \rightarrow CeO_2 + 2\,NO_2$$

The absence of solvent and other by products

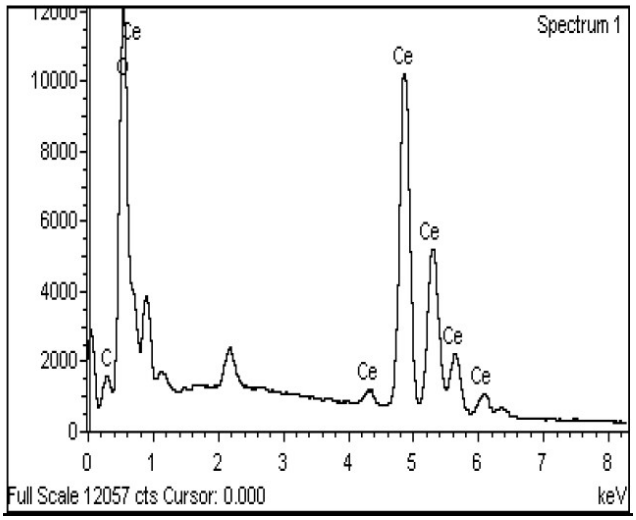

Figure 3 : The EDAX spectrum for the cerium oxide nanoparticle

TABLE 1

Element	Weight%	Atomic%
C K	3.93	14.07
O K	23.69	63.70
Ce L	72.39	22.23
Totals	100.00	

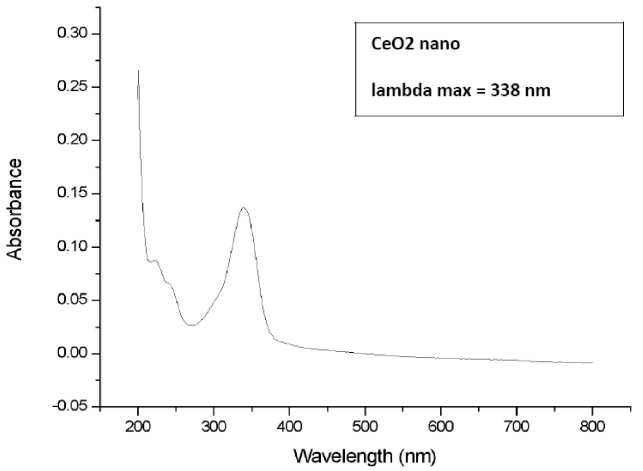

Figure 4 : UV–Visible spectrum of cerium oxide nano particle by calcinations at 800 °C using methanol as solvent

makes the reaction green.

Optical characterization

Optical properties of the sample were characterized by UV absorption and fluorescence spectrophotometer. The slight yellow crystalline powder was insoluble in water and almost in all organic solvents. The UV-Spectra was recorded for the sample dispersed in methanol solution.

Figure 4 shows the typical absorption spectrum of

the synthesized CeO_2 nano particles. A strong blue shifting absorption peak below 400 nm (at 338 nm) is originated from the charge transfer between the oxygen and cerium in CeO_2 [17]. The approximate bandgap value calculated from the λ_{max} using the formula given below.

Energy band gap = $1.2/\lambda_{max}$ (eV) **(2)**

The band gap value calculated from the above equation is around 3.5 eV. The photolumnescence spectrum of cerium oxide was recorded by many groups and a few of properties on photoluminescence have been reported in the literature earlier[18].

The room temperature photouminescence spectrum (RTPL) of the CeO_2 nano particles was recorded at the excitation wavelength 338 nm using fluorimeter is represented in Figure 5

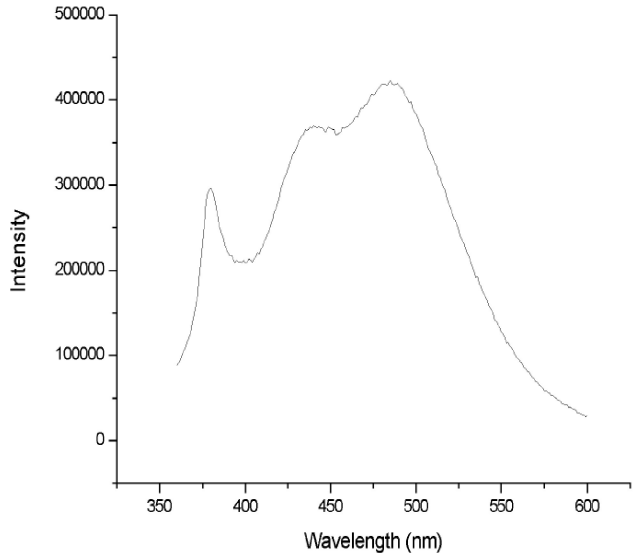

Figure 5 : The fluorescence spectrum of cerium oxide nanoparticle using methanol as solvent

The emission spectrum shows three characteristic peaks one at 378 nm, 438 nm and 484 nm respectively. These three emission peaks are characteristic of rod – like CeO_2 nanoparticles[19]. The investigation showed that the 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. It is suggested that the strong emission peak at 484 nm is related to the abundunt defect such as dislocations which is helpful for fast oxygen transportation.

CONCLUSION

The CeO_2 nanoparticles were successfully synthesized by the solvent free and eco friendly method. The structural and optical characterization were carried out using XRD, SEM, absorption and fluorescence measurements respectively. 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 sample shows absorption maximum at 338 nm and also exhibits room temperature photoluminescence of the blue light at 378 nm, 438 nm and 484 nm respectively. The current investigation proves that this is the simplest method in the synthesis of nano particles.

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