Research Article

Influence of Various Surfactants on Size, Morphology, and Optical Properties of CeO₂ Nanostructures via Facile Hydrothermal Route

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Different surfactants such as sodium dodecyl sulfate (SDS), polyethylene glycol (PEG), and cetyltrimethyl ammonium bromide (CTAB,) assisted cerium oxide (CeO₂) nanoparticles were synthesized by using cerium chloride and potassium hydroxide as the starting materials via facile hydrothermal route. The powder X-ray diffraction (XRD) shows that cubic fluorite-type structure of pure CeO₂ and the average crystallite sizes were calculated to be ~12–16 nm. Raman spectra of various surfactants assisted CeO₂ consist of a single triply degenerated F_{2g} mode characteristic of the fluorite structure. The elongated spherical-like morphology of SDS assisted CeO₂ samples was observed from the SEM and TEM studies. Optical absorption spectra showed a blue shift by the capped CeO₂ due to the quantum confinement effect. Photoluminescence (PL) emission studies shows that there is a change in the intensity of emission peaks by the capping agents, which indicates that the capping layers did result in size changes or increased surface defect.

1. Introduction

Synthesis of nanomaterials with controlled morphology, size, chemical composition, and crystal structure, and in large quantity, is a key step toward nanotechnological applications [1]. Nanocrystalline cerium oxide (CeO₂) materials have received much attention owing to their physical and chemical properties, which are markedly different from those of the bulk materials [2]. Ceria is an important rare-earth oxide with rapidly increasing applications in several fields due to its high refractive nature, strong UV absorption property [3], and high transparency in the visible and IR region [4]. Due to these properties, it has been widely used for a variety of applications such as fuel cells, gas sensors, NO removal, glass polishing material, and UV-blockers and filters [3–7]. It is well known that the new properties and applications of materials are related to their shapes and sizes [8]. Moreover, the morphology of the product can be controlled, through proper choice of the surfactants. A variety of methods, including spray pyrolysis, microwave-hydrothermal, sol-gel,

and hydrothermal and chemical precipitation route, have been successfully used to create ceria nanoparticles [7–12]. Among the other methods, the hydrothermal approach is a better alternative with the advantages of the simplicity of the process, high purity, easy scaleup, narrow particle size distribution, chemical homogeneity, and low environmental pollution.

Cationic, anionic, and nonionic surfactants can play an important role in synthesizing the nanomaterial in different interesting morphologies [13]. It can be used to control the size, shape, and agglomeration among the particles. However, the cationic surfactant (CTAB) assisted nanocrystalline CeO₂ was prepared by organophilic method [14] and the nonionic surfactant (PEG) assisted nanostructured CeO₂ was reported by chemical precipitation route [12]. Mei et al. [15] reported the anionic surfactant (SDS) assisted nanocrystalline CeO₂ powders by hydrothermal method. In this current work, under the influence of different surfactants by using hydrothermal process, the structural, morphological, and optical properties of CeO₂ nanoparticles are investigated.

2. Experimental Procedures

All the chemical reagents were commercial with AR purity and used directly without further purification. Initially, 0.1 M of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was dissolved in 50 mL distilled water under vigorous stirring at room temperature. After that, 0.05 M of SDS was added to the above transparent solution under stirring. Similarly, 0.2 M of KOH pellets was dissolved in 50 mL distilled water in a separate container. Thereafter, the milky-white-colored sol solutions were formed by the slow addition of KOH solution to the above cerium chloride solution under stirring conditions. Then, 3 mL of H_2O_2 was dropped in the mixture within half an hour. After that, the mixed solution was maintained under stirring at room temperature for 12 hrs. The resultant products were transferred into a Teflon-lined autoclave for the reaction at 160°C for 12 hrs, and thus yellowish-white colored precipitates were collected. Finally, yellow-colored CeO_2 nanopowders were formed at 400°C for 2 h. The same procedure was followed for the preparation of CeO_2 nanoparticles, using different surfactants such as CTAB and PEG.

The XRD pattern of the CeO_2 samples were recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using $\text{CuK}\alpha$ ($\lambda = 0.154 \text{ nm}$) radiation, with a diffraction angle between 20 – 80° . The FTIR spectra of the samples were taken using an FTIR model Bruker IFS 66W Spectrometer. Raman spectra were collected using a Bruker RFS 27: stand-alone model Raman spectrometer with Fourier transform. The laser source is Nd: YAG 1064 nm. SEM images were carried out on JEOL, JSM-67001. TEM images were taken using a TEM CM200 with an accelerating voltage of 200 kV. The UV-Vis absorption spectra were recorded using a Varian Cary 5E spectrophotometer in the range of 200–800 nm. The PL spectra of the CeO_2 were recorded by using the Perkin-Elmer lambda 900 spectrophotometer with a Xe lamp as the excitation light source.

3. Results and Discussion

Figure 1 shows the powder XRD patterns of the various surfactants assisted CeO_2 samples calcined at 400°C for 2 h. All the diffraction peaks agreed well with the standard values (JCPDS number 81-0792), indicating that pure cerium oxide was synthesized via the present preparation procedures. The surfactant addition in the precursor improves the crystallinity and enhances the growth of crystallites along certain preferred directions as evident in Figure 1(a–c). It is clearly indicated that the well-crystalline and single phase of pure CeO_2 , which can be indexed to the cubic fluorite structure of CeO_2 with lattice constant of, $a = 5.412 \text{ \AA}$ [8]. The average crystallite sizes of the CeO_2 samples mediated by the SDS, PEG and CTAB were calculated, using Scherrer's equation, as 12.53, 13.24 and 16.07 nm, respectively.

The FTIR spectra of the various surfactants assisted CeO_2 samples are shown in Figure 2(A). The broad absorption in $\sim 3345 \text{ cm}^{-1}$ is assigned to the existence of stretching vibration of hydroxyl groups on the surface of the samples. The weak absorption bands at ~ 2380 and 1430 cm^{-1} are attributed

FIGURE 1: XRD pattern of (a) SDS, (b) PEG, and (c) CTAB assisted CeO_2 nanoparticles.

to the bending vibration of C–H bands of the incorporated surfactant residuals [8]. The absorption band around 1637 cm^{-1} is attributed to the bending vibration of absorbed molecular water, which can be seen in all the specimens. The strong absorption band at $\sim 662 \text{ cm}^{-1}$ is assigned to Ce–O stretching band [16].

Figure 2(B) exhibits the Raman spectra of the various surfactants assisted ceria nanoparticles. According to the literature, CeO_2 with a fluorite structure has one Raman active triply degenerated F_{2g} mode as a symmetric breathing mode of the oxygen atoms around the cerium ions, which is located at 458, 462 and 467 cm^{-1} for SDS, PEG, and CTAB assisted samples, respectively [9, 17]. Among them, the SDS assisted sample exhibits the enhanced intensity of broad peak, which can be ascribed to the smaller crystallite size.

Figures 3(a)–3(c) show the SEM images of the various surfactants assisted ceria nanoparticles. In the case of SDS, the spherical-like elongated particles are observed with the average crystallite size in the range of ~ 10 – 15 nm , and thus it results in small-size particle (Figure 3(a)). PEG is a large molecule polymer; although it could coat onto the CeO_2 particles, they formed flower-petals-like morphology of larger clusters as shown in Figure 3(b). Moreover, it seems that CTAB has a weaker effect on the reduction in particle size rather than SDS or PEG and thus some agglomerated small rods-like ceria particles were observed as shown in Figure 3(c). Since the particle size is too small to be identified by SEM, the SDS-capped CeO_2 nanoparticles were further analyzed by TEM, as shown in Figure 4.

Figures 4(a) and 4(b) show the bright and dark field images of SDS-assisted CeO_2 nanoparticles. The SDS-mediated CeO_2 sample showed the ultrafine spherical-like elongated particles with loosely agglomerated status depicted in the bright field image (Figure 4(a)) and also illustrated by their corresponding dark field image (Figure 4(b)). The average particle size is calculated to be $\sim 12 \text{ nm}$, which is in good agreement with the XRD results. The addition of anionic surfactant (SDS) reduces the surface tension of the cerium precursor solution, which facilitates nucleation

FIGURE 2: (A) FTIR and (B) Raman spectra of (a) SDS, (b) PEG, and (c) CTAB assisted CeO₂ nanoparticles.

FIGURE 3: SEM images of (a) SDS, (b) PEG, and (c) CTAB assisted CeO₂ nanoparticles.

FIGURE 4: TEM images of (a) bright field (b) dark field, and (c) diameter size distribution histogram of SDS assisted CeO₂ nanoparticles.

and allows its easier spreading. The van der Waal's force may be responsible for the formation of CeO₂ agglomerates [18]. The selected area electron diffraction (SAED) pattern of their corresponding image is shown in the inset of Figure 4(a). The appearance of strong diffraction spots rather than diffraction rings confirmed the formation of poly-crystalline cubic fluorite structure of CeO₂, which is in good agreement with the XRD patterns.

From the data obtained by the TEM image, the particle size histogram can be drawn and the mean size of the particles can be determined. Figure 4(c) shows the particle size distribution of the CeO₂ nanoparticles. It can be seen that the particle sizes possess a small- and narrow-size distribution in the range from 3 to 21 nm, and the mean diameter is about 12 nm for the SDS assisted sample.

Figure 5(A) shows the UV-vis absorption spectra of various surfactants assisted CeO₂ nanoparticles. The presence of the various surfactants caused significant absorption shifts into the UV region. It is well known that optical band gap (E_g) can be calculated based on the optical absorption spectra by the following equation:

$$(\alpha h\nu)^n = K(h\nu - E_g). \quad (1)$$

Plotting $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) and extrapolating the linear portion of the curve gives the value of the direct band gap energy (as shown in the inset of Figure 5). The corresponding band gap energies of SDS, PEG, and CTAB assisted CeO₂ nanoparticles can be calculated to be 3.74, 3.67, and 3.61 eV, respectively, which is larger than the bulk CeO₂ ($E_g = 3.19$ eV) [19]. The results show that a blue shift has occurred. Moreover, the blue shift phenomenon might be ascribed to the quantum confinement effect. Optical absorption spectra confirmed the capping effectiveness by the selected capping agents, as the SDS-capped CeO₂ colloids were absorbed at shorter wavelength than the other capped CeO₂ indicating smaller crystal size. Hence, the various surfactants assisted ceria samples should be more efficient for absorption of UV lights.

Figure 5(B) shows the room temperature PL emission spectra of the various surfactants assisted CeO₂ nanoparticles with an excitation wavelength of 300 nm. In the UV emission region, the strong peak at ~337 nm with the corresponding energy of 3.68 eV is called near band edge emission, which is likely to be associated with a band-to-band recombination process, possibly involving localized or free excitons [20].

FIGURE 5: (A) UV-vis absorption and (B) PL emission spectra of (a) SDS, (b) PEG, and (c) CTAB assisted CeO_2 nanoparticles.

In the blue-green emission region, the several weak peaks at ~ 438 , 452, 461, 481, 493, and 510 nm with the corresponding energies of 2.83, 2.74, 2.68, 2.57, 2.51, and 2.43 eV, respectively, are obviously lower than the deduced band gap, which can be attributed to the presence of oxygen vacancies. It is noticed that there is a change in the intensity of emission peaks by the capping agents, which indicates that the capping layers did result in size changes or increased surface defect.

4. Conclusions

Various surfactants assisted cerium oxide (CeO_2) nanoparticles were synthesized by facile hydrothermal route. The XRD and Raman results confirmed the cubic fluorite-type structure of pure CeO_2 nanoparticles. The elongated spherical-like morphology of SDS assisted CeO_2 samples was observed from the SEM and TEM studies. The surfactants assisted CeO_2 nanostructures show strong absorption in the UV region. Therefore, CeO_2 nanostructures may be suitable for UV blocking or shielding materials. PL emission studies show that there is a change in the intensity of emission peaks by the capping agents, which indicates that the capping layers did result in size changes or increased surface defect.

Conflict of Interests

This is the authors' original work. The paper has been written by the stated authors who are all aware of its content and approve its submission, which has not been published previously. It is not under consideration for publication elsewhere; no conflict of interests exists, and if accepted, the paper will not be published elsewhere in the same form, in any language, without the written consent of the publisher.

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