Synthesis and characterization of surfactant assisted CeO$_2$/ZrO$_2$ nanocomposite

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Abstract

This paper reports the synthesis of CeO$_2$/ZrO$_2$ nanocomposite by wet chemical method using cationic surfactant (CTAB). The properties of the obtained nanocomposites were analysed by X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), UV-Diffuse Reflectance Spectroscopy (UV-DRS) and photoluminescence (PL) spectroscopy. XRD results confirm the formation of the crystalline nature and the mixed phase of CeO$_2$/ZrO$_2$ nanocomposites. FTIR and EDX results confirm the formation of Ce-O and Zr-O bond. The TEM studies revealed the spherical morphology of the CTAB assisted CeO$_2$/ZrO$_2$ nanocomposites in the size range of 26.8 nm. The UV-DRS studies revealed the bandgap value of CeO$_2$/ZrO$_2$ nanocomposites. The photoluminescence properties of CeO$_2$/ZrO$_2$ nanocomposites were observed in the strong UV region and several visible region peaks are likely to have originated from the oxygen vacancies.

Keywords: CeO$_2$/ZrO$_2$; CTAB; Wet chemical; Optical.

1. INTRODUCTION

ZrO$_2$ is an n-type semiconductor with wide band gap of Eg = 5.0eV is more valuable for important industrial applications such as photocatalytic, antibacterial, gas sensing and spintronic devices [1]. Recent research lies in doping and mixing metal oxide with ZrO$_2$ which enhance the applications in various fields. Various metal oxides mixed with ZrO$_2$, such as Bi$_2$O$_3$/ZrO$_2$, PbO$_2$/ZrO$_2$ and ZrO$_2$/V$_2$O$_5$ are used in different types of applications because of their enhanced optical and chemical properties [2-4]. In addition, cerium oxide (CeO$_2$) is a good rare earth photo catalyst with the band gap of 3.2eV and CeO$_2$ based materials have received much attention due to their
excellent physical and chemical properties, low cost and environment friendly feature. CeO$_2$ doped and mixed with various metal oxide show its potential applications such as photocatalytic activity, lithium ion batteries etc [5,6]. Likewise, ZrO$_2$ mixed with CeO$_2$, enhanced their properties and show their excellent photo catalytic activity, bio sensor etc [7-10]. Recent research interests lie in the morphological controlled synthesis of heterogeneous photocatalyst due to their enhanced properties and potential applications. This paper manifests the synthesis of CeO$_2$/ZrO$_2$ nanocomposite with well dispersed spherical morphology using cationic surfactant (CTAB) by wet chemical method. This wet chemical method is very simple, inexpensive, non toxic and yield high purity products. The properties of the prepared nanocomposites are characterized by different techniques such as XRD, FTIR, SEM, TEM, UV-DRS, PL, EDX, and SAED.

2. EXPERIMENTAL
2.1 Preparation of CeO$_2$/ZrO$_2$ nanocomposite
CeO$_2$/ZrO$_2$ nanocomposites were prepared by mixing of 0.1 M of cerrous chloride and zirconium oxy chloride octahydrate in water and stirred it for 30 min at room temperature to ensure the formation of the homogeneous mixed salt solution. Then cationic surfactant (CTAB) were added together and stirred for 1 h at room temperature. After the completion of 1 h the aqueous ammonium hydroxide solution was added dropwise to attain the pH-6.5 and stirred continuously for 2 hrs. The resultant product was dried for 12 hrs at 120°C. After that, it was washed with water several times and then calcined at 600°C for 8 hrs.

2.2 Characterisation
The XRD pattern of the nanopowder was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα ($\lambda=1.5417$ Å) radiation. The Fourier transform infrared (FTIR) spectra of the samples were taken using an FTIR model Bruker IFS 66 V spectrometer. High- resolution images and selected area electron diffraction patterns were observed by a JEOL JEM-2200FS transmission electron microscope (TEM) operating at 200 kV. The morphological studies of the samples were carried out by the SEM (Philips model CM 20) with EDX analysis. The optical absorption spectrum was obtained on a CARY 5E UV–VIS–NIR spectrophotometer. The photoluminescence emission spectra were carried out on a Fluoromax-4 spectrofluorometer with a Xe lamp as the excitation light source.

3. RESULTS AND DISCUSSION
The X-ray diffraction pattern of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite are shown in Fig. 1. The four peaks in the pattern with 20 values of 29.8, 34.4, 49.6 and 59.1 correspond to the (101), (002), (022) and (203) planes which indicates the formation of tetragonal and monoclinic structure of ZrO$_2$ that are matched well with the reported values in JCPDS card 17-0923 and JCPDS card 37-1484. Similarly, the five peaks with 20 values 28.6, 33.2, 47.6, 56.4 and 69.6 that are correspond to the (111), (200),
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(220), (311) and (400) planes that indicates the formation of pure phase CeO$_2$ in a cubic fluorite structure [7,8]. Moreover, the XRD patterns exhibit the sharp peaks which reveal the well crystalline nature of the synthesized CeO$_2$/ZrO$_2$ nanocomposites. No peaks were observed due to the impurities which confirm the formation of pure CeO$_2$/ZrO$_2$ nanocomposite. The average crystallite size of the sample was calculated by using the Debye-Scherrer’s equation (Equation 1) from full width at half maximum (FWHM) values of the CeO$_2$ and ZrO$_2$ planes.

$$D = \frac{0.89 \lambda}{\beta \cos \theta}$$

Where $\lambda$ represents the wavelength of the X-ray, $\theta$ indicates Bragg’s angle, and $\beta$ is the FWHM of the characteristic peaks. The average crystallite size of the sample was found to be 26.8 nm.

![XRD pattern of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.](image)

**Fig. 1:** XRD pattern of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.

The FTIR spectrum of CeO$_2$/ZrO$_2$ sample prepared at three different pH values are shown in Fig. 2. From the spectra, the vibrational peaks observed at 3418 and 1639 cm$^{-1}$ are due to the vibrations of $\ce{-OH}$ and $\ce{H_2O}$ functional groups. The absorption band observed in the region 549 cm$^{-1}$ is associated with the stretching vibrations of Zr-O-Zr and Ce-O stretching vibration which are in close agreement with the reported values [11,12]. The band observed at 715 cm$^{-1}$ is due to the Ce-Zr bridge formation, which is in close agreement with the reported literatures [13]. The peak observed at 2924 cm$^{-1}$ can be attributed to the residual organic components.
Fig. 2: FTIR spectrum of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.

Fig. 3(a) shows the SEM micrograph of the CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite. The SEM image shows the dispersed spherical morphologies were observed for the sample. The EDX spectra of CeO$_2$/ZrO$_2$ nanocomposite are presented in Fig. 3(b). The peaks corresponding to Zr, Ce and O are clearly observed in the EDX spectrum at their normal energy and the results are clearly indicating the formation of CeO$_2$/ZrO$_2$ nanocomposite.

Fig. 3(a) SEM image and Fig. 3(b) EDX pattern of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.

Fig. 4 shows the TEM image of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite. The well dispersed spherical morphologies were observed the TEM images. TEM result reveals the surfactant play key role to controlling the nucleation and crystal orientation. In the crystallization process, the surfactant molecules adsorbed on the crystal nuclei, as a result the dispersed spherical nanostructure were produced. The surfactant influences
the formation process and prevents the particle agglomeration. The SAED results clearly demonstrate the poly crystalline nature of the prepared sample as shown in the inset of Fig.4. The schematic formation of the CeO$_2$/ZrO$_2$ nanocomposites is shown in Fig. 5.

![TEM image of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite (SAED pattern inserted).](image1)

**Fig. 4** TEM image of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite (SAED pattern inserted).

![Schematic formation of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite](image2)

**Fig. 5** Schematic formation of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite

The DRS-UV absorption spectrum of the CTAB assisted CeO$_2$/ZrO$_2$ nanocomposites are shown in Fig. 6 with absorption region at 409 nm. Further, the optical band gap energy of all prepared samples was calculated using the following relation.

\[
E_g = \frac{hc}{\lambda} \text{ (eV)}
\]

Where, \(E_g\) represents the band gap energy (eV), \(h\) is the Planck constant, \(c\) is the velocity of light in meters and \(\lambda\) represents lower cutoff wavelength in nanometer. The corresponding band gap values are 3.03 eV. The shifted band gap value revealed
the formation of the mixed metal oxide CeO$_2$/ZrO$_2$ nanocomposites and it suggests a potential material for photocatalysis and opto-electronic devices [6].

![Fig. 6 UV-DRS spectrum of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.](image)

Fig. 6 UV-DRS spectrum of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.

Fig. 7 shows the room temperature PL emission spectrum of the CTAB assisted CeO$_2$/ZrO$_2$ nanocomposites. The strong and weak UV emission peak at 323 and 396 nm is ascribed to the nearest band edge emission of the excitons. In addition, the strong blue green emission peak at 468 nm, weak blue green emission peaks appearing in 451, 484 and 494 nm, are likely to have transition in defect states [14]. Furthermore, it can be seen that the CTAB assisted CeO$_2$/ZrO$_2$ nanocomposites exhibit the higher luminescent peaks in both UV and visible region and it might be used for optoelectronic devices and photocatalytic applications.

![Fig. 7 Room temperature PL emission spectrum of CTAB assisted CeO$_2$/ZrO$_2$ nanocomposite.](image)
4. CONCLUSION

In summary, nanocomposites of CeO$_2$/ZrO$_2$ with spherical morphology were prepared by using the wet chemical method together with CTAB as a surfactant. XRD and FTIR results confirm the formation of the well crystalline nature of ZrO$_2$ and CeO$_2$. The UV-DRS studies revealed the band gap of the CTAB assisted CeO$_2$/ZrO$_2$ nanocomposites and this result implying the improvement of surface oxygen vacancies may open up a new avenue for environmental remediation for the treatment of waste water and gas sensing. The PL results exhibit the CeO$_2$/ZrO$_2$ nanocomposites might be used for optoelectronic devices.

REFERENCES


