

Optical and structural properties of sol–gel derived nanostructured CeO₂ film

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Abstract: Sol–gel derived nanostructured CeO₂ film was deposited on glass substrate using by dip-coating technique with annealing at 650 °C. X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), UV/vis and photoluminescence (PL) spectroscopy studies were employed to analyze the structural and optical properties of the sol–gel derived nanostructured CeO₂ film. The average crystallite size was estimated from the XRD pattern using by Scherrer equation as about 3–4 nm. An SEM micrograph shows that the film was porous in nature and crack free. The UV-visible absorption spectroscopic measurement results showed that the products had conspicuous quantum size effects. The absorption spectrum indicates that the sol–gel derived nanostructured CeO₂ film has a direct bandgap of 3.23 eV and the photoluminescence spectra of the film show a strong band at 378 nm: it may have a promising application as an optoelectronic material.

Key words: sol–gel derived nanostructured CeO₂ film; band gap; photoluminescence; UV/VIS

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1. Introduction

Nanostructured metal oxides have attracted considerable attention from many researchers due to their diversity of applications in various technological fields of science and technology^[1–4]. These nanostructured metal oxides have unique physical and chemical properties, which are significantly different from their bulk counterparts^[5, 6]. In particular, cerium oxide is a promising material which shows a potential application in gas sensors^[3, 7], fuel cells^[8], solar cells^[4] and as a coating material^[9]. Several studies have been reported on the size dependent properties that can increase the attention due to size-induced changes in physical and chemical properties^[10, 11]. The optical properties of CeO₂ could be tuned for their specific applications by adopting suitable chemical and physical synthesis processes^[12]. Ceria (CeO₂) films are prepared by a large variety of techniques which include spray pyrolysis^[13], sonochemical and microwave assisted thermal decomposition^[12, 14, 15], fluxing and hydrothermal treatments^[9, 16], sol–gel^[17, 18], PECVD^[19]. These have been successfully used to create ceria nanoparticles and thin films^[20]. Among these wet chemical deposition techniques, sol–gel processing has been widely used to deposit a variety of films, including metal oxides containing a single cation, as well as more complex oxides^[8, 9, 18, 20–23]. The sol–gel technique for facile fabrication of large-area coatings at low cost offers some advantages of controlling the composition and nanostructure of the particles, an asset for eventual technological applications^[20]. Apart from this, fabrication of nanostructured CeO₂ films is lacking, which is intensively studied because of their unique chemical and physical properties for coating on solar cell and sensor applications. They are derived from their low dimensionality and possible quantum-confinement effects. For extensive application of nanostructured CeO₂ film, an economical mass production method must be developed.

This article describes a modified sol–gel process for the

fabrication of nanostructured CeO₂ film via the dip-coating method. The films were characterized using X-ray diffraction, SEM, FTIR, UV-visible and PL spectroscopy.

2. Experimental

2.1. Chemicals and reagents

All chemicals such as (NH₄)₂Ce(NO₃)₆, NH₄OH, HNO₃ and ethanol were of analytical grade and purchased from Merck India Ltd, Mumbai, India. Borosile glass plates were procured from Borosile Mumbai, India. The deionized water obtained from a Millipore water purification system (Milli Q 10 TS) was used for the preparation of solutions and buffers.

2.2. Sol preparation

A modified method has been used for the fabrication of CeO₂ nanostructured film^[20]. Diluted ammonia solution (1 M) was added into a deionized water dissolved cerium ammonium nitrate [(NH₄)₂Ce(NO₃)₆] solution drop-wise under vigorous stirring. Upon adding the ammonia solution, precipitation of Ce(OH)₄ occurred. Excess ammonia solution was added drop-wise until a solution of pH 10 was achieved, obtaining a gray colored precipitate. The resulting mixture was left to magnetically stir continuously at 70 °C for 3 h for the reaction to complete. After stirring to get a pale yellow precipitate of Ce(OH)₄ which was subsequently washed several times with deionized water and centrifuged to remove residual reactants NH₄⁺, Cl[−], NO₃[−] and neutral pH was achieved. Cerium hydroxide was dispersed in distilled water and an equimolar quantity of HNO₃ (pH = 1) was added; an orange-colored semitransparent viscous sol was obtained. The semitransparent solution was heated to 90 °C with stirring for 4 h, and turned into a colorless transparent sol. The transparent sol was stable for several months when kept in air at room temperature.

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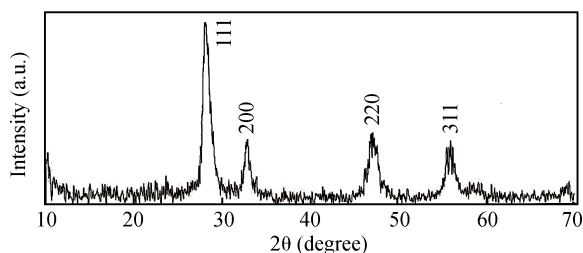
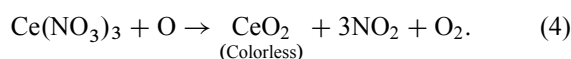
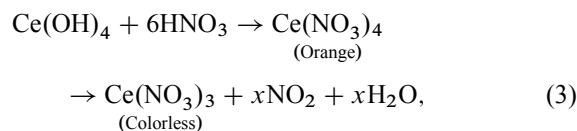
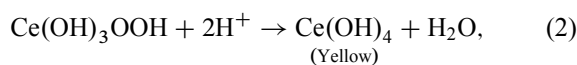
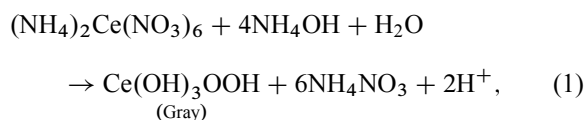


Fig. 1. X-ray diffraction pattern of sol-gel derived nanostructured CeO₂ film.

2.3. Film preparation

A glass substrate was used for film fabrication, and was carefully pre-cleaned with chromic acid, liquid laboratory detergent and water. The substrate (glass) was further cleaned with de-ionized water, washed with acetone and dried. The film was deposited onto glass substrate using the dip-coating method with a selected pulling speed of 10 cm/min. The prepared film was dried in air at room temperature and afterward heated at 650 °C for 30 min. The reaction for the sol-gel prepared nanostructured CeO₂ film deposited on glass plate is given by the following equations.



2.4. Characterization of sol-gel derived nanostructured CeO₂ film

Phase identification of the fabricated sol-gel derived CeO₂ films was carried out by an X-ray diffractometer using CuKα radiation (Rigaku). A scanning electron micrograph (SEM), JSM-5600 LV (JEOL, Japan) was utilized to observe the morphology of the sol-gel derived CeO₂ film. Fourier transform infrared spectra (FTIR) were recorded on a Perkin-Elmer, Model 2000 in the wave number range 400–4000 cm⁻¹. The optical absorption spectra of the sol-gel derived CeO₂ film were recorded on a Shimadzu UV-2100 spectrophotometer in the wavelength range 200–600 nm. Photoluminescence (PL) spectra were measured at room temperature with a spectrophotometer (Perkin Elmer L-55).

3. Results and discussion

3.1. Structural properties

Figure 1 shows the results of X-ray diffraction (XRD) studies carried out for the sol-gel derived CeO₂ film. The XRD pattern reveals all of the major peaks of CeO₂, corresponding

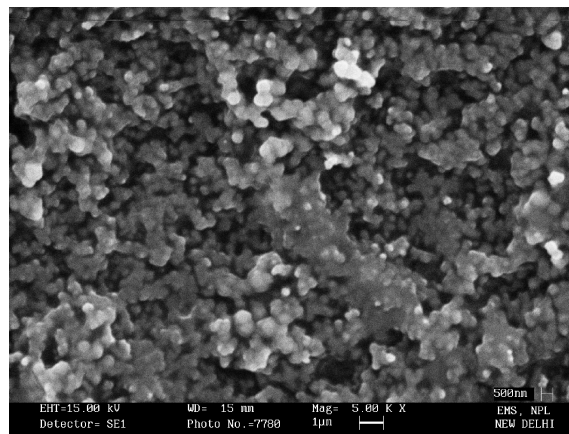


Fig. 2. SEM micrograph of sol-gel derived nanostructured CeO₂ film.

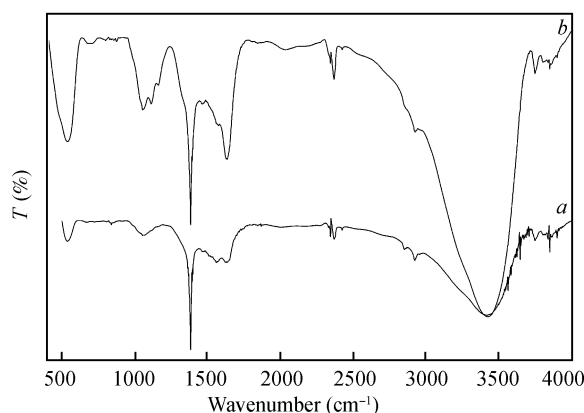


Fig. 3. FTIR spectra of (a) bulk CeO₂ and (b) sol-gel derived nanostructured CeO₂ film.

to the (111), (200), (220) and (311) crystallographic plane cubic fluorite structure (space group Fm3m (225)) as identified using the standard data JCPDS Card No. 34-0394. The intensities and positions of the peaks are in perfect agreement with the literature values. No peak of any other phase is detected indicating the high purity of the product. The broadening of the reflections in the diffractogram distinctly indicates the formation of nano-dimensional crystals. The average crystallite size has been estimated by the analysis of the broadening of (111) and (220) reflections and has been found to be 3–4 nm.

Figure 2 shows an SEM image of sol-gel derived nanostructured CeO₂ film deposited on glass substrate via the dip-coating technique. The SEM micrograph results illustrate that the nanostructured CeO₂ film on glass substrate is quite uniform, crack free, continuous and very porous. The prepared film shows high stability and does not show any leaching in strong acids such as nitric acid, hydrochloric acid and sulphuric acid.

3.2. Optical properties

Figure 3 shows the result of the FTIR spectral measurement carried out for sol-gel derived nanostructured CeO₂ film together with bulk CeO₂ powder film deposited on glass via the drop-casting method. The FTIR spectra show all principal vibrational modes, which are in good agreement with those in

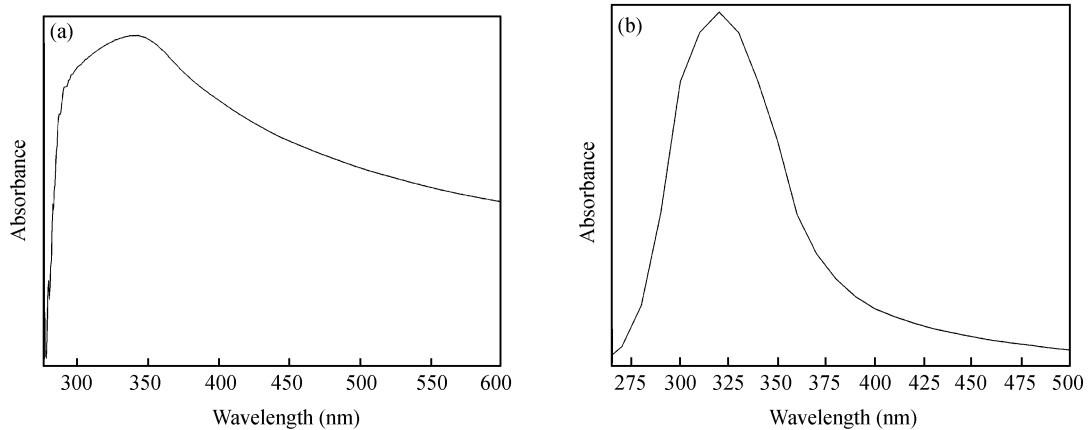


Fig. 4. Absorption spectra of (a) bulk CeO₂ and (b) sol-gel derived nanostructured CeO₂ film.

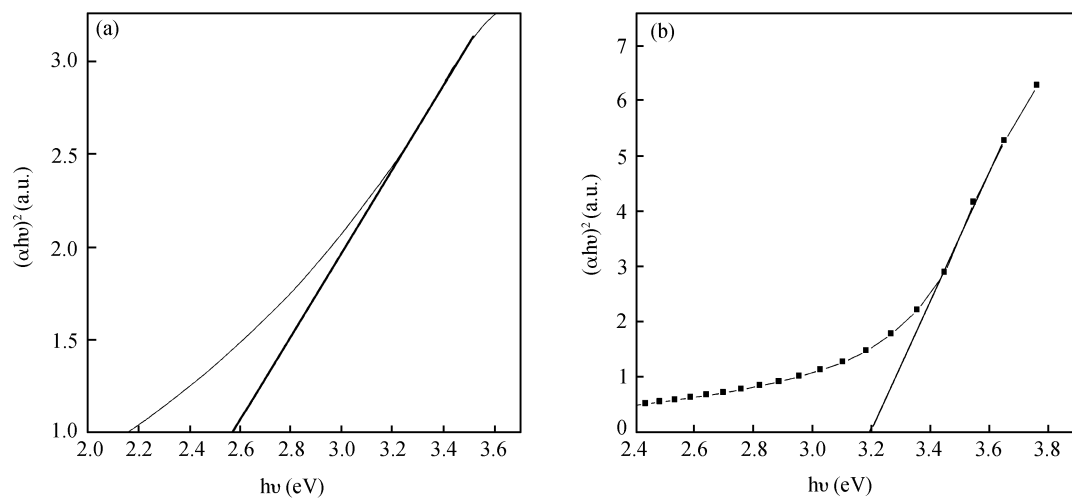


Fig. 5. (a) Plots of $(\alpha h\nu)^2$ versus photon energy for bulk CeO₂. (b) Plots of $(\alpha h\nu)^2$ versus photon energy for sol-gel derived nanostructured CeO₂ film.

Refs. [5, 11, 26]. A diffuse band at about 3417 cm^{-1} is observed, attributed to the stretching vibration of the physically associated water (O–H) molecule on the film surface. Another two bending vibrational bands of physically adsorbed water molecules are also observed at 1632 and 1381 cm^{-1} [11]. A weak peak appears at about 533 cm^{-1} , produced by CeO₂, which is assigned to the Ce–O stretching band [5].

Figure 4 shows the optical absorption spectra of sol-gel derived nanostructured CeO₂ film and bulk CeO₂ powder film (bulk CeO₂ powder was dispersed in ethanol and film was deposited on glass substrate via the drop-casting method). The spectrum of sol-gel nanostructured CeO₂ film and bulk CeO₂ shows a broad absorption band located at 320 and 337 nm in the UV range, respectively, originating from the charge transfer transition from O²⁻ (2p) to Ce⁴⁺ (4f) orbitals in CeO₂ [14, 15]. These spectral profiles indicate that the charge transfer transition of Ce⁴⁺ overlaps with the 4f¹–5d¹ transition of Ce³⁺ [27]. The absorption peak of sol-gel derived nanostructured CeO₂ film is significantly blue-shifted compared to the bulk CeO₂, due to the decreasing particle size. This blue-shifting phenomenon in the absorption spectrum of nanostructured CeO₂ has attracted the interest of many researchers in

recent years [5, 14, 15, 27]. Since sol-gel derived nanostructured films have smaller grain sizes and random orientation, one could suggest that the higher concentration of grain boundaries is responsible for broadening the absorption edge and the apparent shift toward lower energies of the band gap [15, 27]. An estimate of the optical band gap E_g can be made by using the following equation for a semiconductor: $\alpha h\nu = C(h\nu - E_g)^n$, where α is the absorption coefficient, $h\nu$ is photon energy, C is a constant, $n = 2$ for a directly allowed transition, and $n = 1/2$ for an indirectly allowed transition [5]. The optical absorption coefficient α is calculated according to the equation $\alpha = (2.303 \times 10^3 A\rho)/lc$, where A is the absorbance of a sample, ρ is the real density of CeO₂ (7.28 g/cm^3), l is the path length, and c is the concentration of the ceria suspensions [14, 27]. For direct transition, the plots of $(\alpha h\nu)^2$ versus photon energy for nanoporous CeO₂ film are shown in Fig. 5(b); this reveals that the band gap increases from 2.56 to 3.23 eV as the particle size decreases. The value of (E_d) for CeO₂ is consistent with the results reported in Refs. [15, 25, 27]. The absorption edge of the present sol-gel derived nanostructured CeO₂ film is mostly larger ($(E_d) = 3.23\text{ eV}$) compared with that of the bulk CeO₂ powders ($(E_d) = 2.08\text{ eV}$), which mainly

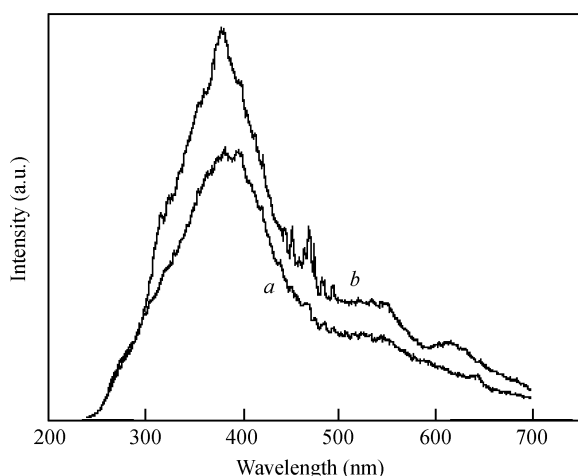


Fig. 6. PL spectra of (a) bulk CeO_2 and (b) sol-gel derived nanostructured CeO_2 film.

results from quantum confinement effect^[5]. Masui *et al.* have reported that the blue shift is due to a charge-transfer optical transition rather than the quantum size effect, explained as being due to the valence state of the Ce ion following charge transfer, and also due to the quantum size effect by decreasing the crystal size. At present, both interpretations may account for the blue shift of the absorption edge.

Figure 6 shows the photoluminescence spectra of sol-gel derived nanostructured CeO_2 film and bulk CeO_2 powder film excited at a similar wavelength (220 nm) at room temperature. Upon excitation at 220 nm, a strong blue-green emission is observed from the Ce^{4+} ions in CeO_2 film. A significant enhancement in the emission band is observed in the spectrum of sol-gel derived nanostructured CeO_2 film compared to the bulk CeO_2 powder film; this may be due to the change in particle size and the quantum size effect. This emphasizes the fact that the d electrons of cerium couple differently to the lattice phonon in the cubic fluorite structure, leading to a higher Stokes shift. A broad band, peaking at 378 nm, is ascribed to the charge transition from the 4f band to the valence band of CeO_2 as previously reported for CeO_2 film^[14, 25]. The excitation of CeO_2 is supposed to originate from the initial “ $\text{Ce}^{4+} - \text{O}^{2-}$ ” CT transition in the host lattice absorbing the excitation light. This phenomenon has been explained by charge transfer transition from the 4f band to the valence band of CeO_2 ^[14, 25].

4. Conclusion

Sol-gel derived nanostructured CeO_2 film has been fabricated on glass substrate through dip-coating via the sol-gel technique. Optical and structural properties were discussed and correlated with the bulk counterpart. The observed optical spectral results indicated that the direct band gap increases from 2.08 to 3.23 eV after film annealing at 650 °C. Such a difference in band gap was possibly ascribed to the different grain sizes in the two samples. The CeO_2 film shows a remarkable enhancement in PL intensity with respect to the bulk CeO_2 powder due to the small grain size development of pores in the films because of the creation of oxygen vacancies. Efforts should be made to utilize these sol-gel derived nanostructured CeO_2 films in gas sensors, biosensors, fuel cells, solar cell coat-

ings and development of sensors, because of the good porosity of the films.

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