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Ce^{3+} and oxygen vacancy mediated tuning of structural and optical properties of CeO_2 nanoparticles

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ABSTRACT

Ceria nanoparticles were synthesized by hydrolysis of cerium nitrate in basic medium. The cubic fluorite structure of ceria was confirmed by XRD. From TEM studies ceria nanoparticles were found to be spherical in shape with an average diameter of 5 nm. The prepared nanoparticles have a predominant orientation along (2 2 2) crystallographic plane. Oxygen vacancies and Ce^{3+} lead to the lattice expansion and strain in CeO_2. Peak asymmetry and broadening of Raman active mode peak further confirms the presence of these defects. Total concentration of oxygen vacancies that are present in the ceria nanocrystallites is calculated to be 1.234×10^{20} cm^{-3}. These oxygen vacancies and ceria related defects result in an effective red shifting of the band gap by changing its structural regularity. The visible luminescence peaks are also caused by these Ce^{3+} and oxygen vacancy centers.

1. Introduction

CeO_2 based nanomaterials have tremendous possibility for use in diverse applications such as three way catalysts (TWC) for exhaust gas treatment from vehicles, oxide ion conductors in solid oxide fuel cells, electrode materials for sensors, high temperature superconducting materials, ultraviolet blocking materials, as photocatalyst, sunscreen cosmetics and luminescent materials [1–6]. The usability of CeO_2 for most of these applications depends on its ability to release or uptake oxygen. Ceria has large oxygen storage capacity depending on Ce^{4+}/Ce^{3+} redox cycles which in turn depends on the concentration and types of oxygen vacancy in the lattice structure. Larger is the amount of oxygen vacancies, more efficient it is for storing oxygen [7]. Reduction in grain size of ceria nanoparticles in nanoregime has effect on the optical, electrical properties compared to bulk one due to surface defects, phonon confinement, internal strain etc. [8–10]. In ceria a size dependency variation of lattice parameter takes place due to the difference in Ce^{3+} and Ce^{4+} sizes which results in the growth of lattice and development of strain arising from loss of oxygen from surface region [11–13]. In ceria the oxygen nonstoichiometry are present in the grain boundary and these vacancies play an important role on the stable grain boundary structure of ceria [14]. Quantum mechanical calculations reported that the most favorable defect structure in CeO_2 is $Ce^{3+}–O_v–Ce^{3+}$ [15,16]. Raman spectroscopy is a valuable tool to understand the presence of internal strain and oxygen vacancy which results in asymmetry and peak shifting of active mode peak. This is because of the sensitivity of the lattice vibration to local environment [17–19]. The formation of Ce^{3+} has effect in the red shifting of the band gap of CeO_2 nanostructures [20]. Photoluminescence in ceria arises due to strong light absorption through the charge transfer between O^{2-} and Ce^{4+} [21]. CeO_2 based nanostructures, thin films are prepared by adopting different synthesis procedures including solvothermal [4], sol–gel [22] hydrothermal [23], pulsed electron beam deposition [24] etc. In this report we have adopted sol–gel route to synthesize CeO_2 nanoparticles. We have attempted to investigate how oxygen vacancies and cationic Ce^{3+} defects, present in ceria, affect the band gap property by changing its structural regularity and also control the visible luminescence in the material.

2. Experimental details

2.1. Synthesis of CeO_2 nanoparticles

CeO_2 nanoparticles are prepared by basic hydrolysis of cerium nitrate hexahydrate, $Ce(NO_3)_3{\cdot}6H_2O$. In a typical synthesis 0.1 M solution of cerium nitrate hexahydrate are prepared in 46 ml of water. The mixture was stirred for 20 min after which aq. NH_3 solution was added to the above solution dropwise to make the pH of the solution 8–9. The solution adopts a whitish color which ultimately turns into yellow at the end of 2 h. The yellow sol was then kept unstirred for 3 h after which it was centrifuged and sonicated in water followed by ethanol for 3–4 times. The washed product

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was kept in oven at 80 °C for drying and then annealed at 430 °C to increase the crystallinity.

2.2. Characterization

The crystalline structure of CeO_2 was recorded with Miniflex Rigaku X-ray diffractometer equipped with intense Cu Kα radiation (0.154 nm), at a scan rate of $1^\circ\,min^{-1}$ and in the scan range from 10 to 80°. Phase identification was achieved by comparing the diffraction data of the prepared CeO_2 nanoparticles with international centre for diffraction data (ICDD) standards JCPDS (joint committee on powder diffraction standards) software. The size and shape of the particles was analyzed on a JEOL JEM 3010 high resolution transmission electron microscope (HRTEM) operating at an accelerating voltage of 300 kV. Raman spectra were recorded with LabRAM HR (Horiba-Jobin Yvon) high resolution Raman spectrometer using 633 nm He–Ne laser with a spectral resolution of $0.5\,cm^{-1}$. Diffuse reflectance spectra (DRS) were collected with a Shimadzu 2450 UV-Vis spectrophotometer taking $BaSO_4$ as the reference. Luminescence spectra were recorded with a Perkin Elmer LS 55 fluorescence spectrometer.

3. Results and discussion

CeO_2 has a fluorite structure in which Ce^{4+} is surrounded by eight equivalent O^{2-} ions forming the corner of a cube, with each O^{2-} co-ordinated to four Ce^{4+} ions [12,22]. The exact structure of CeO_2 nanoparticles is shown in the X-ray diffraction (XRD) pattern in Fig. 1a. The observed pattern matches to the cubic fluorite structure of CeO_2 (JCPDS-340394) [5,29]. Without considering the strain, the average crystallite size is found to be 8 nm as determined from Scherer's formula $d = 0.9\lambda/\beta \cos\theta$, where d is the crystallite size, λ is the wavelength of X-ray radiation and β is the full width at half maximum (FWHM) in radian. The lattice constant a is calculated by X-ray peak broadening of (1 1 1) peak. The lattice parameter we have got in this case is 0.5416 nm which is slightly higher than that of bulk CeO_2 ($a = 0.5411$ nm) reported in the standard JCPDS-340394 [25,29].

XRD peak broadening is controlled by both size and lattice strain which is appropriately expressed by Williamson–Hall (W–H) equation [26,27].

$$\frac{\beta\ \cos\theta}{\lambda} = \frac{1}{D} + \eta\frac{\sin\theta}{\lambda} \tag{1}$$

where β is the FWHM in radians, λ is the wavelength of X-ray radiation, θ is the Bragg angle of the corresponding peak, D is the effective crystallite size and η is the effective strain. In Fig. 1b $\beta \cos\theta/\lambda$ is plotted against $\sin\theta/\lambda$ and after linear fitting the intercept gives the effective crystallite size (D) and slope gives the strain (η). Usually oxygen vacancy and Ce^{3+} leads to the generation of strain and hence expansion of the lattice structure of nanoparticles [12]. In the small sized ceria, the number of Ce^{3+} is higher than in its bulk counterpart. Ce^{3+} is formed by the reduction of Ce^{4+} by the electrons left behind when an oxygen vacancy is created in the lattice. The size variation in Ce^{4+} and Ce^{3+} and oxygen vacancies distort the local symmetry of ceria and generate strain in the lattice [11,12]. By undergoing lattice expansion, CeO_2 releases the internal strain [12,13]. However, surface stress in the small sized nanoparticles may also be partially responsible for this expansion [23]. In our analysis, a positive strain of 0.00961(η) resulted in a size (D) of 12.3 nm. Since W–H plot gives the effective crystallite size with considering strain, so this value is higher than that of the size obtained from Scherer's formula where the strain term is not considered. A schematic view of fluorite structure of CeO_2 along with oxygen vacancy and Ce^{3+} in the lattice site is shown in Fig. 2.

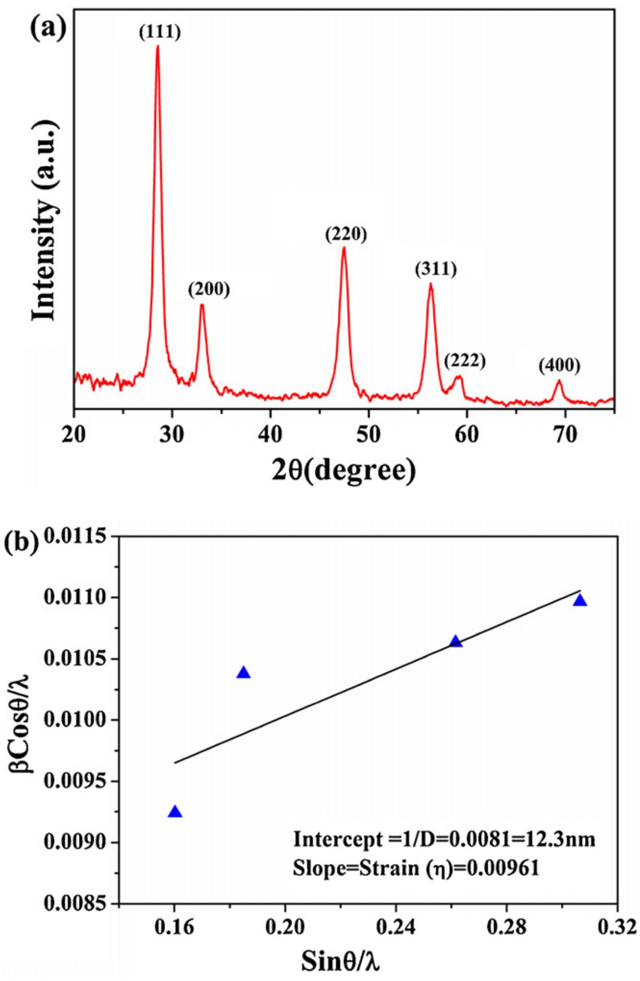

Fig. 1. X-ray diffraction of (a) CeO_2 nanoparticles and (b) observation of positive strain in the material confirms lattice expansion.

In CeO_2, the crystallites have a preferred growth direction or preferred orientation along a particular plane. This can be found out by calculating the texture coefficient ($TC_{h k l}$) of each XRD peak [28].

$$TC_{h\ k l} = \frac{I_{(h k l)}/I_{0(h k l)}}{(1/n)\sum_n I_{(h k l)}/I_{0(h k l)}} \tag{2}$$

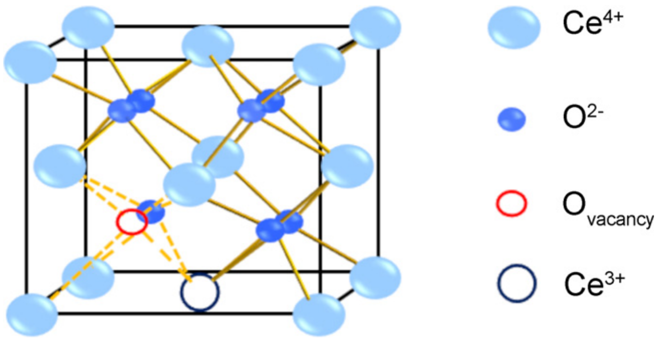

Fig. 2. Schematic representation of cubic fluorite structure of CeO_2. The light blue ball is of Ce^{4+}, the dark blue ball is of O^{2-} on lattice site, red circled ball is of oxygen vacancy and the unfilled blue ball represents Ce^{3+} on lattice site formed after the removal of oxygen either from surface or from interior of CeO_2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)