Structural and optical properties of zirconium oxide (ZrO$_2$) nanoparticles: effect of calcination temperature

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Abstract

In this article, we report the structural and optical properties of zirconium oxide (ZrO$_2$) nanoparticles synthesized via chemical co-precipitation method. The effect of calcination temperature on structural and optical properties of ZrO$_2$ nanoparticles is investigated through XRD, FESEM, EDX, FTIR, UV–Vis absorption, fluorescence emission and life time measurements. XRD spectrum reveals the tetragonal phase at calcination temperature 600 °C and crystallinity of samples increases with calcination temperature. At 800 °C the phase transition from tetragonal to tetragonal-monoclinic mixed phase is noticed. The FESEM images show the particles are of irregular shape and highly agglomerated. FTIR spectra also confirm the formation of ZrO$_2$ in crystalline phase. From UV–vis absorption spectra it is found a strong quantization and varying band gap with calcination temperature. The change in emission wavelength and intensity with phase change is observed from fluorescence emission spectra. At higher calcination temperature emission intensity is decreased which may be due to the phase change and the formation of surface defects. The life time measurements also reveal the different trap states and life time with calcination temperature.

1. Introduction

Wide band gap metal oxide nanoparticles have attracted scientific attention due to their wide range applications. Zirconium oxide (ZrO$_2$) also known as zirconia with its excellent chemical and physical properties have applications such as fuel cells [1], gas sensors [2], optoelectronics [3], catalyst [4], and corrosion resistant material [5]. With band gap ≈5 eV, ZrO$_2$ is an important luminescent material with good optical transparency [6] and a potential candidate for photocatalytic applications due to its high surface area and presence of large number of oxygen vacancies [7]. It comes in three crystal phases namely tetragonal, monoclinic and cubic. The existence of these polymorphs depend on the synthesis process, particle size, calcination temperature and defects. There are contrasting reports on the existence of the phases with calcination temperature. Although monoclinic ZrO$_2$ is believed to be more stable at room temperature than the other two polymorphs but the tetragonal phase can also be stabilized at room temperature depending on the synthesis process [8]. In literature there exist various methods of synthesis of ZrO$_2$ nanostructures like sol-gel [9], hydrothermal [10], combustion [11], and co-precipitation [12, 13].

Calcination temperature not only modifies the morphology and size of nanoparticles but also create the defects and thus generating new energy levels. Further, the calcination temperature modifies the phase of the materials and it affects the optical and structural properties. Photoluminescence is sensitive to structure, chemical composition and defects is an important property to study in ZrO$_2$. The photocatalytic activity of ZrO$_2$ and other metal oxide semiconductor have been well studied [14–17]. Ilkhechi and group have reported the
effect of calcination temperature on optical properties of various metal doped TiO$_2$ and ZrO$_2$ nanopowders [7, 17]. They have shown the rate of calcination and calcination temperature significantly modifies the optical properties. There are many contrasting reports on broad PL emission of ZrO$_2$ nanostructures. Due to defects and excess vacancies the PL band position of ZrO$_2$ depends on excitation wavelength ranging from 340 nm to 240 nm [18]. It has been shown that the PL intensity of nano-ZrO$_2$ decreases with increase in calcination temperature because of oxygen vacancies as well as due to phase transformation [19]. Further, it is noticed that PL intensity depends on the excitation wavelength clearly pointing the different trap levels due to defects. ZrO$_2$ nanotube arrays fabricated by anodization have exhibited different types of photoluminescence peaks with annealing temperature [20]. The calcination temperature induced phase transformation from tetragonal to monoclinic and mixed phase was noticed for different temperature and its effect on optical properties was investigated by Kumar et al [21]. Ioy et al [22] have studied the effect of annealing temperature on photoluminescence properties of ZrO$_2$ thin films and shown $\lambda_{ex}$ changes with coating. Sidhu et al [23] have shown that PL intensity depends on annealing temperature due to change in crystallinity and surface defects. 

However, there are no detailed reports on the effect of calcination and phase transformation on life time of carriers and photoluminescence. Very little attention is paid to the life time measurement of ZrO$_2$ nanoparticles. In the present work, we report the effect of calcination temperature on structural and optical properties including that of life time measurement of ZrO$_2$ nanoparticles synthesized via chemical co-precipitation method using zirconium sulphate and sodium hydroxide as a sources materials. The method is simple, low cost and the required starting materials are less.

2. Experimental section

2.1. Synthesis

Zirconium sulphate (SRL Chem. Pvt Ltd), sodium hydroxide pellets and ethanol are of analytical grade and used as received. In typical procedure, 0.01 mole (2.834 g) of zirconium sulphate was dissolved in 100 ml of deionised water and stirred uniformly using a magnetic stirrer at room temperature. Sodium hydroxide solution was obtained by dissolving 0.04 mole (1.6 g) of sodium hydroxide pellets in 50 ml deionised water. Sodium hydroxide solution was added drop wise under continuous stirring to Zr(SO$_4$)$_2$ solution. During the addition of sodium hydroxide, colourless solution changes into a white precipitate. The resulting precipitate was filtered and purified by washing with deionised water and ethanol, then dried at 90 °C in hot air oven for an hour. Thereafter white colour powder was heated in deionised water on sand bath at 250 °C for 5–6 h to recrystallize and remove impurities. Then nanopowder were filtered by using whatman filter paper. Finally, the powder was calcinated at temperatures 600 °C and 800 °C for 2 h in muffle furnace. Hereafter we refer the as- prepared sample as S0 and the samples calcinated at 600 °C and 800 °C as S1 and S2, respectively.

2.2. Characterization techniques

The synthesized samples were characterized through XRD, FESEM, EDX, FTIR and optical properties are investigated by UV–vis absorption, Fluorescence emission spectroscopy and Life time measurements. The structural properties of ZrO$_2$ nanopowder are studied through the X-ray diffractometer (Rigaku, Ultima-IV). The surface morphology and size of nanoparticles is investigated through Field Emission Scanning Electron Microscopy (JEOL, JSM-7100F). FTIR spectroscopy (Nicolet-6900 spectrophotometer) was used to know the presence of functional group in ZrO$_2$ nanoparticles. The optical studies of samples were carried out by UV–vis absorption spectrophotometer (JASCO, V-670) and fluorescence emission spectrophotometer (HORIBA, Fluoromax-4) at room temperature with optimized excitation wavelength of 310 nm. Time resolved fluorescence spectra of samples were recorded by Chronos BH, ISS spectrofluorometer.

3. Results and discussion

3.1. XRD analysis

Figures 1(a)–(c) depict the X-ray diffraction spectra of ZrO$_2$ nanoparticles at different calcination temperatures. XRD spectrum of S0 sample (figure a), shows that the amorphous phase is formed. Diffraction peaks of sample S1 (figure b), confirms the formation of the tetragonal phase and well matched with JCPDS No. 81–1455 [24]. The diffraction peaks located at 2θ are 30.27°, 35.22°, 50.26°, 59.16°, 60.17°, 62.94°, 74.54°, 81.76° and 85.04° corresponding to the (111), (101), (110), (121), (211), (202), (220), (213) and (310) lattice planes respectively. Small diminish peaks at 28.20° shows the beginning of phase transition from tetragonal to monoclinic phase. XRD pattern of sample S2 (figure c) clearly show that the tetragonal–monoclinic mixed phase is formed. The peaks observed at 28.33° and 31.54° corresponding to the (−111) and (111) plane of monoclinic phase and is well matched with JCPDS No. 37–1484.[25, 26] The intensity of diffraction peaks corresponding to tetragonal
phase were reduced as compared to the sample S1 due to the growth of monoclinic phase. The volume fractions of tetragonal and monoclinic phases of the ZrO$_2$ were calculated using the peak intensity ratio formula [27].

\[
\%T = \left( \frac{I_{T}(101) + I_{T}(110)}{I_{T}(101) + I_{T}(110) + I_{M}(-111)} \right) \times 100,
\]

where \(I\) represents the diffraction intensity of the crystalline plane. Calculated values of phase volume fraction and lattice constants evaluated from (110) and (101) planes for samples S1 and S2 are given in table 1. We have also estimated the crystallite size from the most intense peak (101) of tetragonal structure by using Scherer formula.

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Here \(D\) is the crystallite size, \(K\) is the shape factor, being equal to 0.9, \(\lambda\) is the X-ray wavelength, \(\beta\) is the full width at half maximum of the diffraction peak, and \(\theta\) is the Bragg diffraction angle in degree. The estimated value of crystalline size of the samples S1 and S2 are 12.56 nm and 14.50 nm, respectively.

It is found that the particle size increases with increasing calcination temperature and there is a noticeable phase transition.

### 3.2. Morphological analysis

Figures 2(a)–(c) shows the surface morphology investigations of samples by the FESEM at different calcination temperature. It is found that the particles are in almost irregular shape and highly agglomerated. Further, it is found that the agglomeration is different for different calcination temperatures and increase in particle size is also be noticed.

### 3.3. Elemental analysis

To know the elemental composition of ZrO$_2$ nanoparticles, we have also made EDX characterisation. Figure 3 shows the EDX spectra of ZrO$_2$ nanoparticles. Graphs a–c respectively, represent EDX spectrum of sample S0, S1 and S2. The EDX spectra of all samples clearly show the strong intense peaks relating to Zr and O. From EDX spectra, weight and atomic percentage of Zr and O, respectively, for sample S0 is 80.65, 43.28 and 17.45, 53.41 and for S1 is 67.89, 27.05 and 32.11, 72.95 and that of sample S2 is 79.03, 39.80 and 20.97, 60.20. The presence of Si in the sample S0 may be due to the fact that S0 is amorphous and the grid used for the sample holding is coated.

#### Table 1. Volume fraction of tetragonal and monoclinic phases and lattice parameters.

| Samples | % Tetragonal | % Monoclinic | Particle size (nm) | Lattice parameter (Å) |
|---------|--------------|--------------|--------------------|-----------------------|
|         |              |              |                    | a         | c         |
| S1      | 91.04        | 8.96         | 12.56              | 3.5968    | 5.1519    |
| S2      | 82.87        | 17.13        | 14.50              | 3.5988    | 5.2110    |

Figure 1. XRD spectra of ZrO$_2$ nanoparticles. Graphs a–c respectively, represent XRD spectrum for the samples S0, S1 and S2.
with Si. The sample S0 being amorphous in nature, the crystallinity of samples S1 and S2 increases with increase in calcination temperature. As the calcination temperature increases clearly the weight percentage of Zr and O changes. For 800 °C calcination temperature the decreases in O weight and atomic percentage is due to creation of oxygen vacancies.

Figure 2. FESEM images of ZrO$_2$ nanoparticles. Images (a–c) represent the sample S0, S1 and S2 respectively.
3.4. FTIR analysis

FTIR spectroscopy is used to assess the formation and quality of the samples. Figure 4 shows the FTIR spectra of ZrO$_2$ nanoparticles. Curves a-c represent FTIR spectrum for samples S0, S1, and S2, respectively. The strong absorption band observed in the range from 3200 to 3800 cm$^{-1}$ due to the stretching vibration $\text{–OH}$ group of water molecule adsorbed on the surface of ZrO$_2$ nanoparticles and peak centered at 1632 cm$^{-1}$ refers to characteristic bending vibration of $\text{–OH}$ group of water molecule [28, 29]. The peaks at 2360 cm$^{-1}$ indicates the...
stret=ching vibration of hydroxyl zirconium (Zr–OH) bond [30]. Sharp peaks observed around at 500 cm\(^{-1}\) corresponding to the stretching vibration of Zr–O of ZrO\(_2\) phase [20, 21, 31] and this confirms the formation of ZrO\(_2\) as crystalline phase. The intensity of higher absorption band decreases with calcination temperature which is inferred that the removal of water molecules from sample and particle growth.

3.5. UV-vis absorption spectroscopy

UV–vis absorption spectroscopy is a non-destructive tool to analyse the optical properties of semiconductor nanostructures. Absorption spectra of samples were recorded using JASCO V-670, UV–vis absorption spectrophotometer by dissolving the nanopowder in ethanol in the wavelength range of 700 nm to 200 nm. Figure 5(i) shows the UV–vis absorption spectra of ZrO\(_2\) nanoparticles for different calcination temperature. Curves a–c respectively, represent absorption curves for samples S0, S1, and S2. Inset graph shows the absorption spectra to all samples for limited wavelength range. It is seen that absorption edge of ZrO\(_2\) is different for different calcination temperature. Optical band gap of nanoparticles is calculated by using Tauc formula.\[ (\alpha h\nu)^n = A(h\nu - E_g) \]

Here, \(\alpha\) is the absorption coefficient calculated by normalizing the absorption data with respect to path length, \(h\nu\) is the energy of photon and \(E_g\) is the energy gap and the value of \(n\) depends on the nature of transition; it takes values as 2, 2/3, 1/2, and 1/3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden, respectively[32]. The variation of \((\alpha h\nu)^n\) versus \(h\nu\) is linear at the absorption edge which confirms that ZrO\(_2\) is semiconductor with direct band gap. In figure 5(ii), curves a–c respectively, depict Tauc plots for the samples S0, S1, and S2. The estimated direct band gap of S0 sample is found to be 5.50 eV and that for S1 and S2 are found to be 5.46 eV and 5.42 eV respectively. We have observed that energy band gap of ZrO\(_2\) decreases with calcination temperature which may be inferred that increase in grain size and surface defect such as oxygen vacancies.

3.6. Fluorescence emission spectroscopy

Fluorescence (FL) emission spectroscopy is extensively used to study the various point defects such as vacancies, interstitials, and impurities. FL intensity depends on solvents, surrounding environment, starting materials, processing time and calcination temperature. In order to vary the defect related levels, the sample are calcinated at 600 °C and 800 °C and its effect on FL intensity is studied. Figure 6 depicts the fluorescence spectra of ZrO\(_2\) nanoparticles. The optimized excitation wavelength \(\lambda_{ex} = 310\) nm was fixed for all the samples. Curves a–c respectively, represent emission intensity for S0, S1 and S2 recorded in the range of 320–500 nm. Inset graph shows the FL spectra to all samples for limited wavelength range. Clearly, we see that there is a noticeable change in the emission wavelength and emission intensity for the ZrO\(_2\) nanoparticles with calcination temperature. Luminescence in ZrO\(_2\) nanoparticles is described by three kinds of mechanisms: impurities, intrinsic self-trapped excitons and intrinsic defects [33]. The emission peaks observed at 425, 471 nm may be due to the capture of electrons by mid-band gap trap states such as oxygen vacancies and surface defects [33, 34].

We have noticed that there is a significant decrease in the FL intensity for sample S2 in comparison with S1. This decrease in FL intensity is due to the phase transition from tetragonal to tetragonal-monoclinic mixed phase. There is also a shift in FL peak towards higher wavelength. This is because of increase in grain size with
calcination temperature and due to the electron trapping at oxygen vacancies. Similar behaviour is noticed in ZrO$_2$ nanoparticles by Reddy et al$^{[35]}$. They have reported the decrease in FL intensity and shift in FL peak due to phase transition of ZrO$_2$ from monoclinic to monoclinic–cubic mixed phase. The FL peak at 343 nm corresponds to the ionized oxygen vacancies from the conduction band to the valence band$^{[36]}$. The study reveals that luminescence of ZrO$_2$ nanoparticles is due to oxygen vacancies and surface defects.

3.7. Fluorescence life time measurement

To know more about contribution to the emission from band-edge and trap states that lie within the band gap, we have made a fluorescence life time measurement from a time resolved fluorescence using time correlated single photon counting. Figures 7(a)–(c) shows the fluorescence decay curves for sample S0, S1 and S2 respectively. The curves are fitted with multiexponential function$^{[37]}$.

$$I = \sum_{i=1,2,\ldots} A_i \exp \left( \frac{-t}{\tau_i} \right)$$

where $\tau_i$ represents the fast or slow decay component and $A_i$ is corresponding amplitude. The fitting constants are given in table 2. The two components are associated with band edge recombination (faster) and recombination of trapped electrons (slower). The emission from exciton recombination is likely to contribute to the fast decay components. Conduction electrons constrained in shallow trap states may repopulate the conduction band. The long lived decay components may be attributed to radiative decay from electron–hole recombination on the surface involving surface localized states$^{[38]}$. However ZrO$_2$ nanoparticles have large number of surface defect such as oxygen vacancies, the $\tau_1$ for all samples is larger than $\tau_2$, because of the electrons are captured by these defects states. The average life time of carriers is estimated using the relation given by$^{[39]}$.

$$\tau_{ave} = \frac{\sum_{i=1,2} A_i \tau_i^2}{\sum_{i=1,2} A_i \tau_i}$$

where, $\tau_{ave}$ is the average life time of carriers. It is found that an average life time of sample S2 is longer than S1 due to the larger volume fraction of monoclinic phase. This is in agreement with our XRD and FL emission results. Monoclinic phase is less symmetric than that of tetragonal due to the deficiency of oxygen. These oxygen–deficiency in $m$-ZrO$_2$ acts as accepters to trap electrons and shallow trappers for holes. The direct recombination of electrons and holes is avoided by trapping of carriers in oxygen vacancy, because of this reason mixed phase has longer life time.
4. Conclusion

In this work we have synthesized ZrO$_2$ nanoparticles by chemical co-precipitation method using zirconium sulphate and sodium hydroxide as a starting materials. Effect of calcination temperature on structural and optical properties of ZrO$_2$ nanoparticles were investigated. XRD spectra confirms the tetragonal phase at calcination temperature 600 $^\circ$C and crystallinity of samples increases with increase in calcination temperature. At the calcination temperature 800 $^\circ$C the phase transition from tetragonal to tetragonal-monoclinic mixed phase is noticed. The FESEM images show that the particles are of irregular shape and of nanometer scale. Energy dispersive X-ray analysis (EDX) reveals the elemental composition of ZrO$_2$ nanoparticles. The FTIR spectra confirms the formation of ZrO$_2$. The optical band gap is calculated from UV–vis absorption measurement. It is found that the strong quantization and varying band gap with calcination temperature. The fluorescence emission spectra shows change in emission wavelength and intensity with calcination temperature. At calcination temperature 800 $^\circ$C emission intensity is decreased which may be due to the phase change and the formation of surface defects such as oxygen vacancy and interstitials. Significant modification were observed in structural, photoluminescence and life time measurements due to calcination temperature and thus makes ZrO$_2$ a promising material for optoelectronic applications.

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Figure 7. Fluorescence decay of ZrO$_2$ nanoparticles. Graphs a-c respectively, represent FL decay for the samples S0, S1 and S2.
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