

Synthesis, structural and optical properties of TiO₂-ZrO₂ nanocomposite by hydrothermal method

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ABSTRACT

A series of TiO₂-ZrO₂ mixed oxide samples with various ZrO₂-TiO₂ content (10, 30, 40, 60, 70 and 90 mol %) were prepared by hydrothermal method. These nanocomposites were characterized by XRD, SEM, UV-vis spectroscopy and Photoluminescence spectroscopy. XRD data identified Anatase and Rutile phases in the TiO₂ rich samples while Tetragonal and Monoclinic phases in ZrO₂ rich samples. The average crystallite size of the samples was between 9 to 26 nm. As per Uv-Vis spectra, the band gaps of TiO₂-ZrO₂ composites vary from 1.34 eV to 2.48 eV. The absorption spectra show a shift of the absorption edge of TiO₂-ZrO₂ towards longer wavelength region. The decreased band gap is attributed to the surface trap states. The PL spectrum shows very strong blue-green PL band under excitation at 300 nm. The occurrence of emission peaks in the visible region is attributed to the presence of defect levels below the conduction band. Copyright © 2013 VBRI Press

Keywords: Nanocomposite; hydrothermal; photoluminescence; anatase; rutile.



conducting polymers.

Laxmi J. Tomar received her M.Sc (Applied Physics) degree from The M.S. University of Baroda, India in 2010. She is pursuing her Doctoral degree from The M. S. University of Baroda. She is working on optical absorption, emission and photoelectric properties of rare earth and transition metal doped TiO₂/ZrO₂ compounds. Her current research is focused mainly on nanomaterials for Dye Sensitized Solar cell, natural dyes for DSSC and



Dye sensitized solar cells, up conversion phosphors and its application in bio imaging, Polymer composites, sulfide nanomaterials and its optical properties.

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Introduction

TiO₂ is the most common material used for dye sensitized solar cell. As a chemical, it is relatively inert, cheap and can be synthesized (by different) process offering flexibility and scalability. Unlike silicon solar cells, very high purity is not required. It exists in various forms, mainly anatase, rutile and brookite. Anatase has a high band gap (3.2 eV compared to rutile's 3.0 eV) which gives several advantages. It absorbs very little of the solar spectrum, meaning it is transparent to incoming light source (the dyes rather than the metal oxide is activated by light). In addition, the larger band gap than rutile means that recombination is slower (the energy gap law) – some reports have determined a 30% lower efficiency with rutile. Mixing of the oxides can produce new crystallographic phases with quite different properties than the original oxides [1]. The use of mixed oxides in many technological fields is an attractive strategy to produce materials with superior properties than the single components [2]. In particular, mixed oxides have been widely used in catalysis, because the surface characteristics of the individual oxides can be changed due to the formation of new sites in the interface between the components, or by the incorporation of one oxide into the lattice of the other. It was reported that ZrO₂ doped titanium solid solution showed enhanced photocatalytic activity from UV light. The authors attributed it to the increase of oxygen vacancy

concentration. The main reason was that the size difference between titanium and zirconium caused the increase of lattice parameters and cell volume leading to structure defects. It has been reported that incorporation of ZrO_2 into TiO_2 leads to decrease in particle size of TiO_2 and increase in surface area due to the dissimilar nuclei and coordination geometry [3]. A mixture of ZrO_2 and TiO_2 was used as an electrode for dye-sensitized solar cell [4]. Many properties of this nanostructured mixed metal oxides were reported to be better than that of TiO_2 . These include the BET specific surface area, which can improve the amount of adsorbed dye molecules. TiO_2 absorbs only uv radiation while ZrO_2 absorbs uv to infrared radiation.

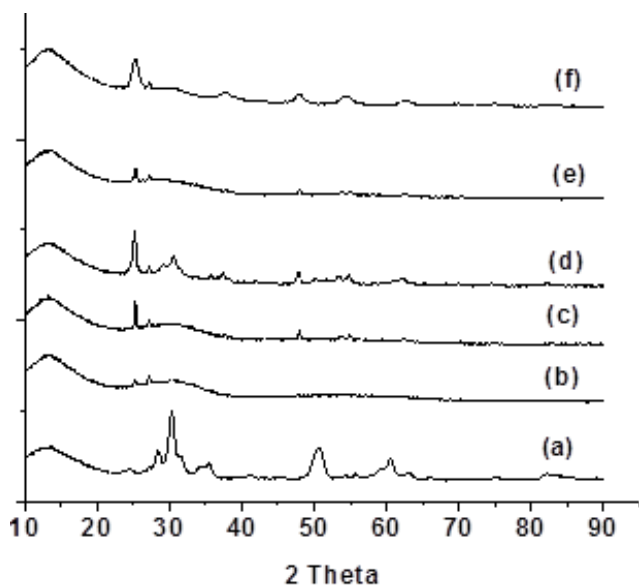


Fig. 1. XRD pattern of (a)10/90% TiO_2 - ZrO_2 , (b)30/70% TiO_2 - ZrO_2 , (c) 40/60% TiO_2 - ZrO_2 , (d) 60/40% TiO_2 - ZrO_2 , (e) 70/30% TiO_2 - ZrO_2 , (f) 90/10% TiO_2 - ZrO_2 .

Experimental

Materials synthesis

A series of Titania–Zirconia mixed oxides with various ZrO_2 - TiO_2 content (10, 30, 40, 60, 70 and 90 mol %) were prepared by the hydrothermal method. Titanium isopropoxide, Zirconium propoxide and isopropanol were used as starting chemicals. All chemicals were analytical grade and used as received. The synthesis was carried out as follows: Ti isopropoxide and Zr propoxide were diluted in isopropanol (ROH) to obtain oxides in a 10/90, 30/70, 40/60, 60/40, 70/30 and 90/10 ZrO_2 / TiO_2 molar ratio. A $H_2O + HNO_3$ mixture was drop-wise added to the alkoxides solution kept under vigorous stirring at ~ 273 K (Ts). The ROH/alkoxide., H_2O /alkoxide., and HNO_3 /alkoxide molar ratios used were 65, 20 and 0.05, respectively. After alkoxide hydrolysis the alcogel was obtained. The solids were obtained by transferring the alcogel to a stainless steel autoclave. The temperature was raised to $240^\circ C$ and the sample was maintained under autogenic pressure for 24 h. Then, the sample was oven-dried at $100^\circ C$ (2 h) and finally calcined at $450^\circ C$ for 4 hours under static air atmosphere.

Characterization

The composition of the sample was examined by A Bruker D8 Advance X-ray Diffractometer. The morphologies of the sample were analyzed with scanning electron microscopy (SEM) on a machine of JEOL make MODEL JSM 5810 LV. The fluorescence characteristics of the samples were recorded on a Fluoromax 4 instrument of Horiba Jobin Yvon make, USA. The slit width for the excitation as well as emission monochromators was fixed at 1 nm to ensure optimization and uniformity. The absorption spectra were recorded on a Thermo Scientific (Evolution 600 UV-Vis).

Results and discussion

XRD analysis

The XRD patterns of TiO_2 - ZrO_2 mixed oxides (10, 30, 40, 60, 70, and 90 mol %) are given in **Fig. 1**. By matching the d values of the samples with JCPDS data it can be seen that Anatase and Rutile phase of TiO_2 are formed whereas Monoclinic and Tetragonal structure of ZrO_2 are formed. As the percentage of ZrO_2 content increases most of the peaks match with Monoclinic and Tetragonal Structure of ZrO_2 and as the percentage of ZrO_2 content decreases most of the peaks match with Rutile and Anatase phase of TiO_2 . The peaks of almost all the samples are intense and broad. The formation of material with low crystallinity is also indicated from some patterns. The crystallite size was calculated by using the Sherrer formula. Looking to the peak broadening and FWHM values, small crystallite size is expected. The calculations confirmed this. The average crystallite size for each sample is shown in **Table 1**. The sample with 30 mol% titania was amorphous. The amorphous structure is produced by the large number of aquo and hydroxo bonds present in the zirconia precursor, which gives rise to a fast condensation and avoids crystallization [5].

Table 1. Crystallite size of TiO_2 - ZrO_2 composites.

Sample	Size (nm)
10% TiO_2 - ZrO_2	11.34
30% TiO_2 - ZrO_2	22.12
40% TiO_2 - ZrO_2	26.66
60% TiO_2 - ZrO_2	16.75
70% TiO_2 - ZrO_2	19.06
90% TiO_2 - ZrO_2	09.33

SEM analysis

Typical SEM micrographs of TiO_2 - ZrO_2 composites are shown in **Fig. 2**. It can be seen from the **Fig. 2. (a), (b), (c), (d), and (e)** that the particles are highly agglomerated. The porosity is observed to be very high. It is seen that the agglomerates in **Fig. 2(b)** consist of almost spherical crystalline particles with the average size of 22 nm. The cloudy structure can be seen for the sample with 70 mol% titania. The particles are round in shape for the 30 mol % TiO_2 . Fully porous materials were obtained for 10, 30, 40, 60 and 70% TiO_2 doped Zirconia. **Fig. 2(f)** shows the SEM

micrograph of 90% TiO₂ doped Zirconia. The particles are hard in nature. They are irregular in shape. The particles have sharp edges and the growth is highly non uniform. The structure is pore free. The hard crystal like structure can be seen for the 90 mol% TiO₂.

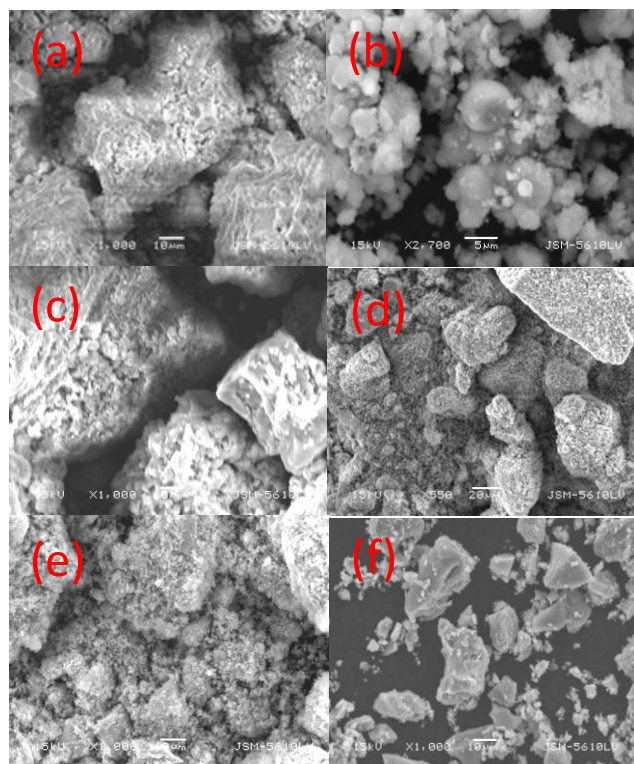


Fig. 2. SEM images of (a) 10/90% TiO₂-ZrO₂, (b) 30/70% TiO₂-ZrO₂, (c) 40/60% TiO₂-ZrO₂, (d) 60/40% TiO₂-ZrO₂, (e) 70/30% TiO₂-ZrO₂, (f) 90/10% TiO₂-ZrO₂.

Fig. 3 shows the PL spectra of the TiO₂-ZrO₂ composite at room temperature. The excitation wavelength for curve (a) is 300 nm. A very strong blue-green PL band can be observed which is ranging from 398 nm to 492 nm under excitation at 300 nm. This band consists some PL peaks situated at 411 nm, 436 nm, 452 nm, 469 nm, 474 nm, 483 nm, 492 nm.

Photoluminescence (PL) study

Two PL peaks situated at 558 nm and 572 nm can also be observed under same excitation. All the samples have same broad band emission under excitation at 300 nm. The PL peak position and intensity are obviously different under different excitation wavelengths. The main peak is respectively located at about 439, 460, 493 and 516 nm under excitation at 400, 420, 450 and 470 nm respectively. All the samples have same emission peak under the same excitation but their intensities are different.

The occurrence of emission peaks in the visible region is due to the presence of defects levels below the conduction band [6]. The peak observed in the visible region is attributed to the electronic transition mediated by the defect levels such as oxygen vacancies in the band gap [7]. The surface trap states are attributed to oxygen vacancy

levels [8]. The high PL intensity of TiO₂-ZrO₂ clearly shows the surface states of material are well below and hence, the easy transfer of the electron from VB to CB may occur even with a low energy.

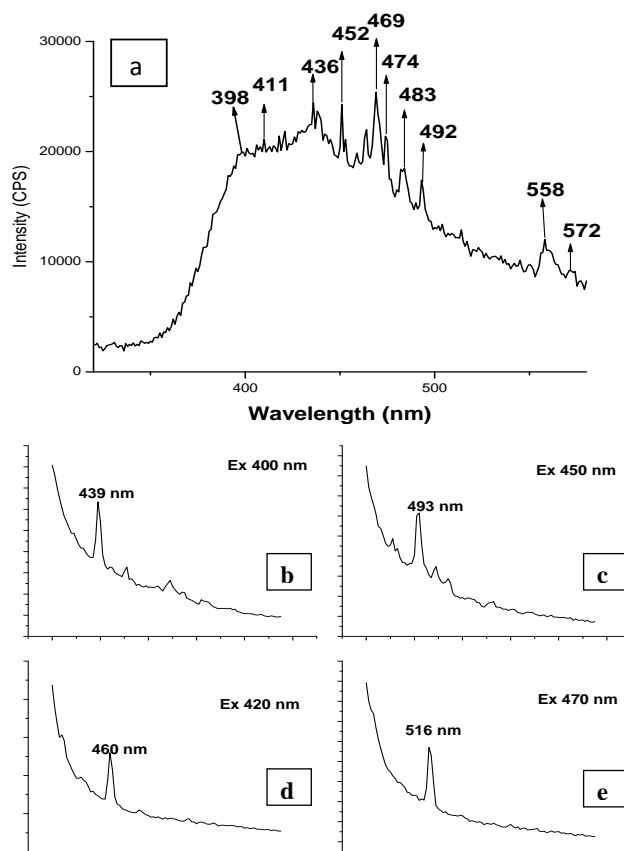


Fig. 3. Fluorescence spectra of TiO₂-ZrO₂ composites under excitation at (a) 300 nm, (b) 400 nm, (c) 420 nm, (d) 450 nm, (e) 470 nm.

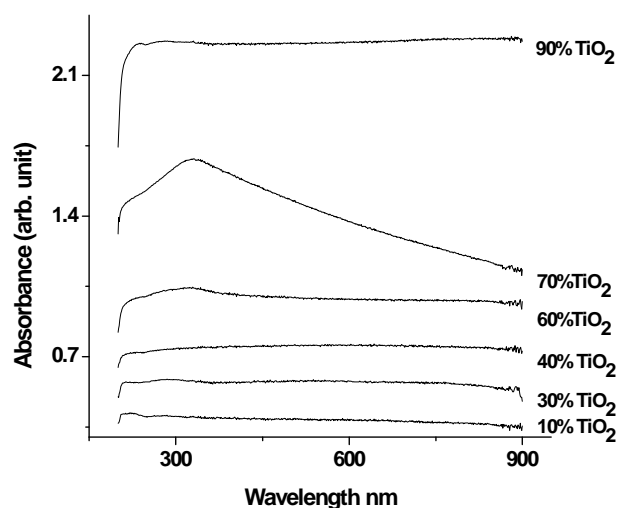


Fig. 4. Absorption spectra of TiO₂-ZrO₂ nanocomposite.

UV-visible spectroscopy

Fig. 4 shows the absorption spectra of TiO₂-ZrO₂ composite. A shift of the absorption edge of the TiO₂-ZrO₂ towards longer wavelength region of light is observed. This shift depends on the amount of ZrO₂ incorporated. The observed absorptions are not attributed to the TiO₂ or ZrO₂ bandgap absorption but rather to the additional sub-bandgap absorptions [9]. These sub band gap absorption may arise from surface states of the TiO₂-ZrO₂ material. The surface states are surface localized electronic states within the material bandgap, involving complex species such as dangling bonds, defects and atoms adsorbed on the surface [10, 11]. The optical bandgap of TiO₂-ZrO₂ composite is obtained by establishing the relation between $h\nu$ and $(ah\nu)^2$. The corresponding calculated bandgap values are given in **Table 2**. The bandgap of pure TiO₂ and ZrO₂ are 3.2 eV and 4.6 eV respectively whereas the calculated bandgap of TiO₂-ZrO₂ mixed oxide varies from 1.34 eV to 2.48 eV. The energy level of TiO₂ both for the valance band and conduction band correspond well within bandgap of ZrO₂ which is shown in **Fig. 5**. When the electrons are excited, most of the electron from the conduction band of ZrO₂ can easily transfer to the conduction band of TiO₂ and thereby, the bandgap may be decreased [12].

Table 2. Band gap energy of TiO₂-ZrO₂ composites.

Sample	Band gap
10/90% TiO ₂ -ZrO ₂	2.48 eV
30/70% TiO ₂ -ZrO ₂	1.72 eV
40/60% TiO ₂ -ZrO ₂	1.34 eV
60/40% TiO ₂ -ZrO ₂	1.7 eV
70/30% TiO ₂ -ZrO ₂	1.49 eV
90/10% TiO ₂ -ZrO ₂	1.49 eV

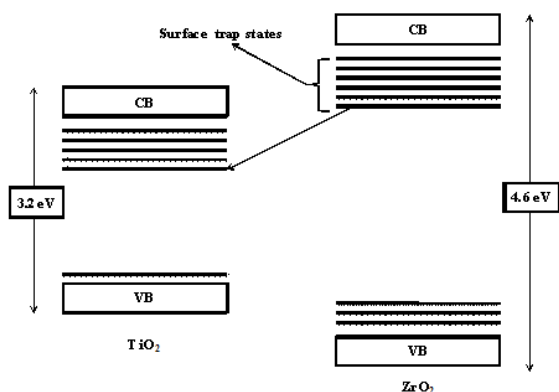


Fig. 5. Schematic Energy level diagram.

Conclusion

In conclusion, we have successfully fabricated TiO₂-ZrO₂ nanocomposite with various molar ratios using a hydrothermal method. The XRD pattern showed the

formation of both TiO₂ and ZrO₂. It can also be concluded from the XRD pattern that Anatase and Rutile phases of TiO₂ have been formed and Monoclinic and Tetragonal structure of ZrO₂ have been formed. The average crystallite sizes of all the samples were found to be 9 to 26 nm. The SEM images showed that the particles are somewhat round shaped. The SEM images confirmed the formation of highly porous material. The shift in the absorption edge towards longer wavelength indicates the sub band gap absorption arised from surface states of the TiO₂-ZrO₂ material. The peak observed in the visible region of PL spectra is attributed to the defect levels created by oxygen vacancies.

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