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Effect of Preparation Method on Optical and Structural Properties of TiO_2/ZrO_2 Nanocomposite

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Abstract: The comparison of preparation method is shown in the present work. TiO_2/ZrO_2 Nanocomposite was synthesized by two different precipitation and hydrothermal method. The structural properties of the prepared samples were analyzed by X-ray diffraction spectroscopy. The average crystallite sizes were calculated by Sherrer formula. From the XRD it was confirmed that the TiO_2 exists in two different phases Anatase and Rutile where as ZrO_2 exists in two different phases monoclinic and tetragonal. The surface morphology was studied by Scanning Electron Microscopy. The optical absorption was measured by UV-Visible spectroscopy. The absorption spectra were taken in the wavelength range 200-900 nm. The optical bandgap was calculated by establishing relation between $(\alpha h\nu)^2$ and hv. All other optical constants such as refractive index, extinction coefficient, absorption coefficient and optical conductivity were calculated from absorption spectra.

Keywords: Hydrothermal, Precipitation, Nanocomposite, Optical constants.

1. Introduction

TiO_2 has been most widely used photocatalyst because of its non toxicity, inexpensiveness and chemical stability. TiO_2 has photoelectrochemical properties suitable for its use as a photoelectrode for hydrogen generation through the decomposition of water using solar energy [1].

Zirconium oxide is used as photocatalyst, refractory material and photoelectric material. Zirconium oxide is an important catalyst support, since it can present acidic and basic properties. During the last decades, nanocrystalline zirconia has been produced by using different methods [2-8].

In this paper, the comparison of two preparation method of TiO_2/ZrO_2 mixed oxide has been shown here. We have prepared TiO_2/ZrO_2 mixed oxides by two different methods i.e precipitation and hydrothermal

2. Experimental

TiO_2/ZrO_2 mixed oxide was prepared by precipitation and hydrothermal method. Titanium isopropoxide, zirconium propoxide and titanium tetrachloride were purchased from sigma Aldrich. All other chemicals were purchased from Loba chemicals. All the chemicals were used as received.

Precipitation

Titanium tetrachloride and zirconium oxy chloride were mixed. The solution was stirred at room temperature for 30 min. Then urea and ammonia solution was added slowly. The solution was stirred for 30 min at room temperature. The solution was refluxed for 10h at 100□C. Precipitates were dried in oven at 120□C for 12h. Finally sample was kept in a furnace for 5h at 450□C.

Hydrothermal

TiO_2/ZrO_2 nanopowder was prepared by hydrothermal method in which titanium isopropoxide; Zirconium propoxide and isopropanol were used as starting chemicals. The TiO_2 and ZrO_2 were prepared in 50/50% molar ratio. Ti isopropoxide and Zr propoxide were diluted in 5 ml isopropanol to obtain oxides in a 50/50 TiO_2/ZrO_2 molar ratio. A (0.5 ml H_2O + 0.5 ml HNO_3) mixture was drop-wise added to the alkoxides solution kept under vigorous stirring at room temperature. The alcogel was obtained after the alkoxide hydrolysis. The solids were obtained by transferring the alcogel to a teflon lined autoclave. The temperature was raised to 240 ºC and the sample was maintained under autogenic pressure for 24 h. Then, the sample was oven-dried at 100 ºC (2 h).

3. Results and Discussions

XRD Analysis

X-ray diffraction pattern was recorded on a Bruker D8 Advance X-ray Diffractometer to study the composition of material. The XRD patterns of TiO_2-ZrO_2 mixed oxide is 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 where as Monoclinic and Tetragonal structure of ZrO_2 are formed. For the sample prepared by precipitation method no monoclinic phase was observed. The peaks of both the samples are intense and broad. The formation of material with high crystillanity is indicated from 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 of TiO_2/ZrO_2 mixed oxide was found to be 18.94nm and 31.89nm for samples prepared by precipitation and hydrothermal method respectively.

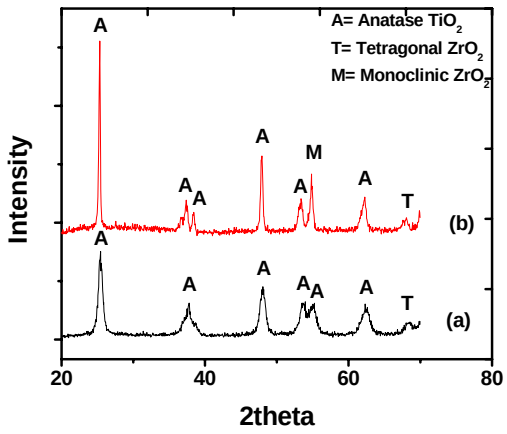

Fig.1: XRD pattern of TiO_2/ZrO_2 mixed oxide prepared by (a) precipitation method, (b) Hydrothermal method.

SEM Analysis

Typical SEM micrographs of TiO_2/ZrO_2 nanocomposites are shown in Fig.2. The nanosized particles are can be seen from the SEM micrographs. It is seen from Fig. 2(a) that sample prepared by precipitation method consist of almost spherical crystalline particles with the average size of 18.94 nm. It can be seen from the Fig.2. (b) that the particles are highly agglomerated and the porosity is observed to be very high.

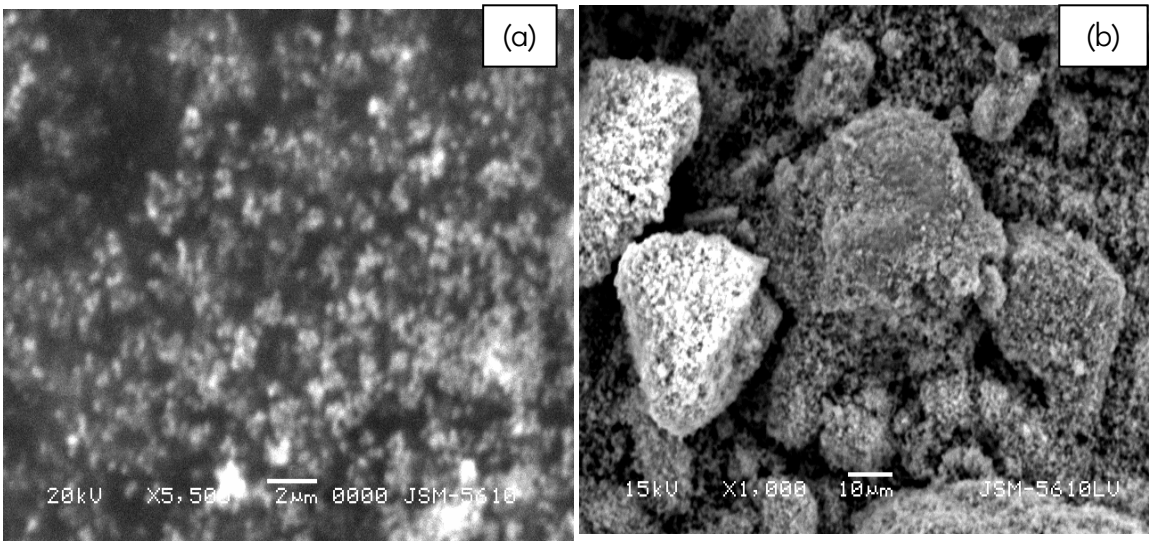

Fig.2: Scanning electron micrographs of TiO_2/ZrO_2 mixed oxide prepared by (a) Precipitation method, (b) Hydrothermal Method.

UV-Visible Spectroscopy

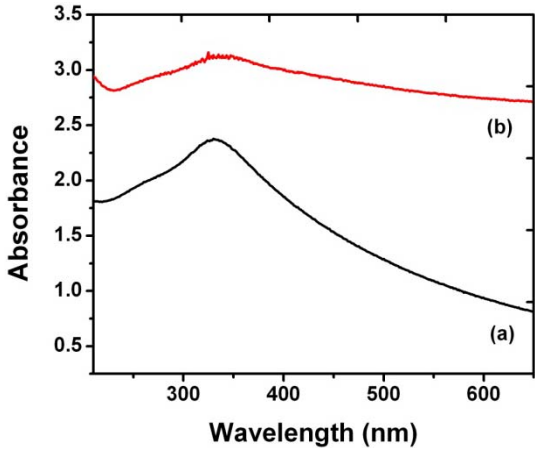

Fig.3: UV-Visible Absorption spectra of TiO_2/ZrO_2 mixed oxides prepared by (a) Precipitation method, (b) Hydrothermal method.

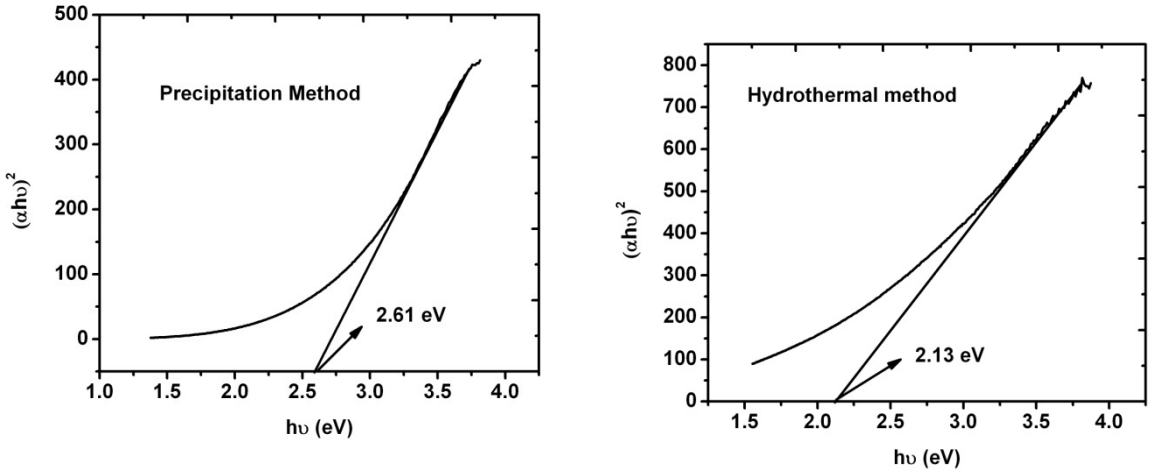

Fig. 4: Tauc's plot of TiO_2/ZrO_2 mixed oxides prepared by precipitation method and hydrothermal method.

The absorption spectra were recorded on a Thermo Scientific (Evolution 600 UV-Vis). Fig.3 shows the absorption spectra of TiO_2/ZrO_2 mixed Oxides. The optical band gap was evaluated by Tauc's plot which is shown in Fig. 4. The bandgap for pure TiO_2 and ZrO_2 is 3.2 eV and 4.6 eV respectively whereas the calculated bandgap of TiO_2/ZrO_2 is 2.61 eV and 2.13 eV for precipitation and hydrothermal method respectively. The energy level of TiO_2 both for the valance band and conduction band correspond well within bandgap of ZrO_2. When the electrons are excited, most of the electron from the conduction band of ZrO_2 can easily transfer to the conduction band of TiO_2 and thereby, the bandgap may be decreased [9].

Different optical constants such as Extinction coefficient, refractive index and optical conductivity were also evaluated using absorption spectra. The values of calculated different optical constants for TiO_2/ZrO_2 mixed oxides are given in the Table 1.

Table 1: Different optical constants for TiO_2/ZrO_2 mixed oxide

Preparation method	Optical bandgap eV	Refractive index	Extinction co efficient	Optical conductivity $(ff cm)^{-1}$
Precipitation	2.61	2.47	1.22×10^{-5}	1.91×10^{10}
Hydrothermal	2.13	2.63	2.94×10^{-5}	3.99×10^{10}

The amount of light lost due to scattering and absorption was evaluated by calculating extinction co efficient using the following relation [10].

$$K = \alpha\lambda/4\pi \qquad (1)$$

Where α = absorption coefficient and λ = absorbed wavelength. . The variation of extinction co efficient with wavelength is shown in Fig. 5. From the graph it can be seen that extinction coefficient increases with increase in wavelength for both the samples. The extinction coefficient decreases after 350nm for the sample prepared by precipitation method.

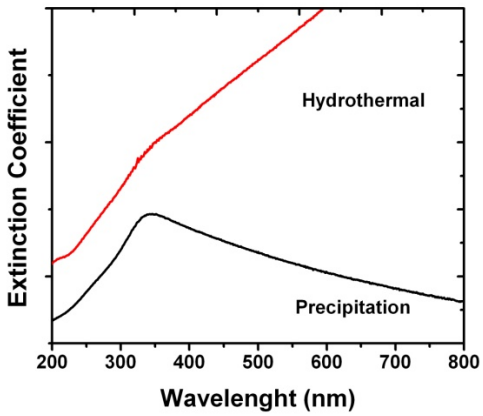

Fig.5: Variation of Extinction coefficient with wavelength for TiO_2/ZrO_2 mixed oxides.

V. Kumar and J.K. Singh have proposed relation between energy bandgap and refractive index [11]. Using this relation the refractive index of both samples was evaluated.

$$n = KE_g^{\,C} \qquad (2)$$

Where n = Refractive index, Eg = bandgap, K and c are the constants having values K = 3.3668 and C = -0.32234.

The optical conductivity determines the optical response of the material which is given by the relation [12].

$$\sigma = \alpha nc/4\pi \qquad (3)$$

Where c = velocity of light, α = absorption co efficient and *n* = refractive index of the material. Optical conductivity is dependent on refractive index and absorption coefficient of the material. Fig.6 shows the variation of optical conductivity of TiO_2/ZrO_2 with photon energy. From the fig. 6 it is clearly visible that the optical conductivity increases with the increase in photon energy for TiO_2/ZrO_2 mixed oxide prepared by precipitation method in lower energy region and decreases abruptly after 3.5 eV. The optical conductivity for TiO_2/ZrO_2 mixed oxide prepared by hydrothermal method decreases with increase in photon energy.

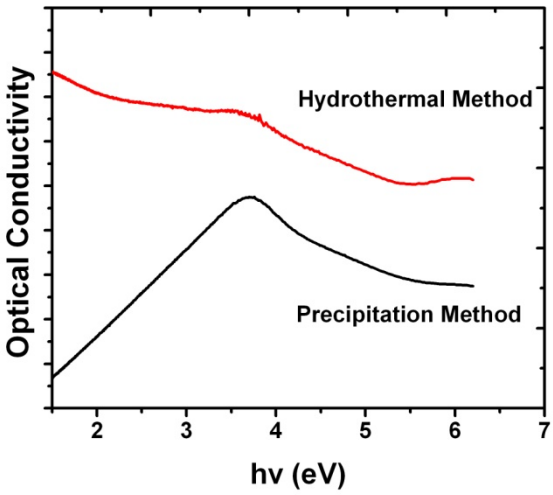

Fig.6: Variation of Optical conductivity with photon energy for TiO_2/ZrO_2 mixed oxides.

4. Conclusion

In conclusion we can say that we have successfully prepared TiO_2/ZrO_2 mixed oxides by using precipitation and Hydrothermal Method. The average crystallite size was found to be 18.94 nm and 31.89 nm for the sample prepared by precipitation and hydrothermal method respectively. The SEM images shows material is porous prepared by hydrothermal method. Spherical and round shaped particles are formed by precipitation Method. The optical bandgap was found to be 2.61 eV and 2.13 eV for samples prepared by precipitation method and hydrothermal method respectively. The evaluation of optical constants shows that particles prepared by hydrothermal method are more optically active.

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