

The Effect of SnO₂-TiO₂ Composite and Mixed-Oxide Nanoparticles Prepared by Sol-Gel Method

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Abstract: SnO₂-TiO₂ composite and mixed-oxide nanoparticles have been prepared by sol-gel technique from titanium tetra chloride and stannous chloride in the laboratory. The prepared materials were characterized by XRD, SEM-EDAX, FT-IR spectroscopy and UV-vis diffuse reflectance spectroscopy. The results indicate that compared to pure TiO₂, SnO₂-TiO₂ nanoparticles calcined 400°C show higher thermal stability, large surface area, greater band gap energy and smaller crystalline size. From XRD analysis, SnO₂-TiO₂ nanoparticles average crystalline size was estimated using the Debye-scherrer's formula. From the FTIR results, peaks were observed at 3435 cm⁻¹ and 1630 cm⁻¹ in both samples due to stretching and bending vibrations of O-H group and H-O-H co-ordinate water. Visible absorption at (1450 & 1900 nm) the absorption ability UV-Visible light was enhanced after composite especially 500 nm.

Keywords: Sol - gel, Mixed-oxides, Composite, SnO₂-TiO₂ nanoparticles.

1. Introduction

Nanoparticles have various technological applications in areas such as ceramics, magnetic recording, semiconductors, electronic, magnetic and optical properties compared with those of conventional bulk materials. However, many applications required the nanoparticles with a very strict nanosize and narrow size distribution, therefore, the development of synthesis methods, control of size and morphology, and assembly of desired nanostructure still remains challenge in this field [1]-[3] nanostructured materials are defined as those materials whose structural elements have dimensions in the 1-100 nm range [4], [5]. In recent years for the production of TiO₂ nanopowders, such as gas condensation [6], Sol-gel [7] and hydrothermal devices [8], owing to improved optical property [9] Photo catalytic action and solar cells for low-cost photovoltaic devices [10], [11].

Titanium dioxide (TiO₂) is one among the important inorganic pigments used in the plastic and paint industry [12], [13]. TiO₂ exists mainly in three naturally occurring crystallographic forms, namely anatase, brookite and rutile. Nanoscale materials exhibit different or superior properties than bulk materials. However, the wide energy band gap of TiO₂ (3.2eV) is frequently studied in optic fields, especially as an excellent photo catalytic material applied in photo degradation and solar energy conversion [14], [15].

Tin dioxide (SnO₂) is an important n-type semiconductor metal oxide with wide band gap (3.6eV). Because of its unique electronic, optical, electrochemical and catalytic properties [10], SnO₂ were extensively used in solar cell, transparent conducting electrodes, soiled-state sensors, rechargeable Li batteries and optoelectronic devices [16].

Doping TiO₂ with different anions like N, S, Cl and Br [17], [18] or cations like Gd, V, Cu, Sn, Fe, Cr etc. [19], [20] has been tried to reduce the bandgap and to increase the visible light absorption. However, these dopants can form isolated localized levels within the bandgap and trap electrons and can lead to adverse effect in photocatalytic hydrogen generation. Enhancements in photo catalytic H₂ production

over coupled semiconductors including SnO₂/TiO₂ [21] have been investigated extensively.

2. Experimental

2.1 Materials

All reagents used were of analytical grade purity and were produced from Merck Chemical Reagent Co. Ltd. India.

2.2 Preparation of SnO₂-TiO₂

The titanium composite was prepared by the following method. The sol-gel composition method was carried out as follows. The solution A titanium tetra chloride was used as a pre-cursor added drop by drop in the ethanol solution maintained continuous stirring for 1hour, kept at a room temperature and maintain p^H range of 1 to 2. The colorless solution turned into yellowish color. Deionized water (10 ml) added drop by drop to the solution A. The stirred solution is maintained at temperature 60°C for 1hour.

The solution B was prepared by 1 mole of stannous chloride is added with deionized water and kept in constant stirring at room temperature for 15 minutes. As prepared solution B was added drop by drop to solution A. The yellowish solution is changed into white colored.

The final solution was stirred for 1hour at the temperature of 40°C and the gel was formed. Finally the gel was dried at room temperature and powder-mixed oxide was heated at 400°C for an hour.

2.3 Characterization

The prepared nanoparticles were characterized for the crystalline structure using D8 Advance X-ray diffraction meter (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using CuK α radiation (λ = 0.15406 nm). The crystal size was calculated by Scherrer's formula. Surface morphology was studied by using SEM-EDAX (Model JSM 6390V, JOEL, USA), UV-Vis diffuse reflectance spectra were recorded with a Carry 5000 UV-

Vis-NIR spectrophotometer (Varian, USA) and FTIR spectra were measured on an AVATAR 370-IR spectrometer (Thermo Nicolet, USA) with a wave number range of 4000 to 400 cm^{-1} .

3. Result and Discussion

3.1 X-Ray Diffraction – Estimation of Structural Parameters

XRD was used to investigate the phase structures and average particle size of the pure TiO_2 & SnO_2 - TiO_2 nanoparticles annealed at 400°C . That characteristic peaks of 2θ degrees were recognized corresponding to the hkl Miller indices respectively Fig-1 (a) & (b). Presence of anatase and rutile is confirmed for both TiO_2 & SnO_2 - TiO_2 nanoparticles. The strongest peaks for anatase and rutile were observed at $2\theta = 25.4^\circ$ (101) [22] and $2\theta = 27.5^\circ$ (110) [23] respectively. No characteristic peaks of SnO are observed in the XRD patterns, indicating that phase-pure SnO_2 can be formed on the surface of TiO_2 [24]. As can be noticed, the nanopowders showed a low degree of crystallization, and a thermal treatment was necessary in order to increase it and to stabilize the nanoparticles [25]. The result of XRD powder patterns indicated that the experimental data are in good agreement with the simulated XRD powder patterns based on the reference data. The Broadening of the peaks indicated that the particles were of nanometer scale. The particle size can be estimated from the XRD pattern using Scherrer's formula show at table: 1 & 2 [26].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where **D** is the crystalline size, **k** is a geometrical factor taken to be 0.89, $\lambda = 1.5406 \text{ \AA}$ is the X-ray wavelength, θ is the diffraction angle and β the peak width at half maximum of the most prominent peaks. We found that pure TiO_2 & SnO_2 - TiO_2 crystal domains are in the range from 12 to 15 & 7 to 28 nm in diameter. The average particle size which is calculated from Debye Scherrer's formula is 14.35 & 15.681 nm. X-ray structural analysis of doped samples showed that the samples had typical peaks of rutile structures without any detectable dopant related peaks. The dopant ions Sn may have been moved either into interstitial positions or substitutional sites of the TiO_2 nanocrystal structure, or their concentration was too low to be detected [27].

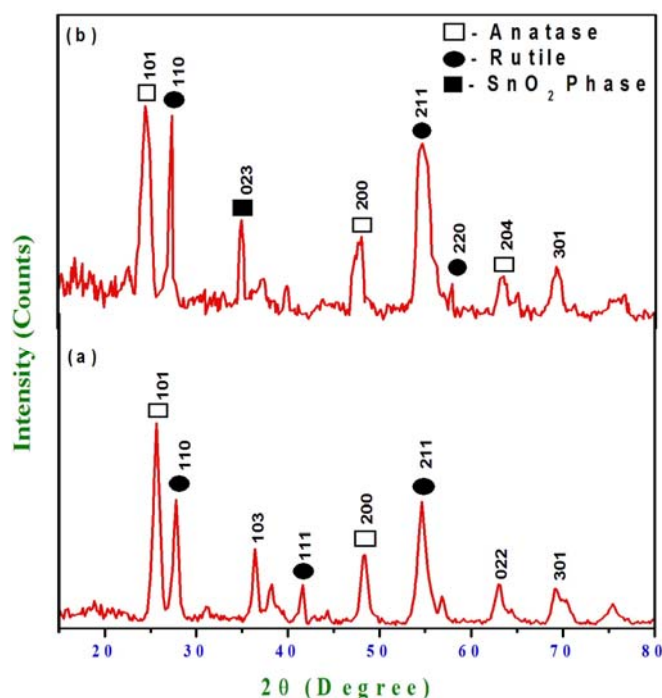


Figure 1 (a) & (b): X-Ray Diffraction Pattern of Pure TiO_2 & SnO_2 - TiO_2

Table 1: To determine the Particle Size of TiO_2

S.No	2θ	FWHM	β $\times 10^{-3}$	Particle Size (nm)
1.	25.643	0.717	12.50	12.16
2.	27.762	0.559	9.75	15.88
3.	54.618	0.904	15.76	15.01

Table 2: To determine the Particle Size of SnO_2 - TiO_2

S.No	2θ	FWHM	β $\times 10^{-2}$	Particle Size (nm)
1.	25.458	1.075	1.874	7.58
2.	27.578	0.446	0.778	18.34
3.	35.650	0.571	0.995	27.99
4.	48.378	0.856	1.493	16.53
5.	62.721	1.044	1.821	7.965

3.2 Scanning Electron Microscope Analysis (SEM)

Fig-2 (a) & (b) shows the SEM image of pure TiO_2 & SnO_2 - TiO_2 nanoparticles. The surface morphology of the SnO_2 - TiO_2 nanoparticles is analyzed by scanning electron microscope. Compared with the pure TiO_2 , the size of SnO_2 - TiO_2 nanoparticles was enlarged and uniform, so its surface area was larger. The growth of the fine particles of TiO_2 in regular pattern is observed on the surface of the sample. The size and morphological evaluations of SnO_2 - TiO_2 is also dependent on the reaction time. To verify the morphology scheme obtained from XRD the data from the scanning electron microscopy was studied [28].

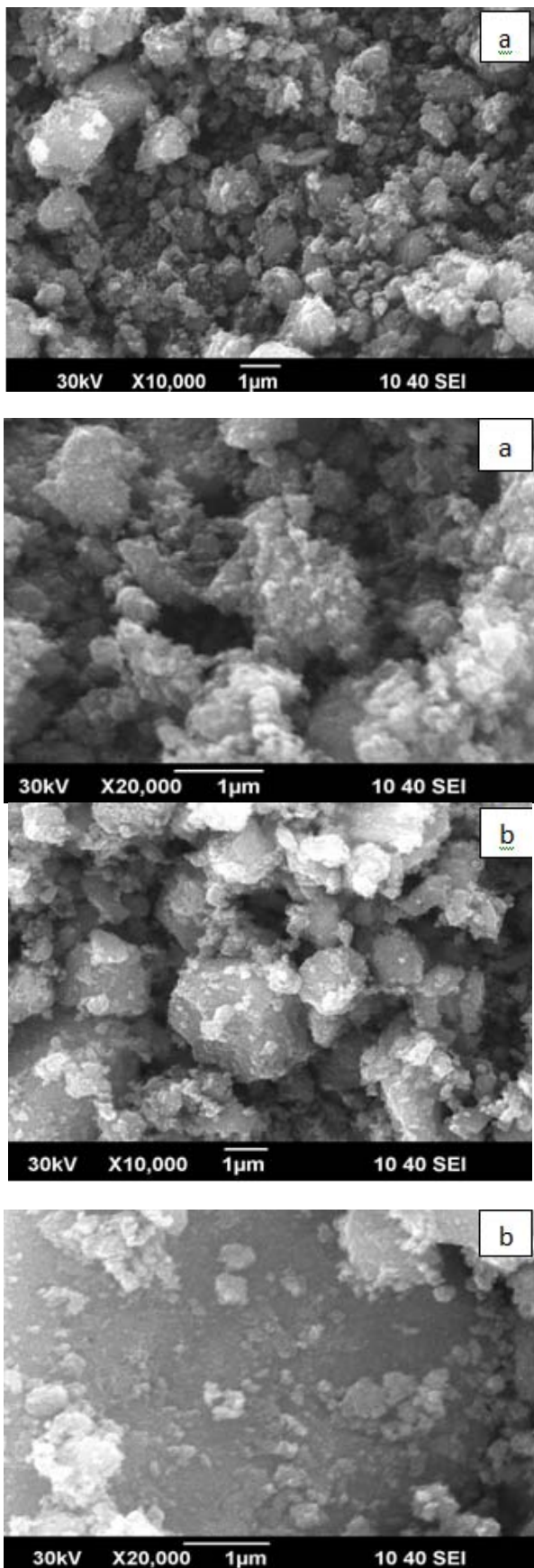
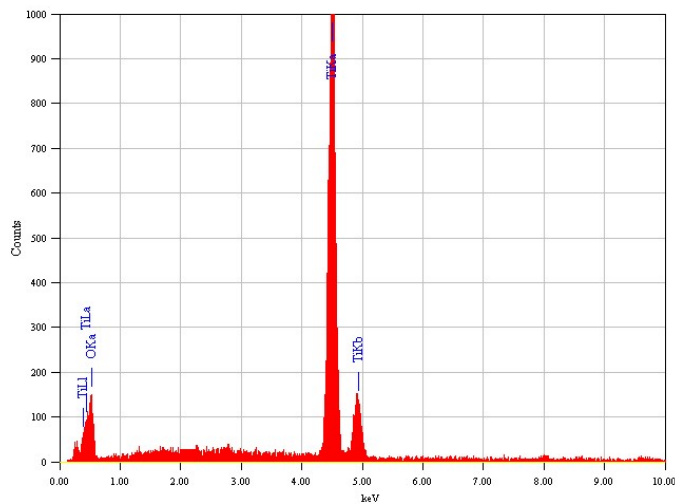


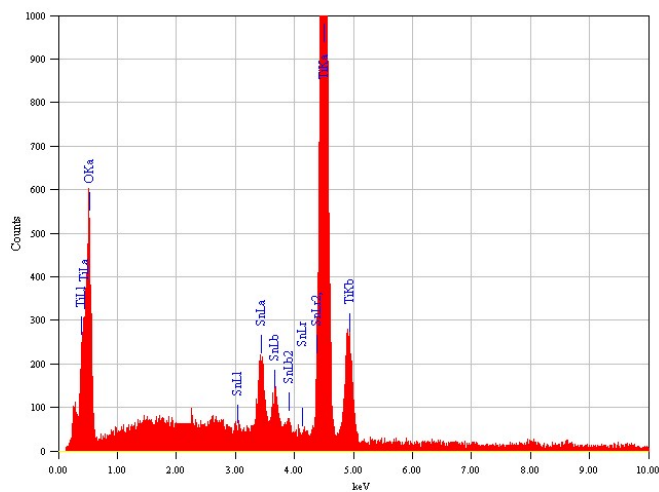
Figure 2 (a) & (b): SEM micrograph of the as-synthesized pure TiO₂ & SnO₂-TiO₂ nanoparticles at various magnifications

3.3 Energy Dispersive X-Ray Analysis (EDAX)

EDAX analysis fig 3 (a) & (b) demonstrates that there are Sn, Ti and O elements on the surface of the obtained powder. Further demonstrating that SnO₂ is directly deposited on the TiO₂ nanoparticles powder substrate table 2 & 3.



(a)



(b)

Figure 3 (a) & (b): EDAX spectrum of pure TiO₂ & SnO₂-TiO₂ nanoparticles

Table 2: The Percentage of Atoms present in the pure TiO₂

Element	(keV)	Mass%	Atom%
O	0.525	4.82	13.17
Ti	4.508	95.18	86.83

Table 3: The Percentage of Atoms present in the SnO₂-TiO₂ nanoparticles

Element	(keV)	Mass%	Atom%
O	0.525	8.54	23.71
Ti	4.508	76.1	70.54
Sn	3.443	15.36	5.75

3.4 FTIR Spectroscopy Analysis

The FTIR spectrum of the samples reveals the presence of strong bond around 1500 cm⁻¹. Fig 4(a) & (b) shows the FTIR spectra of the pure TiO₂ & SnO₂-TiO₂ nanoparticles comparing bands shows that the broad band around 3435 cm⁻¹ is assigned to O-H vibration where as the band around 1630 cm⁻¹ is the H-O-H bending of the coordinate water, the IR absorption band at 541cm⁻¹ is attributed to the Ti-O-Ti stretching vibrations [29]. Comparing the spectra of SnO₂-TiO₂ mixed oxides with the standard samples of TiO₂

anatase, TiO₂ rutile and SnO₂ the change in the line shape of SnO₂-TiO₂ at 610 cm⁻¹. Due to the low concentration of SnO₂ the dopant ions may be present in interstitial positions or substitutional sites [30].

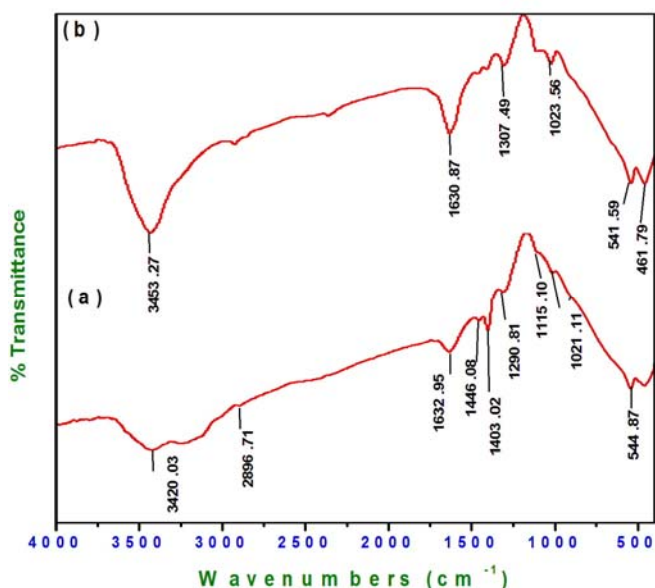


Figure 4 (a) & (b): FTIR spectrum of pure TiO₂ & SnO₂-TiO₂ nanoparticles

3.5 UV Visible Spectrum

The optical properties of these compounds were probed by the UV visible diffuse reflectance spectroscopy and converted to the transmittance spectra. However, since the crystallite size in pure TiO₂ & SnO₂-TiO₂ nanoparticles prepared by sol-gel method is smaller, quantum size effect appears, resulting in pseudo-“blue shift” of the absorption edge [31]. Fig- 5 & 6 (a) & (b) shows pure TiO₂, SnO₂-TiO₂ its basic absorption and transmission spectrum. Visible absorption at 1450 & 1900 nm the absorption ability UV-visible light was enhanced after composite especially 500nm. This result indicates that the new material may be good for solar cells [32]. At shorter wavelengths, the transmittance first slightly, and then decreased rather quickly, finally approached zero. The fast decrease below 350 nm was due to the absorption of light caused by the excitation of electrons from the valance band to conduction band of TiO₂ is 3.2 eV, So SnO₂-TiO₂ it absorption edge should be 385 nm [33].

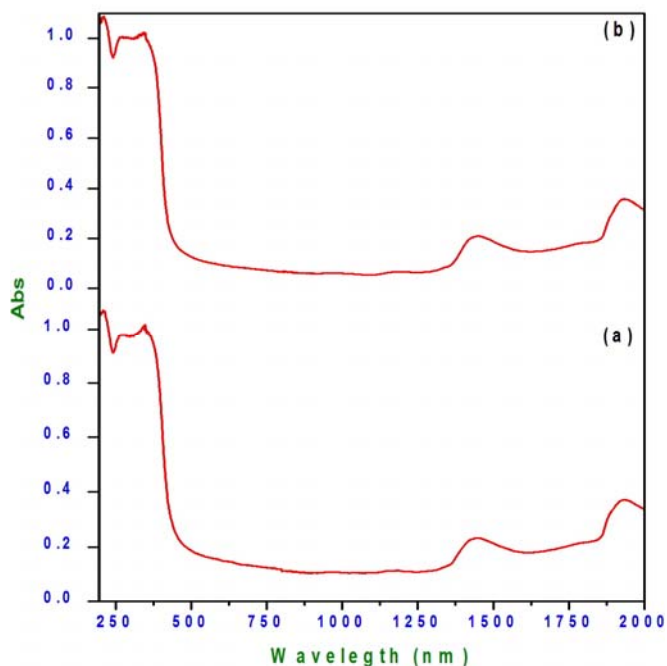


Figure 5 (a) & (b): UV visible absorption spectrum of pure TiO₂ & SnO₂-TiO₂ nanoparticles

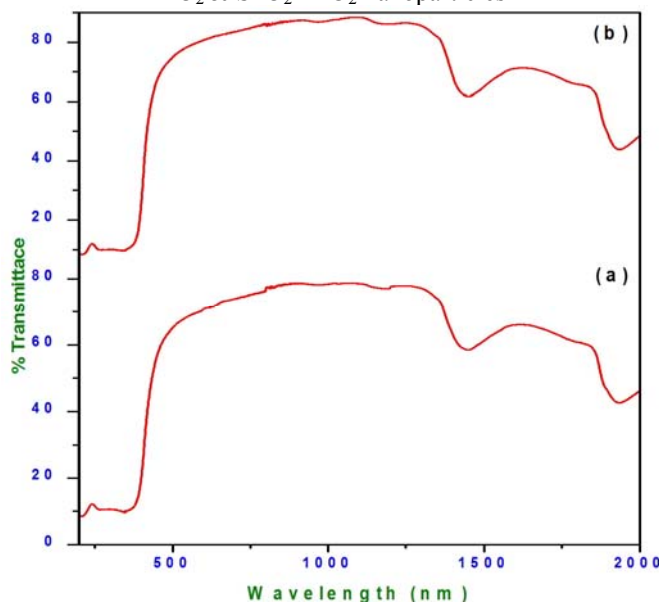


Figure 6 (a) & (b): UV visible transmittance spectrum of pure TiO₂ & SnO₂-TiO₂ nanoparticles

4. Conclusion

Highly dispersed TiO₂, SnO₂-TiO₂ composite and mixed-oxides nanoparticles have been synthesized by solution-gel method annealed at 400°C. The X-ray diffraction investigations showed that pure TiO₂, SnO₂-TiO₂ nanoparticles have perfect crystalline structure. The average particle size which is calculated from Debye Scherrer’s formula is 14.35 & 15.681 nm. From SEM analysis shows the growth of the fine particles SnO₂-TiO₂ in regular pattern is observed on the surface of the sample. The EDAX spectrum reveals that the stoichiometric is maintained. The product is highly pure and the corresponding SnO₂ with an average atomic percentage ratio about 6%. The functional group in the molecules was identified using FTIR spectrum. The spectral analysis gave the information related to the chemical spectroscopy which showed a various bonding

nature corresponding to different frequencies varied between 500- 4000cm⁻¹. The UV visible absorption spectrum shows wide absorption range the absorption edge of the SnO₂-TiO₂ nanoparticles is about 300nm.

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