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Preparation and characterization of SnO₂ nanoparticles by hydrothermal route

Ganesh E Patil¹, Dnyaneshwar D Kajale², Vishwas B Gaikwad¹ and Gotan H Jain^{1*}

Abstract

This paper demonstrates the synthesis of SnO₂ nanoparticles using a simple hydrothermal route in the presence of the surfactant hydrazine at 100 °C for 12 h. X-ray diffraction (XRD), field emission scanning electron microscopy, and transmission electron microscopy (TEM) were employed to characterize the as-prepared product, and optical property was studied by UV-visible diffuse reflectance spectroscopy (DRS). The XRD pattern of the as-prepared sample is indexed to the tetragonal structure of SnO₂, and the calculated particle size is 22.4 nm, which is further confirmed by TEM. The selected area electron diffraction patterns showed continuous ring patterns without any additional diffraction spots and rings of secondary phases, revealing their crystalline structure. Analysis of the DRS spectrum showed the bandgap of the synthesized SnO₂ to be 3.6 eV. The anionic surfactant hydrazine plays a key role in the formation of the SnO₂ nanostructures. A probable reaction for the formation of SnO₂ nanoparticles is proposed.

Keywords: SnO₂ nanoparticles, Hydrothermal route, FESEM, TEM

Background

Nanomaterials have attracted great interest due to their intriguing properties, which are different from those of their corresponding bulk state. In the past few years, SnO₂ is an important n-type wide-energy-gap semiconductor ($E_g = 3.64$ eV, 330 K) which has a wide range of applications such as in solid-state gas sensors [1], transparent conducting electrodes [2], rechargeable Li batteries [3], and optical electronic devices [4]. During the past decade, SnO₂ nanostructures have been one of the most important oxide nanostructures due to their properties and potential applications [5,6].

Many processes have been developed to the synthesis of SnO₂ nanostructures, e.g., spray pyrolysis [5], hydrothermal methods [6-8], evaporating tin grains in air [9], chemical vapor deposition [10], thermal evaporation of oxide powders [11], rapid oxidation of elemental tin [12], the sol-gel method [13], etc. Davar et al. [14] reported the synthesis of SnO₂ nanoparticles by thermal decomposition using [bis(2-hydroxyacetophenato)tin(II)], [Sn(HAP)₂], as precursor. Salavati-Niasari et al. [15] synthesized zinc blend ZnS nanoparticles by a thioglycolic

acid (HSCH₂COOH)-assisted hydrothermal technique via the reaction between a new inorganic precursor [bis(2-hydroxyacetophenato)zinc(II)], [Zn(HAP)₂], and thioacetamide (CH₃CSNH₂). Gnanam and Rajendran [16] synthesized nanocrystalline tin oxide powders of about 8 to 13 nm in size using different surfactants such as cetyltrimethyl ammonium bromide, sodium dodecyl sulphate, and polyethylene glycol via hydrothermal reaction at 160°C for 12 h and studied their structural and photoluminescence properties.

A simple hydrazine-assisted hydrothermal route was employed to synthesize nanocrystalline SnO₂ powders in this study, and structural, morphological, microstructural, and optical properties were discussed.

Methods

All reagents used were of analytical grade without further purification. First, 3.505 g of SnCl₄·5H₂O (0.1 M) was dissolved in 100 ml of distilled water, and then 1.2800 g of hydrazine hydrate (0.01 M) was added with stirring. N₂H₄·H₂O immediately reacted with SnCl₄ in the solution to form a slurry-like white precipitate of the hybrid complex between N₂H₄ and SnCl₄. After 10 min of stirring, the solution was transferred into a Teflon-lined stainless steel autoclave with a capacity of 200 ml

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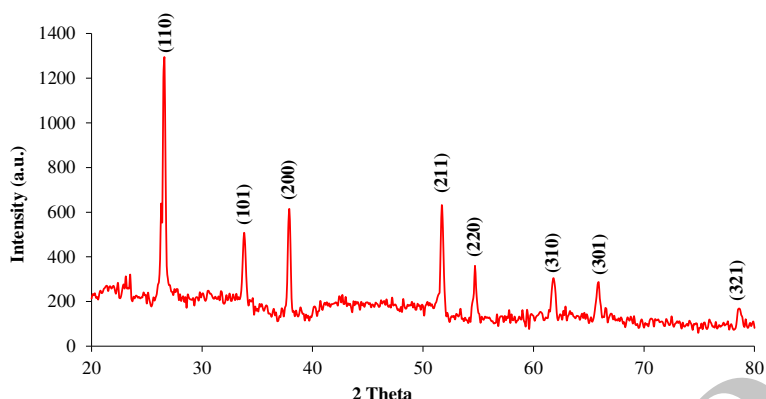
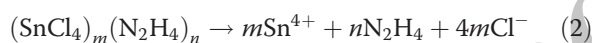
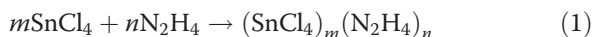


Figure 1 XRD pattern of the SnO₂ sample.

and then sealed. The autoclave was maintained at 100°C for 12 h and cooled naturally to room temperature. The product was centrifuged, filtered out, and rinsed with methanol and distilled water several times, and then dried at 120°C for 1 h in air.

The possible reaction of SnCl₄·5H₂O with hydrazine produced SnO₂ nanoparticles via Sn⁴⁺ reaction with NH₄OH. The process can be expressed as follows:



Prior to the hydrothermal process, the (SnCl₄)_m(N₂H₄)_n complex clusters were formed via reaction (1), and at the same time, the clusters were agglomerated into the slurry-like white precipitate mentioned above. As represented in reaction (2), the (SnCl₄)_m(N₂H₄)_n clusters underwent dissociation when the solution was heated to 100°C during

the hydrothermal stage. In reaction (3), OH⁻ ions were formed via the dissociation of N₂H₄ into NH₄OH and N₂ [17]. Reaction (4) represents the formation of the SnO₂ nanoparticles via the reaction between Sn⁴⁺ and OH⁻ ions formed in reaction (3).

The synthesized sample was characterized by X-ray powder diffraction (XRD) using the XRD Make-Bruker D-8 model (Bruker AXS, Inc., Madison, WI, USA) with CuKα radiation with a wavelength λ = 1.5418 Å at 2θ values between 20° and 80°. Transmission electron microscopy (TEM) images were recorded from a transmission electron microscope (CM-200, Make-PHILIPS, Amsterdam, The Netherlands). The UV-visible (UV-vis) diffuse reflectance spectrum (DRS) was obtained from a JASCO UV-vis/NIR spectrophotometer V-670 model (Easton, MD, USA).

Results and discussion

Structural properties by XRD

The XRD pattern of the product is shown in Figure 1. The peaks at 2θ values of 26.6°, 33.8°, 37.9°, 51.8°, 54.7°, and 78.1° are indexed to the SnO₂ (JCPDS card no. 04-07-876) [18].

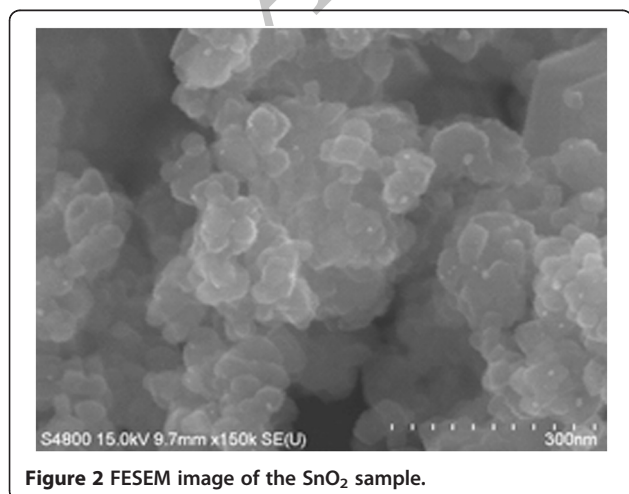


Figure 2 FESEM image of the SnO₂ sample.

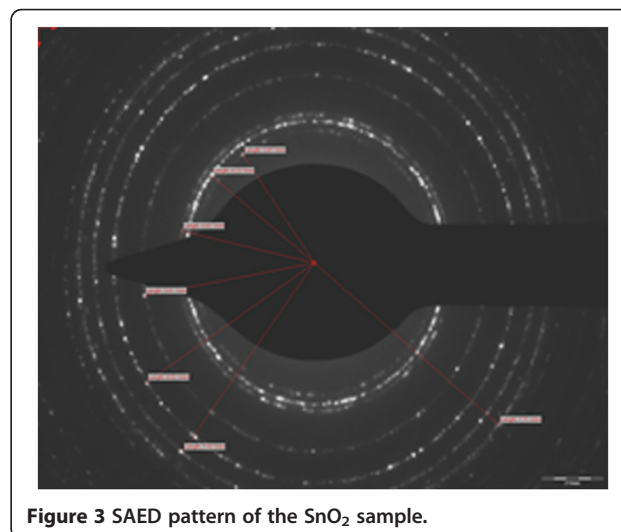


Figure 3 SAED pattern of the SnO₂ sample.

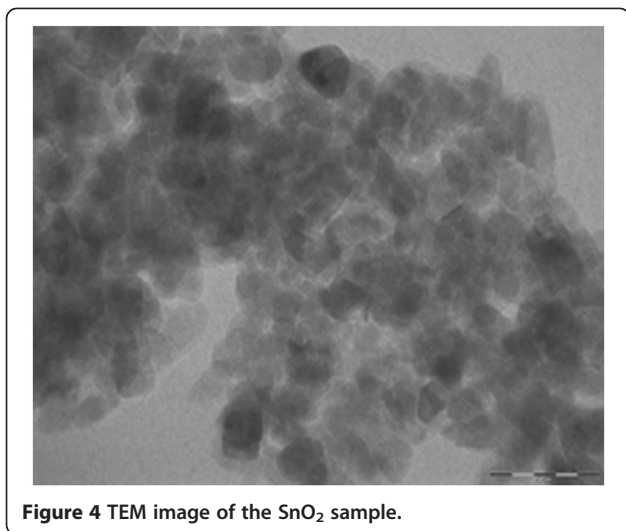


Figure 4 TEM image of the SnO₂ sample.

61.9°, and 65.9° can be associated with (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0), and (3 0 1), respectively. A matching of the observed and standard (*hkl*) planes confirmed that the product is of SnO₂ having a tetragonal structure, which are in good agreement with the literature values (JCPDS card no. 41-1445). The average particle size (*D*) was estimated using the Scherrer equation [18]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \quad (5)$$

where *D* is the crystallite size, λ is the X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle of the diffraction peaks. The average particle size was found to be 22.4 nm.

Morphological properties by FESEM

Figure 2 shows the field emission scanning electron microscopy (FESEM) micrograph of the synthesized SnO₂ sample. Clustering of particles seems to have occurred on the surface. In this image, cubic structures can be easily seen.

Microstructural properties by TEM and SAED pattern

Figure 3 shows the electron diffraction patterns of the sample. It is clear from the figure that the SnO₂ particles are crystalline in nature. The electron diffraction patterns show continuous ring patterns without any additional diffraction spots and rings of secondary phases, revealing their crystalline structure. Seven fringe patterns corresponding to planes (1 1 0), (1 0 1), (2 0 0), (2 1 1), (2 2 0), (3 1 0), and (3 0 1) are consistent with the peaks observed in the XRD patterns. XRD and TEM studies confirmed pure tetragonal structure of SnO₂ as evidenced from Figures 1 and 4, respectively. The ring-to-the-center distance of each ring is measured as 3.01, 4.23, 4.41, 5.61, 6.52, 7.10, and 7.71 and expressed in terms of nm⁻¹. The reciprocal of these values gives the interplanar distance *d*. Details are given in Table 1.

Optical properties by UV-vis DRS

To determine the optical bandgap of synthesized SnO₂, the reflectance spectra of the SnO₂ thick film prepared by screen printing technique [19] on a glass substrate was measured. The reflectance (*R*) spectra of the SnO₂ thin film were shown in Figure 5.

As seen in Figure 5, the reflectance spectra show a strong decrease after 360 nm. This decrease is related to optical transitions occurring in the optical bandgap. In order to determine the precise value of the optical bandgap of the SnO₂, the reflectance values were converted to absorbance by application of the Kubelka-Munk function [20,21].

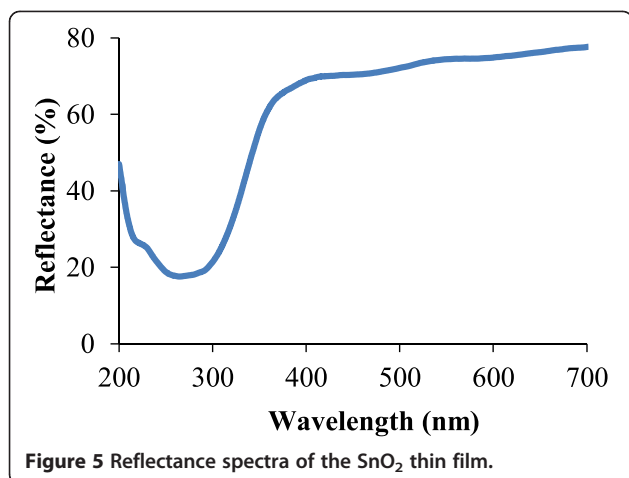
The Kubelka-Munk theory is generally used for the analysis of diffuse reflectance spectra obtained from weakly absorbing samples. The Kubelka-Munk formula is expressed by the following relation:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{K}{S}, \quad (6)$$

where *F*(*R*) is the Kubelka-Munk function which corresponds to the absorbance, *R* is the reflectance, *K* is the absorption coefficient, and *S* is the scattering coefficient.

Table 1 *d* values obtained from XRD and TEM

Reported <i>d</i> values (Å)	XRD <i>d</i> values (Å)	Electron diffraction (TEM)		Planes (<i>hkl</i>)
		Reciprocal of <i>d</i> values δ_{hkl} (nm ⁻¹)	<i>d</i> values d_{hkl} (Å)	
3.35	3.342	3.01	3.320	(1 1 0)
2.64	2.604	4.23	2.364	(1 0 1)
2.37	2.372	4.41	2.267	(2 0 0)
1.76	1.770	5.61	1.782	(2 1 1)
1.67	1.653	6.52	1.533	(2 2 0)
1.50	1.501	7.10	1.408	(3 1 0)
1.41	1.418	7.71	1.297	(3 0 1)



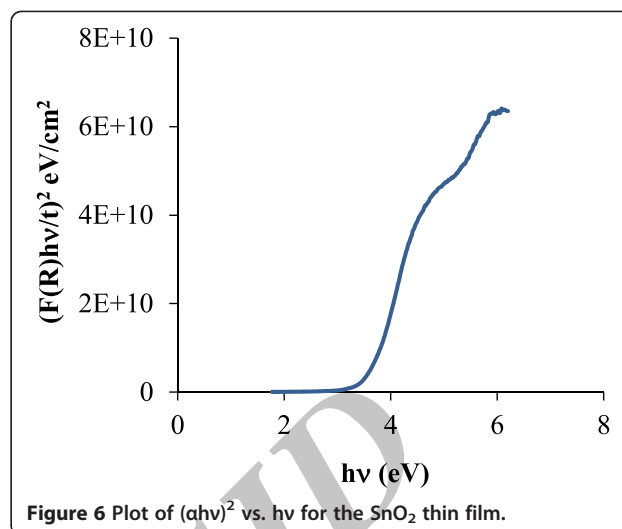
It is well known that the optical transitions in semiconductor materials are taken place by direct and indirect transitions. The absorption coefficient α for direct transitions is expressed by the following relation [22]:

$$\alpha hv = A(hv - E_g)^n, \quad (7)$$

where α is the linear absorption coefficient of the material, A is an energy-independent constant, E_g is the optical bandgap, and n is a constant which determines the type of optical transitions: for indirect allowed transition, $n = 2$; for indirect forbidden transition, $m = 3$; for direct allowed transition, $n = 1/2$; and for direct forbidden transition, $m = 3/2$. The $F(R)$ values of the SnO₂ film were obtained using the $\frac{(1-R)^2}{2R}$ relation in Equation 6 [23,24] and the Kubelka-Munk function $F(R)$ is directly proportional to the absorbance. Therefore, $F(R)$ values were converted to the linear absorption coefficient by means of the $\alpha = \frac{F(R)}{t} = \frac{\text{Absorbance}}{t}$ relation [25], where t is the thickness of the SnO₂ film. The curve of $\left(\frac{F(R)hv}{t}\right)^2$ vs. hv for the SnO₂ film was plotted, as shown in Figure 6. The optical bandgap (E_g) of the SnO₂ film was determined from the curve of $\left(\frac{F(R)hv}{t}\right)^2$ vs. hv and was found to be 3.6 eV. The optical bandgap of the SnO₂ studied is similar to that of undoped SnO₂ materials obtained by various methods [26,27]. This suggests that the optical bandgap of SnO₂ semiconductors changes with respect to the synthesis method used.

Conclusions

SnO₂ nanoparticles have been successfully synthesized by a simple hydrothermal method at low temperature using hydrazine hydrate as a mediator. The structural, morphological, microstructural, and optical properties of a SnO₂ sample were investigated. XRD spectra indicated that the as-prepared product is polycrystalline in nature.



It was also shown from these spectra that the crystallite structure was observed to be tetragonal. The surface morphology was investigated by FESEM. The crystallite size (22.4 nm) of the SnO₂ nanoparticles, estimated by XRD, is confirmed by TEM. The optical bandgap of the SnO₂ film was found to be 3.6 eV.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

GEP synthesized the nanocrystalline SnO₂ materials, carried out the characterization, and drafted the manuscript. DDK participated in the discussions and interpretation of all characterization results. VBG and GHJ gave the final approval of the version to be published. All the authors read and approved the final manuscript.

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