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ORIGINAL ARTICLE

Synthesis and characterization of SnO_2 nanoparticles by co-precipitation method

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Abstract

Tin oxide (SnO_2) nanoparticles were synthesized by co-precipitation method and the synthesized nanoparticles were annealed at different temperatures for characterization. The powders were investigated with X-ray diffraction, scanning electron microscopy and optical spectroscopy. The structural characterization was carried out by X-ray diffraction which confirms the crystalline nature of the films with a tetragonal structure. SEM analysis of the powders enabled the conclusion that the prepared nanoparticles are spherical particles which are smaller in size composed of clustered and agglomerated nanoparticles. From the absorption spectra the type of transition and band gap of the synthesized nanoparticles were estimated. The optical (UV-visible) spectrum exhibits a well defined absorption which in considerably blue shifted related to the peak absorption of bulk SnO_2 indicating quantum size effect.

Keywords: *Morphological Properties; Optical Properties; Quantum Size Effect; Structural Properties; Tetragonal Structure; Tin Oxide Nanoparticles.*

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INTRODUCTION

Nanomaterials have attracted great interest due to their intriguing (unique electrical, physical, chemical, and magnetic) properties, which are different from those of their corresponding bulk state. Enormous efforts are being taken towards the development of nanometer sized materials in studies related on one hand to their fundamental mechanism such as the size effect, the quantum effect and on the other hand towards application of these materials. With decreasing particle size the band structure of the semiconductor changes; the band gap increases and the edges of the bands splits into discrete energy levels. These so-called quantum size effects occur [1-11]. Nanometer sized material and semiconductor particles have a large potential for industrial applications. Metal oxide semiconductors are low cost and effective gas sensing material. Among the various metal oxide semiconductors, SnO_2 have been attracting much attention since they are highly conducting, transparent and sensitive to gases. SnO_2 is highly interesting as it is an n-type semiconductor with direct band gap of 3.6 eV between the full oxygen 2p Valence band and the tin states at the bottom of the conduction band and offers many technological applications such as catalysts for oxidation of organics, solid state gas sensors, conducting films, environmental monitoring, biochemical sensor, lithium rechargeable batteries, solar cells [12], dye-sensitized solar cells. [13-17].

Earlier workers synthesized SnO_2 nanoparticles by various methods like Sol Gel [18] Micro Wave technique [19] Solvo-thermal [20], Hydro thermal [21], Sonochemical [22] Mechanochemical [23], Co-precipitation [24]etc., Of the various methods Co-precipitation method is simple, inexpensive and does not require high temperature and pressure. In this method the size and shape of the particle can be controlled by altering pH of the

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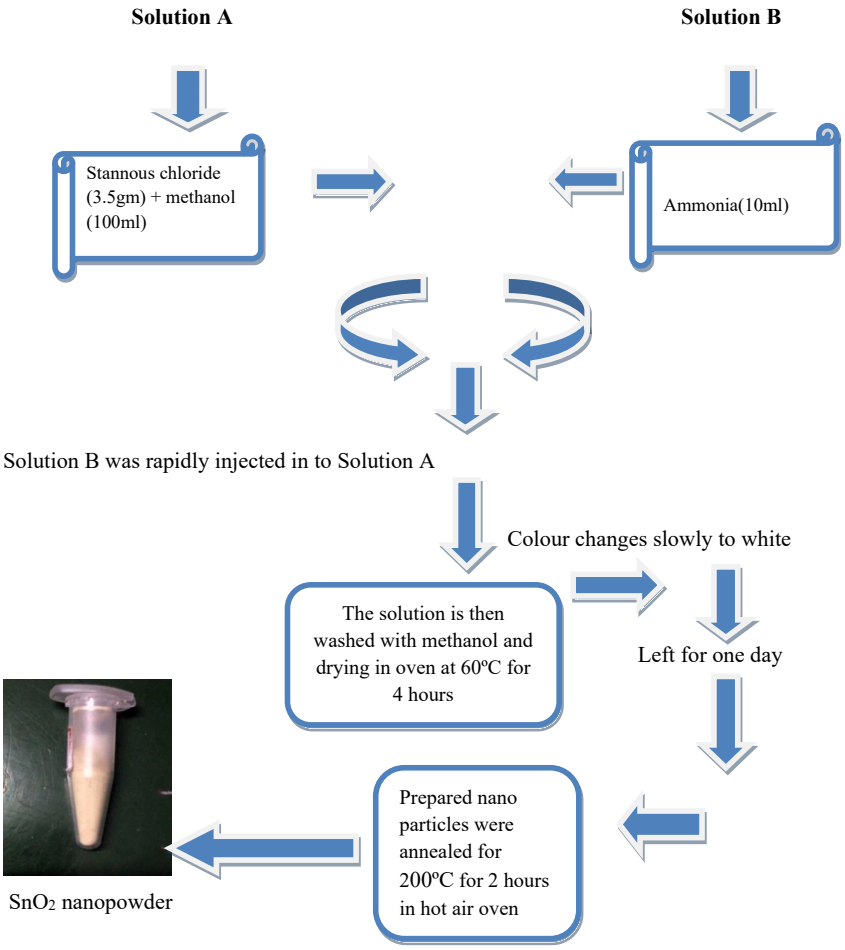

Fig. 1. Schematic representation of synthesis of SnO_2 nanoparticles.

medium, concentration of the precursor and precipitating reagents. Impurities in the precipitate were easily eliminated by filtration and repeated washing and after some time the particles undergo aggregation. Therefore focus has been given to synthesize pure and highly crystalline SnO_2 nanoparticles using Co-precipitation method.

EXPERIMENTAL DETAILS

In the present work Tin oxide (SnO_2) nanoparticles were synthesized by co-precipitation method using precursor's stannous chloride and methanol. Solution A contains 3.5gm of stannous chloride which was dissolved in 100ml of methanol and kept in a magnetic stirrer for 20-30 minutes. Solution B contains 10ml of Ammonia (NH_3), was rapidly injected in to solution A under continuous stirring for 30 minutes. Following rapid injection, a white precursor was obtained and the reaction system gradually becomes transparent and the color changes slowly, now the color changes from transparent to white. The white colour precipitate was taken out by filtering and then the filtered powder was washed with methanol for once. The washed nanoparticles were dried at 60 ºC for 4 hours by using hot air oven. The prepared nanoparticles were annealed 200 ºC for 2 hours in hot air oven for characterization. The schematic representation of synthesis of SnO_2 nanoparticles is presented in Fig 1. Structural characterization of these films was carried out by using Shimadzhu (Lab X-6000) x-ray diffractometer with Cu Kα (λ = 1.5406 Å) line in 2θ range from 20 to 80 degrees. A JASCO (V570: UV-VIS-NIR) double beam spectrophotometer was used for optical studies in the wavelength range 400–2500 nm.

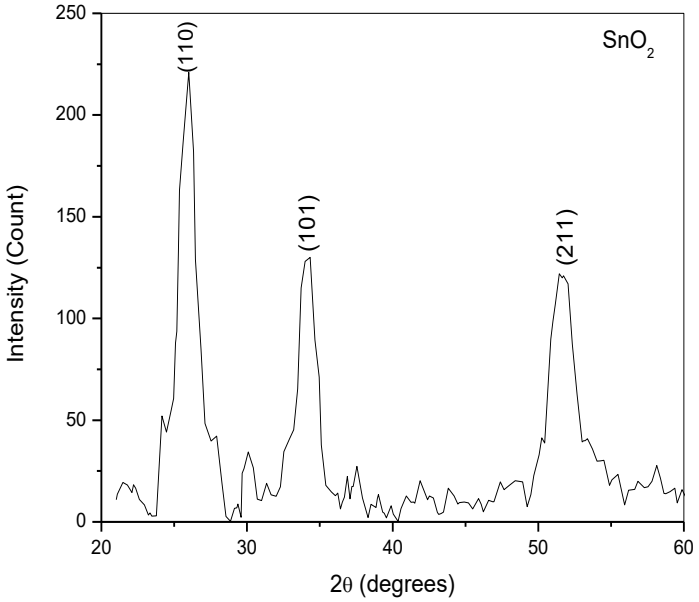

Fig. 2. XRD diffractogram of SnO_2 nanoparticles.

Table 1: Structural parameters of SnO_2 nanoparticles.

Sample	Interplanar spacing 'd' (nm)	2θ (degrees)	(hkl) Planes	Lattice constants		Crystallite size(nm)
				'a'(Å)	'c' (Å)	
SnO_2	3.3670	26.46	(110)	4.1610	-	20.45
	2.6582	33.70	(101)	4.7730	3.200	29.49
	1.7741	52.40	(211)	4.7660	3.201	27.71

RESULTS AND DISCUSSION

Structural Analysis of SnO_2 nanoparticles

The X-ray diffraction pattern of SnO_2 nanoparticles prepared by Co-Precipitation method is presented in Fig. 2, which confirms the polycrystalline nature of the prepared SnO_2 nanoparticles. Similar X-ray diffractograms were reported for SnO_2 nanoparticles prepared by different methods by the earlier researchers [1-3, 17, 25-28].

From the diffraction profile the diffraction angles and the intensity of lines were measured with greater accuracy. The predicted peaks (110) (101) and (211) are reported as the identifying peaks for SnO_2 nanoparticles by earlier reporters [1-3,17, 25-28] and JCPDS file of SnO_2 (JCPDS 41-1445). From the diffraction profile it has been found that the prepared SnO_2 nanoparticles are polycrystalline in nature [28] with tetragonal structure, having the preferential orientation along (110) plane. The intensity of the peak (110) increases significantly faster than the other peaks.

The lattice parameters 'a' and 'c' for the SnO_2 nanoparticles of tetragonal structure were evaluated by using the relation,

$$\frac{1}{d^2} = \left(\frac{h^2 + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

The crystallite size (D) of the SnO_2 nanoparticles were estimated using Debye Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where, λ the wavelength of the radiation is source (CuKα) and β is the full width at half maximum of the corresponding peak of the XRD pattern.

From the observed 'd' spacing, (hkl) planes, the lattice constants were calculated using the above relation [Table 1] and are in good agreement with earlier reporters [28-31]. The average crystallite size (*D*) evaluated from the XRD spectra using Scherer's formula lies between 20 nm and 27nm, presented in Table [1].

SEM analysis of SnO_2 Nanoparticles

Scanning Electron Microscopy (SEM) was employed to analyze the morphology and growth features of aggregates of the as prepared SnO_2 nanoparticles with different magnification. In Fig. 3 (a, b) SnO_2 particles with nano sized dimension are interconnected, which shows strong agglomeration accompanied with a lot of small spherically shaped particles. This agglomerate actually consists of much larger grains of about 100–200 nm in diameter [17]. Particle size and distribution of nanoparticles mainly depend upon the relative rates of nucleation and growth processes, as well as the extent of agglomeration [29].

It is interesting to note that, when magnification increased SnO_2 particles are fine and some agglomeration of finer particulates to form bigger clusters. However there is some non-uniformity in the shape and the existence of porosity observed in Fig. 3(c & d) [32]. The measured average particle size of the tin oxide particles from the SEM image Fig. 3(e) was around 160 nm.

Optical analysis of SnO_2 Nanoparticles

The most dramatic property of semiconductor nanoparticles is the size evolution of the optical absorption spectra. Hence UV–visible absorption spectroscopy is an efficient technique to monitor the optical properties of quantum-sized particles. The absorption spectrum of the nanoparticles of SnO_2 is shown in Fig. 4. The spectrum exhibits a well-defined absorption feature (peak) at ~328 nm

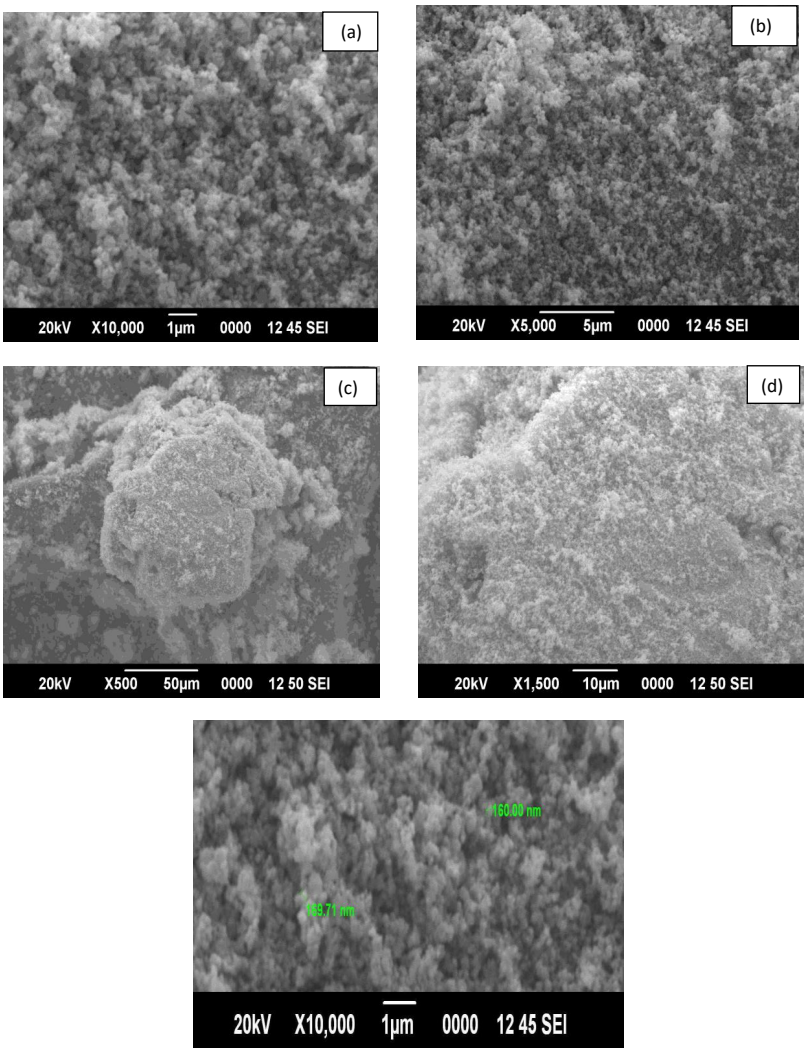

Fig. 3 (a, b, c, d, e). SEM image of SnO_2 nanoparticles (Particle size is indicated in green colour).

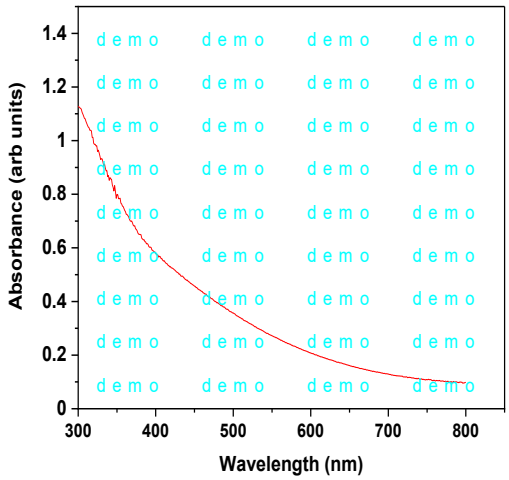

Fig. 4. Optical absorption spectra of SnO_2 nanoparticles.

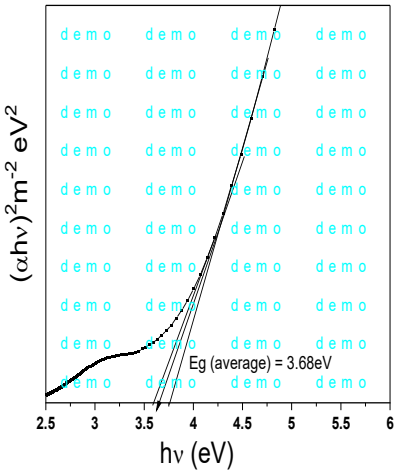

Fig. 5. Plot of $(\alpha h\nu)^2$ vs $(h\nu)$ for SnO_2 nanoparticles.

corresponding to the band gap of 3.77 eV (E=hυ) which is considerably blue-shifted by 0.17 eV relative to the bulk SnO_2 value (3.6 eV). It is clear that the obtained tin oxide has the optical band gap larger than the value of 3.6 eV for bulk SnO2 which can be attributed to quantum confinement effect [24, 28, 33-35].

From a quantum mechanical basis and appropriate selection rules, it is possible to find out the nature of electronic transition from the absorption of photon energy by using the relation,

$$\alpha = \frac{A\left(h\upsilon - E_g\right)^r}{h\upsilon}$$

where A is a constant and E_g is the energy band gap. The optical energy band gap is the minimum energy required to excite an electron from the valance band to the conduction band by an allowed optical transition [36]. $(\propto h\nu)^2$ versus $(h\nu)$ for SnO_2 nanoparticles is shown in Fig. 5. The straight line extrapolated to the energy axis has been rotated many times and the band gap has been estimated each time [37] and the average value is given by 3.68 eV. The observed band gap value is in agreement with earlier reported values and which is considerably blue-shifted by 0.08 eV relative to the bulk SnO_2 value (3.6 eV) [26, 29, 38, 39].

The dependence of particle size of the SnO_2 nanoparticles can be determined experimentally from the band gap energy inferred from the optical absorption spectra, which is expressed from an effective mass model [39, 40]. Using effective mass equation the calculated optical band gap energy for SnO_2 nanoparticles was found to be 3.65 eV. The optical band gap energy (*Eg*) was calculated using effective mass equation and from Tauc's relation as 3.65 eV and 3.68 eV, respectively. Hence the optical band gap energy value appears slightly lower than the calculated band gap energy value (effective mass model Eg = 3.65) due to a tight-binding model used in the experimental data (optical absorption spectra) [39].

Band gap values estimated from different methods were in good agreement with the earlier reporters on SnO_2 nanoparticles. The wide direct band gap makes these particles good material for potential applications in optoelectronic devices such as multilayer dielectric filters and solar cells [41].

CONCLUSION

SnO_2 nanoparticles have been synthesized by co-precipitation method. The XRD analysis confirmed that the crystalline structure of SnO_2 nano particles as tetragonal. The structural parameters such as crystallite size, lattice constants a & c has been calculated [a=4.161 nm, c=3.200 nm] which were in well agreement with JCPDS data and earlier reporters. SEM image of SnO_2 nano particles showed that the present nano sized spheres and some agglomeration with larger grains. The UV-visible spectrum exhibits a well defined absorption peak at ~328 nm corresponding to the band gap of 3.77 eV, optical band gap of 3.68 eV estimated from Tauc's plot and optical band gap of 3.65 calculated using effective mass equation were considerably blue shift, related to the peak

absorption of bulk SnO_2 (3.6 eV) indicating quantum size effect. From the results, the synthesized SnO_2 nanoparticles by co-precipitation method could have large number of potential application in the field of optoelectronic devices and solar cell applications.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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