Structural Study of Tin Oxide Nanopowder Prepared by Jaggery Mediated Gel Combustion Method

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Abstract

Nanocrystalline tin oxide (SnO_2) powder was synthesized through a simple and inexpensive gel combustion method using jaggery as a fuel. Prepared SnO_2 powder was calcinated at 800^oC for 3 hours and characterized by PXRD, FESEM and FTIR. The PXRD and rietveld analysis revealed the tetragonal rutile SnO_2 phase. The cell parameters determined from rietveld analysis and Nelson-Riley plot method were in good agreement with standard data. The grain size was calculated using Scherer equation and W-H plot method and was found to be $\approx$ 9 nm. The FESEM picture showed the loosely held network with agglomerated nanoparticles. The texture coefficient of the prepared sample was found to be slightly higher than 1. The FTIR spectrum revealed the molecular vibrations of chemical bonds associated with SnO_2.

Keywords *Tin oxide, Gel combustion method, Jaggery and Rietveld refinement*

1. Introduction

Tin oxide (SnO2) is a unique semiconductor material, with a wide band gap of 3.6 eV at 300 K [1]. It's optical and electrical properties are allied with good chemical and mechanical stability. It has been widely used for catalytic applications, gas sensing, transparent conducting electrodes and liquid crystal displays, etc., [2].

Jaggery is one of the most important sweeteners in India. It is a concentrated product of cane juice without separation of the molasses. It contains up to 50% sucrose, up to 20% invert sugars with some insoluble matter such as ash, proteins and bagasse fibers [3].

Several methods of synthesizing SnO_2 nanoparticles such as sol–gel, hydrothermal, solvothermal, chemical precipitation, thermal decomposition, microwave assisted combustion method, polyol method, gel combustion method have been reported [1,2,4,5,6,7,8]. Among these, gel combustion synthesis process is relatively cost effective, fast, energy efficient and it provides easy formation of high-quality multielement compounds with complex crystal structures [7]. Also, gel combustion method gives a homogenous, high purity, and high quality nano powders due to the possibility of stochiometric control [8].

Synthesis of tin oxide nanoparticles by gel combustion method using jaggery as a fuel has not been reported. In the present work nanocrystalline tin oxide (SnO_2) powder was prepared by gel combustion method using jaggery as a fuel. Prepared SnO_2 powder was calcinated at 800^oC for 3 hours and characterized by PXRD, FESEM and FTIR.

2. Experimental

2.1 Material Preparation

Tin oxide (SnO2) nanopowder was synthesized using tin metal granules (Sn), nitric acid (HNO_3), and jaggery as starting materials. The stoichiometric amount of tin metal granules were added to the dilute HNO_3 solution (nitric acid: distilled water ratio was 4:1) kept in an ice bath and continuously stirred to get tin nitrate [$Sn(NO_3)_2$] which acts as an oxidiser [9,10,11]. The 20 g of jaggery which is a fuel was dissolved in 20 mL double distilled water. This solution of fuel was added to the oxidizer and heated under constant stirring at a temperature of about 100°C on a hot plate. Then the concentration of the solution slowly became higher and eventually a gel was formed. When the temperature of the hot plate was raised to about 300°C, the gel underwent a strong, self sustaining combustion reaction with evolution of gases in a large volume and yellowish tin oxide powder was formed. The resulting powder was then fired at a temperature of 450°C in a muffle furnace until complete decomposition of the carbonaceous

residues was achieved. The nano powder produced was then calcinated at 800 °C for 3 hours.

2.2 Characterisation

The structural characterization of SnO_2 nanopowder was performed using Rigaku powder X – ray diffractometer (PXRD). The diffraction pattern was recorded at room temperature using CuKα (1.54056 Å) radiation in the range 20° - 80° at a scan rate of 2° min^{-1}. The morphological feature of the sample was observed by using Carl Zeiss Supra 55 field emission scanning electron microscope. FTIR spectrum of the sample was taken with Nicolet spectrometer.

3. Results and Discussion

3.1 PXRD Studies

Peak indexing

Fig. 1 shows the PXRD pattern of the prepared SnO_2 nanopowder. The reflections are consistent with a rutile-type structure (space group, *P*42/*mnm*). The peaks are readily indexed to the tetragonal rutile phase of SnO_2 (JCPDS No. 41-1445).
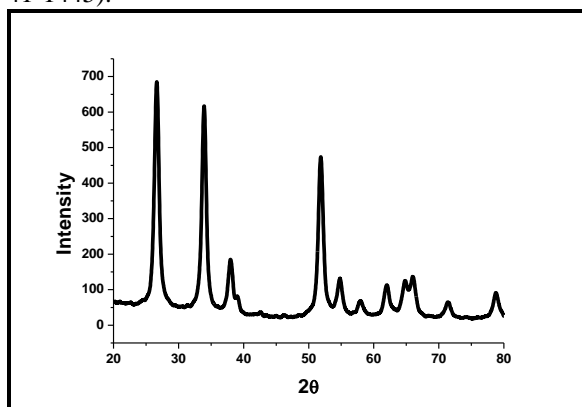

Fig.1 PXRD pattern of SnO$_2$ nanopowder

Particle Size Calculation

The mean crystallite size (D) of the nanopowder was estimated using the Debye-Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where λ, β, θ are the wavelength of X-ray radiation used (1.54056 Å), the full width at half maximum (FWHM) of diffraction peak and the Bragg diffraction angle respectively. The mean crystallite size determined by Scherer's method was found to be 9.33 nm.

Nelson-Riley Plots

The spacing between diffracting planes (d) of SnO_2 was calculated from the Bragg equation:

$$2d.\sin\theta = n\lambda \qquad (2)$$

and the lattice parameters (a = b ≠ c) for the tetragonal phase structure were determined by the equation (3).

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (3)$$

The corrected values of lattice parameters were estimated from the Nelson-Riley [12] plots (Fig. 2). The Nelson-Riley curve was plotted between the calculated lattice parameters for different planes and error function

$$f(\theta) = \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta} \qquad (4)$$

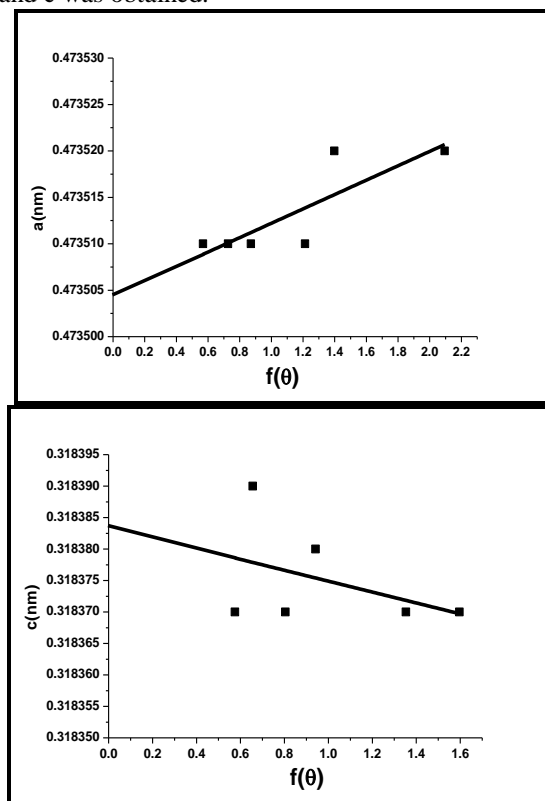by the extrapolation f(θ) against lattice parameter, a and c was obtained.

Fig.2 Nelson-Riley plots of SnO$_2$ nanopowder

The values of lattice parameters a and c, respectively calculated by Nelson-Riley equation are 0.473504 nm (4.73504 Å) and 0.318381 nm (3.18381 Å). They are in good agreement with the results of rietveld refinement and JCPDS data (Table 1).

Table 1. Values of lattice parameters

Lattice Parameter	Nelson-Riley Plot	JCPDS	Rietveld refinement
a	4.73504 Å	4.7382	4.7347
c	3.18381 Å	3.1871	3.1854

Insrumental Broadening

Appreciable broadening in x-ray diffraction lines will occur when particle size is less than 100 nm. Diffraction pattern will show broadening because of particle size and strain. The average size of the particles was determined using the observed line broadening. The total broadening of the diffraction peak is due to the sample and the instrument [13]. The sample broadening is described by Williamson - Hall equation

$$\beta \cos\theta = \frac{0.94\lambda}{D} + 4\varepsilon \sin\theta \qquad (5)$$

where ε is strain and β instrumental broadening. The average particle size D and the strain (ε) of the experimentally observed broadening of several peaks was computed using least squares method. The instrumental Broadening calculations for several planes were plotted against 2θ as in Fig.3. Williamson-Hall plot was also plotted with 4sinθ on the x-axis and βcosθ on the y-axis as in Fig.4. The particle size and strain (ε) were calculated from y-intercept and slope respectively. The calculated particle size D was found to be 8.92 nm and internal lattice strain value is found to be 8.19×10^{-5}.
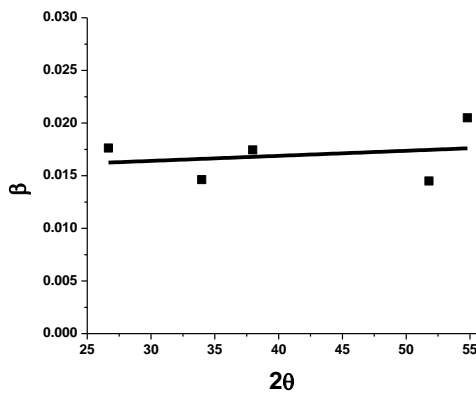

Fig.3 Line broadening value due to the equipment

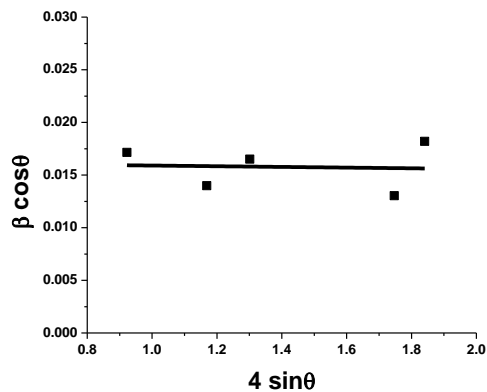**Fig. 4 W–H analysis for SnO$_2$ nanopowder.**

Dislocation Density

The dislocation density (δ) which represents the amount of defects in the powder was calculated from Williamson and Smallman's formula [14]

$$\delta = \frac{n}{D^2} \qquad (6)$$

where, n is a factor, which when equal to unity gives the minimum dislocation density, and D is the average crystallite size. The dislocation density for the prepared tin oxide nanopowder was estimated to be $11.48 \times 10^{15}\,\mathrm{m}^{-2}$.

Determination of Texture Coefficient

The information concerning the preferential crystal orientation can be obtained from the texture coefficient, TC, defined as [15]

$$TC = \frac{\frac{I_{hkl}}{I_O}}{\frac{1}{N}\sum_1^N \frac{I_{hkl}}{I_O}} \qquad (7)$$

where, I is the measured intensity, Io is the standard intensity from JCPDS data and N is the number of diffraction peaks.

If TC≈1 for all the (hkl) planes considered, then the nanoparticles are with a randomly oriented crystallite similar to the JCPDS reference, while values higher than 1 indicate the abundance of grains in a given (hkl) direction. Values 0<TC<1 indicate the lack of grains oriented in that direction. As TC increases, the preferential growth of the crystallites in the direction perpendicular to the hkl plane is greater. We have used three diffraction peaks (110), (101) and (211). It can be seen that the lowest TC was in (211) plane for SnO$_2$ nanoparticles, indicating the lack of grains oriented along that plane and for the other plains TC was found to be slightly higher than 1 .The obtained results are presented in table 2.

Table 2. Texture Coefficient Results

Reference*		SnO$_2$ Nanopowder	
(hkl)	I/I$_O$	I/I$_O$	TC
(110)	1.00	1.00	1.16
(101)	0.75	0.90	1.04
(211)	0.57	0.69	0.79

* (JCPDS – 41-1445).

Rietveld analysis

Rietveld refinement was carried out using FULLPROF software [16] on the powder X-ray diffraction (PXRD) data of SnO$_2$ nanopowder, selecting the space group (P 42/mnm). Fig.5 depicts the observed, calculated and difference PXRD profile for SnO$_2$ nanopowder after final cycle of refinement.

It can be seen that the profile for observed and calculated one is perfectly matching. The value of χ2 comes out to be equal to 0.843, which may be considered to be very good for estimations. The profile fitting procedure adopted was minimizing the χ2 function. The obtained results of rietveld refinement of SnO$_2$ nanopowder are given in Table 3. The obtained lattice parameters have shown a good agreement with the JCPDS data.
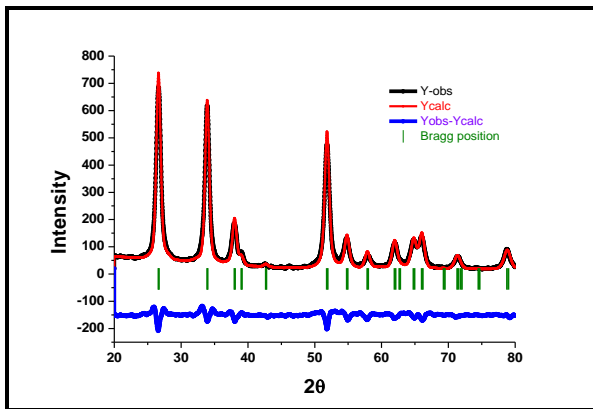
Fig. 5 Rietveld pattern of SnO₂ nanopowder

Table 3. Results of rietveld refinement

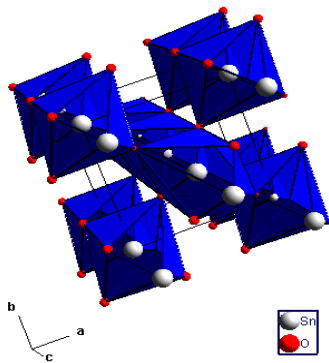| Space Group	P 42/mnm	
Hall Symbol	-P 4n 2n	
Lattice Parameters		**JCPDS No. 41-1445**
$a=b$ (Å)	4.7347	4.7382
c (Å)	3.1854	3.1871
$\alpha=\beta=\gamma$	90°	90°
Reitveld Parameters		
R_p	8.36	
R_{wp}	10.5	
R_{exp}	11.5	
$\chi 2$	0.843	
GoF	0.92	
Density (g/cm³)	7.048	7.020
Unit cell volume (Å³)	71.408	

Fig. 6 Packing diagram of SnO₂ nanopowder

The packing diagram of the SnO₂ nanopowder was drawn using DIAMOND crystal and molecular structure visualization software and is shown in the Fig. 6.

3.2 Morphology Study

Fig. 7 shows FSEM image of tin oxide nanopowder synthesized by gel combustion method using jaggery as a fuel.
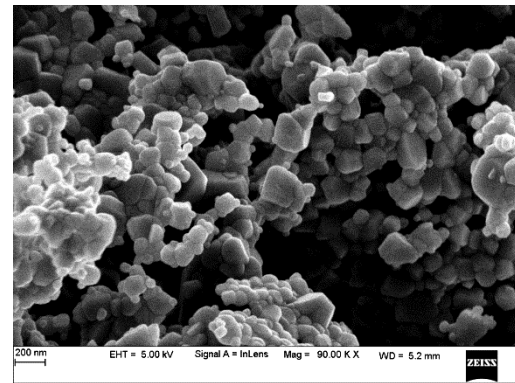

Fig. 7 SEM image of SnO₂ nanoparticles prepared by combustion method using jaggery as a fuel

The FESEM image shows the formation of agglomerated irregular shaped nanoparticles.

3.3 FTIR Study

FTIR is a technique used to obtain information regarding chemical bonding and functional groups in a material. FT-IR spectrum was recorded in solid phase using KBr pellet technique in the region 400–2000 cm⁻¹. The Fig.8 shows the FTIR spectrum of the SnO₂ nanopowder.
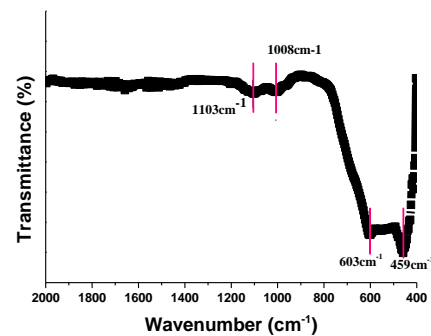

Fig. 8 FTIR spectrum of SnO₂ nanopowder

The bands at 1103cm⁻¹ and 1008cm⁻¹ are attributed to the stretching of water molecules or hydroxyl groups. The bands at 603cm⁻¹ and 459cm⁻¹ refers to Sn-O stretching modes of Sn-O-Sn [17]. The molecular vibrations of chemical bonds observed are all associated with SnO₂ and this shows the purity of the material.

CONCLUSION

Tin oxide nanopowder was synthesized by gel combustion method using jaggery as a fuel. The diffraction pattern of the nanopowder was indexed to tetragonal structure with average crystallite size of 9.33 nm. The FESEM image revealed the formation of agglomerated irregular shaped nanoparticles. The cell parameters determined using Nelson-Riley plot were matched with JCPDS data. The texture coefficient was found to be slightly higher than 1, indicating the abundance of grains oriented in the given hkl direction. The obtained cell parameters from rietveld analysis were in good agreement with

standard data. The FTIR spectra revealed the molecular vibrations of chemical bonds associated with SnO_2 showing the purity of the materials. The gel combustion route is simple, eco-friendly, low expensive and is found to be effective in producing nanoparticles of smaller sizes.

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