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SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMICAL PROPERTIES OF ANTIMONY DOPED MESOPOROUS TIN OXIDE

[1]S.Blessi, [2]V.Maria Vinosel, [3]Dr.S.Pauline*

[1,2,3] *Department of Physics, Loyola College, University of Madras (India)*

ABSTRACT

Antimony-doped Tin Oxide (ATO) nanoparticles were prepared via chemical precipitation technique using $SnCl_4$, $SbCl_3$ as the precursor materials. The doping composition was varied between 1, 3 and 5 wt%. The obtained nano samples were characterized by means of XRD, FTIR, FESEM-EDAX, N_2 adsorption - desorption isotherms and by cyclic voltammogram. The average crystallite size of ATO particles was calculated from the XRD patterns and was found to decrease with increasing proportion of Antimony. Further the N_2 adsorption - desorption isotherms confirmed the porous nature of the material. The electrochemical test by cyclic voltammogram shows better electrochemical performance which proves its application in energy storage systems.

Keywords: Tin Oxide, Cyclic Voltammogram, Surface Area

I INTRODUCTION

Tin Dioxide or Tin oxide (SnO_2), an important n-type semiconductor with a wide band gap (Eg=3.6 eV) exhibits excellent physical, chemical, electrical, optical and high thermal stability both in bulk form and at the nano scale. It crystallizes with the rutile structure wherein Tin atoms are six coordinate and the Oxygen atoms three coordinate and its space group is $P4_2/mnm$. SnO_2 has been extensively studied for transparent conductive electrodes [7], anodes for lithium ion batteries [2], dye-sensitized solar cells [8] and chemical gas sensors [1]. Currently various research works have been focused on to enhance the properties of SnO_2 by adding suitable atoms. For example, Tan Rui-Qin et al reported Pd doped SnO_2 to promote its gas sensing property [9]. X.M Lu et al reported Ti doped SnO_2 to improve its conducting property [10]. N.Kumari et al studied the enhancement of optical conductivity in SnO_2 when it is doped with Al [11]. Accarat Chaoumead studied the electrochemical characteristics of SnO_2 doped with Indium [12]. Among these doping systems Antimony-doped Tin dioxide (ATO) has gained immense interest owing to its potential application such as Lithium ion battery [14], gas sensor, humidity sensor, transparent electrode, electricity conducting coating and so on. During the past decade, much attention has been paid on the synthesis of porous structured materials, since materials of this type exhibit unique physical and chemical properties. In particular, porous nanostructures have additional advantages in enhancing the response of various gas sensors due to their high surface area and high pore volume [14]. A variety of techniques have been reported to synthesize porous tin oxide materials, such as hard templating [3], soft templating, hydrothermal [5], sol-gel [3], microwave assisted [13] etc.,

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This paper reports the synthesis of antimony (Sb) substituted SnO_2 (ATO) nanoparticles (Sb = 1,3,5 wt%) by simple co-precipitation method. The cost effectiveness, small crystalline size, high purity and short preparation time make this synthesis technique more preferred compared to other preparation techniques. The synthesized particles were characterized by several techniques such as XRD, FESEM, FTIR, BET (Brauener-Emmett-Teller) surface area and BJH (Barrett-Joyner-Halenda) pore size distribution. The cyclic voltammetry behavior of the as prepared ATO nanoparticles was also measured.

II EXPERIMENTAL

ATO nanoparticles were synthesized using AR grade chemicals. $SnCl_4$ $5H_2O$ (98% Sigma Aldrich) was used as the source of tin and $SbCl_3$ as the source of antimony (1,3,5 wt%). Stoichiometric amounts of $SnCl_4$ $5H_2O$ and $SbCl_3$ were dissolved in water: ethanol (1:1 wt/wt) solvent. Few drops of hydrochloric acid were added under stirring followed by NH_4OH until the pH of 4 was reached. The precipitate was then washed with water and ethanol to remove the Cl- ions. Then the product was initially dried at 80^0C and then annealed at 600^0C for 2 hours. As per the literature reports [3] annealing changed the color of the product from yellow to blue and became darker as the dopant proportionately was increased.

III RESULTS AND DISCUSSION

3.1 X-Ray Diffraction

The powder XRD patterns of the as synthesized ATO nanoparticles are shown in Figure 1. The diffraction peaks are in good agreement with those of the tetragonal phase tin dioxide. The peaks obtained are found to be in good agreement with the standard data (JCPDS card no:41 - 1445, space group $P4_2/mnm$, a0 = 4.738Å, c0=3.187Å). The spectra clearly show only the peaks related with SnO_2 which indicates that all the doped antimony atoms are successfully incorporated into the crystal lattice. The peaks become broader as the doping was proportionally increased thereby indicating a corresponding decrease in the grain size. The average crystallite size of the particles is tabulated in Table 1. and were calculated using Scherrer's equation for the plane (110) using the Full Width Half Maximum (FWHM). The corresponding lattice parameters were calculated using the XRDA software which are slightly different from standard values of Tin Oxide due to the incorporation of Sb ions [6]. Indeed, the ionic radii of Sn^{4+}, Sb^{3+} and Sb^{5+} are 0.72 Å, 0.90 Å, and 0.62 Å respectively. Therefore, it is expected if the Sb^{5+} ions were substituted for Sn^{4+} the lattice parameter decreases, since the ionic radii of Sb^{5+} ions are smaller than those of Sn^{4+}. On the other hand, if Sb^{3+} ions were substituted, an increase in the lattice parameter can be expected owing to the ionic radii of Sb^{3+} being larger than Sn^{4+} ions [6].

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Table 1.

Samples	Crystallite size (nm)	a (Å)	c (Å)	u=c/a
ATO 1wt%	28	4.7300±0.0022	3.1801±0.0021	0.6723±0.0005
ATO 3wt%	21	4.7269±0.0053	3.1788±0.005	0.6724±0.0012
ATO 5wt%	17	4.7046±0.0068	3.1759±0.006	0.6750±0.0013

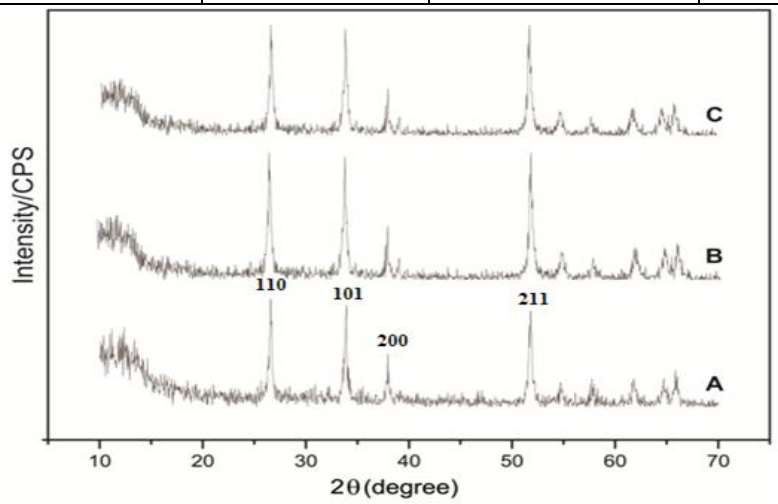

Figure 1. XRD spectra of Sb SnO_2 nanoparticles (A=1%, B=3%, C=5%)

3.2 FTIR Studies

FTIR spectroscopic measurements were performed for all the samples and are shown in Figure 2. Minimum transmittance in the wavelength range of 3400 - 3700 cm^{-1} is related to the OH stretching modes of the water molecule absorbed. The main IR features include resonances at 537 cm^{-1}, 532 cm^{-1} and 482 cm^{-1} were attributed to Sn-O stretching modes of Sn-O-Sn. The remaining low signals could be attributed to some OH groups at the surface probably due to the re-absorption of water from the ambient atmosphere.

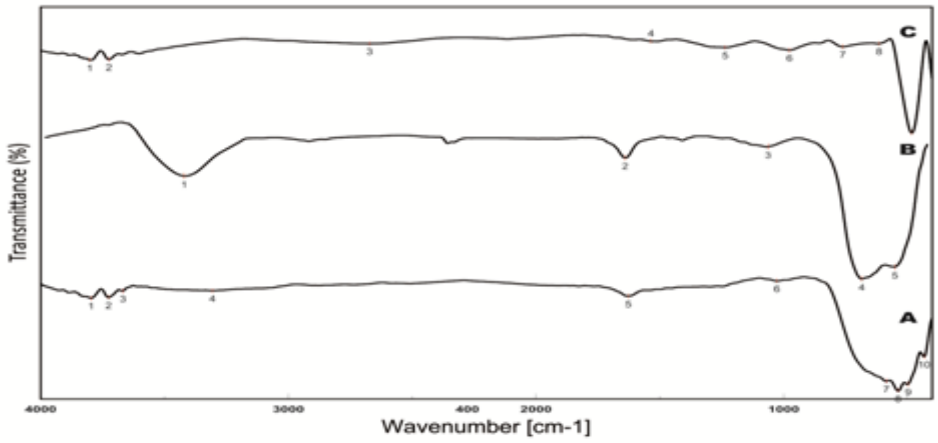

Figure 2. FTIR spectra of Sb doped SnO_2 (A=1%, B=3%, C=5%)

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3.3 Morphological study: FESEM

The surface morphology of ATO nanoparticles are shown in Figure 3. The micrographs clearly indicate spherically shaped particles with little agglomeration. The agglomeration effect depends on the size of the particles. The grain size calculated from the FESEM images are consistent with the crystallite size obtained from the XRD measurements. As the particle size moves into the nano regime, an increase in agglomeration can be noticed. The elemental composition of the synthesized samples was confirmed using the EDAX spectra shown in Figure 4. The spectra did not detect any appreciable impurities thus confirming the complete removal of ammonia and chlorine.

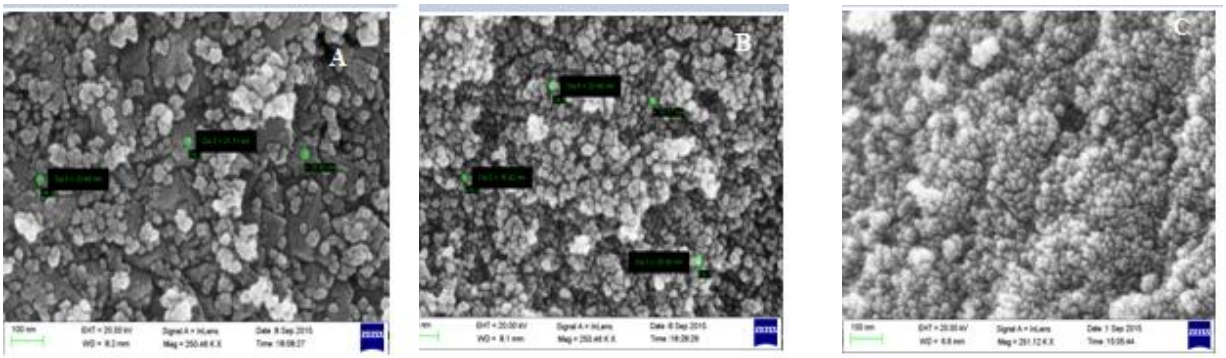

Figure 3. FESEM images of ATO nanoparticles

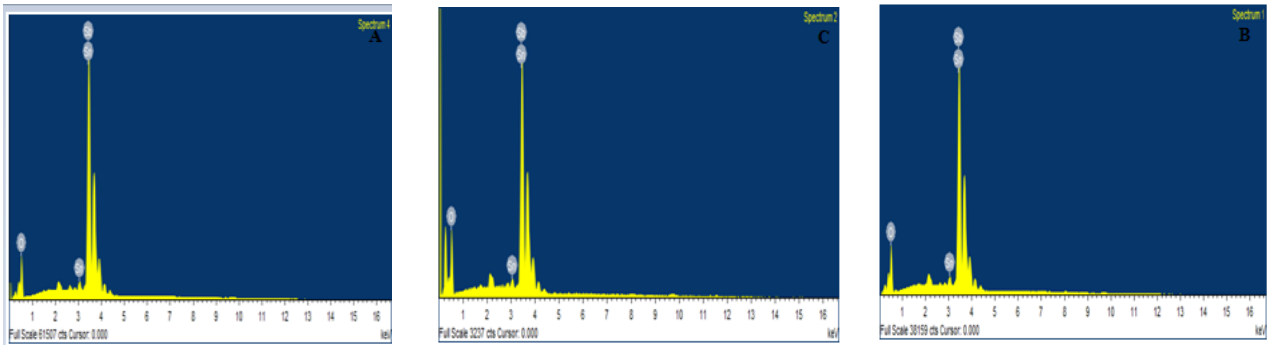

Figure 4. EDAX patterns of Antimony doped SnO_2 particles

3.4 BET and BJH analysis

The porous structure was characterized by N_2 adsorption-desorption isotherm and are presented in Figure 5 and the parameters are summarized in Table 2. The graph clearly shows the gradual increase in N_2 adsorption as the pressure was relatively increased and then decreased, leaving a large hysteresis loop which can be attributed to type IV according to ICPAC. The mesoporous nature of the synthesized materials was hence established. The hysteresis loop observed in the plot is associated with the filling and emptying of mesopores (pores of diameter 2- 50 nm) by capillary condensation. Closure of the loop at P/P_0 (relative pressure) of 0.6 - 1 indicates the presence of very small pores. Pore size distribution was then determined by Barrett-Joyner-Halenda (BJH)

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method (inset of Figure 5) and the pores of average size 2 - 20 nm are dominant in all the resultant product. Thus proved, the method is effective in preparing mesoporous ATO nanoparticle. The specific surface area of Antimony substituted SnO_2 particle of 5 wt% was evaluated to be 38 m^2/g. This high surface area and mesoporous nature is expected to be highly beneficial for absorbing gas molecules [11,15].

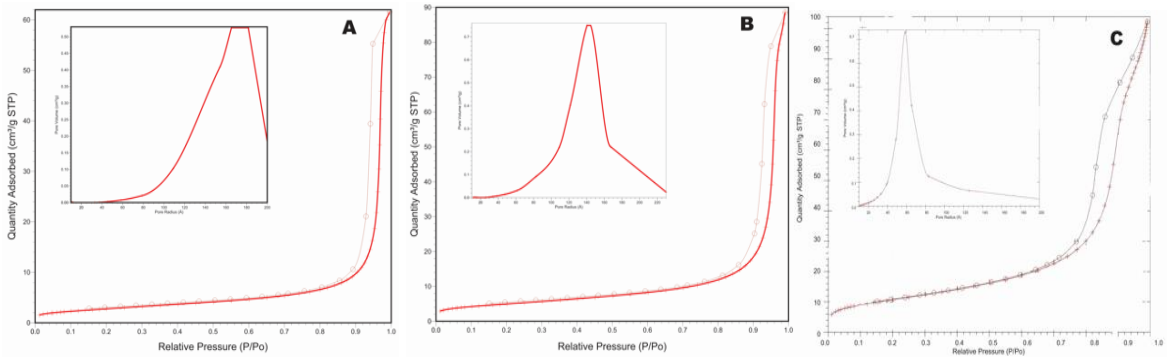

Figure 5. Nitrogen Adsorption - Desorption Isotherms (Inset Shows The BJH Plot)

Table 2

Samples	BET Surface Area (m2/g)	BJH Pore Size (nm)	BJH Pore Volume (cm^3/g)	Crystallite Size(nm) (from XRD)
ATO -1 wt%	10	14.2	0.095	28
ATO - 3wt%	17	12.5	0.136	21
ATO - 5wt%	38	6.2	0.158	17

3.5 Electrochemical Characterization

The electrochemical behavior of the synthesized ATO particles was characterized by cyclic voltammograms and are shown in Figure 6. A three electrode system, ATO (1,3,5%) as working electrode, glassy carbon as reference electrode and platinum wire as counter electrode with H_2SO_4 as the electrolyte were used. The cyclic voltammetry curves were scanned from -1.3V to 1.3V at a scan rate of 10 mV/s.

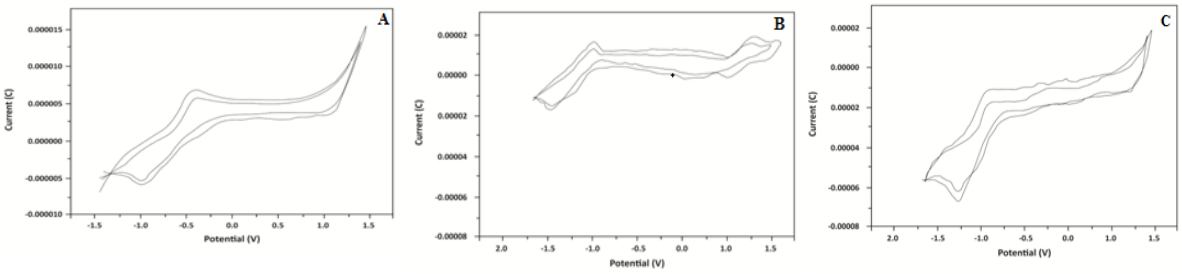

Figure 6. Cyclic voltammogram of ATO nanoparticles at the scan rate of 10mv/s for the first two cycles

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All the three curves showed a pair of redox peaks corresponding to oxidation and reduction process. The cathodic peaks occur at -1.0 V corresponds the reduction and the anodic peaks occur at -1.25V corresponds to oxidation was obtained in all the three graphs. The observed values are comparable with the previous reported values synthesized by other methods [14]. In addition, the peak features and the area of the CV curve in the two cycles remain the same, indicating better electrochemical reversibility of the material.

IV CONCLUSION

Nano sized antimony tin oxide ranging from 17-28 nm were successfully synthesized via chemical precipitation method for the different wt% of antimony. Surface area and the porosity studies confirmed the mesoporous nature of the host material and the maximum surface area was observed in 5% doping of antimony. The structural investigation carried out using the X-ray Diffraction technique indicated the tetragonal rutile phase of the as prepared sample. It is noteworthy to mention that the gradual increase in antimony content showed a decrease in particle size and a corresponding increase in surface area. Cyclic voltammograms measurements indicate that the electrochemical reaction of ATO was a reversible redox reaction with good reversibility and hence makes it a promising material for energy storage applications.

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