Study of Structural and Optical Properties of $\text{Fe}^{2+}$ Doped Tin Oxide Nanoparticles

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Abstract: Tin dioxide nanoparticles ($\text{SnO}_2$) were synthesized by a sol-gel method. And tin tetra chloride ($\text{SnCl}_4$) and ammonium hydroxide ($\text{NH}_4\text{OH}$) were used as the precursor. $\text{NH}_4\text{OH}$ maintain the homogeneity and stoichiometry of solution through pH. The obtained powder subjected to calcination about $110^\circ\text{C}$. The obtained samples are characterized by X-ray diffraction, Scanning electron microscope, Fourier transform infrared spectroscopy and UV-Visible spectroscopy. From the characterizations it is confirmed that the tetragonal structure and the particles are small and nanosizes, The O-H stretching and C=C bending stretching with chemical compositions are analyzed. The improved conduction properties through lower bandgap and the results are further interpreted and discussed.

Keywords: Tin oxide; $\text{Fe}^{2+}$; Sol-gel techniques; Electrical; Optical.

1. Introduction

In recent years the need of semiconductor are very important for functional and active devices. The active devices such as diode, triode and thin film for mass saving purpose are the demand in few decades. Tin oxide semiconductor possess the transparent, highly stable even upto $500^\circ\text{C}$ in air, physical, chemical and good absorber etc., $\text{SnO}_2$ is an IV-VI groups of semiconductor with n-type, the range of band gap from 3.6 to 3.8 eV [1-3]. It is a potential candidate for gas sensing materials such as CO and $\text{O}_2$ for better environment. For this low bandgap and active nature, it can be widely used in many active materials such as semiconductor devices, electrochemical devices such capacitors, condenser, charge storage devices such as batteries and it act as better catalysis rather than other metal oxides [4-6]. It is an ideal candidate used for oxidizing agent for CO, propane, and sometimes used as oxidation reduction in NO, NO$_2$ to N$_2$, esterification, hydrogenation and etc., it is a good catalyst especially for organic compounds [7-9].

Materials ($\text{SnO}_2$) with large surface area lead to large number of contacts with active groups, and they have large chance to produce various active groups CTAB, AOT and etc. The researcher encounter a problem with removal of surfactant from the sample, ie sample free from surfactant, goods and products. $\text{SnO}_2$ can be synthesized by many methods such as combustion, co-precipitations, sol-gel techniques, slow-evaporation, hydrothermal, polymerization and precipitations and etc [10-12].

In this present work the authors adopted a sol-gel method for control over particle size, uniformity, pure and cost effective for synthesis $\text{SnO}_2$ with $\text{Fe}^{2+}$ dopant.

2. Sample preparations

The mixture of tin-tetrachloride-pentahydrate and ammonia water of their purity is 99%. In order to maintain the tin-oxide nanoparticles through $\text{NaOH}$, and from their pH through maintain homogeneity and stoichiometry of the solutions. Initially 2.94 g of tin tetrachloride was added to 50 ml water stirring and added with Ferrous oxide is added to the above mixture and again stirred till its forms the clear solution form a gel phase. The surfactant $\text{NaOH}$ is added to the above sol slowly drop wise while stirring about 30 minutes to form a gel. In this process,
the additional ammonia convert tin chloride into tin hydroxide. After thorough washing the precipitation with deionized water removed the other products. Finally the sample collected through the normal procedure [13, 14].

3. Characterization techniques

The structural and phase identifications of a samples analysis through powder X-ray diffraction technique [14]. The surface features and composition analysis carried out through scanning electron microscope [15]. Type of chemicals, stretching and vibration identified through Fourier transform infrared (FTIR) spectroscopy [16, 17]. The optical absorption study performed through UV-Visible absorption spectroscopy [16].

4. Results and discussions

The crystallographic data of SnO$_2$ powders were collected by using XRD data which is shown in Figure.1. From the observation the (hkl) planes depicts the sample is SnO$_2$ with tetragonal structure and it matches well with standard reference (JCPDS card no. 41–1445). The XRD pattern of the sample exhibit the characteristic peak at $2\theta = 26.6^\circ$. The peak at this angle causes more broadened, it meant for nanosized particles. The size of the particles are computed from the XRD observation through the known Scherer formula

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

where, $D$ is the average particle size, $\lambda$ – wavelength of X-ray source, $k$ - constant (0.9) and $\beta$ – full width half maximum (FWHM) in radians for the diffraction angle ($2\theta$). The diffractions angles with hkl values are given in Table.1 is 26.6, 33.8, 37.9, 51.8, 54.7, 61.9, 65.9 and 78.4 with 100, 101, 200, 211, 220, 310, 301 and 321 respectively. The average particle sizes determined at the intense peaks of (110) at 26.6 degree (20). By this sol-gel method the growned particle is 63.68 nm [17].

![Figure 1](https://example.com/figure1.png)

**Figure 1.** X-ray diffraction pattern of Fe doped tin oxide powder prepared by sol-gel method

| Peaks (2θ) | hkl |
|-----------|-----|
| 26.6      | 110 |
| 33.8      | 101 |
| 37.9      | 200 |
| 51.8      | 211 |
| 54.7      | 220 |
| 61.9      | 310 |
| 65.9      | 301 |
| 78.4      | 321 |

The SEM micrographs of SnO$_2$ nanoparticles at various magnifications are shown in Fig. 2. (a) and (b) of 500nm and 2µm magnification respectively. From the figures it can be observed that the particles are fine, finer and forms large clusters. The mean size of particles from this SEM analysis 69 nm, and it is slightly greater than XRD analysis [12]. These marginal changes in sizes may due to different shape of molecules and texture. Even though, both these experimental observations confirmed that the synthesized particles are in nano phase.
The FTIR spectrum of Fe doped SnO$_2$ nanosized particles in the range of 400-4000 cm$^{-1}$, are shown in Figure 3. From the same Figure 3, the O-H stretching at observed at 3389.86 cm$^{-1}$, aromatic C=C bending stretching at 1631.56 cm$^{-1}$, alkyl methyl at 1400.75 cm$^{-1}$, alkenes at 899.69 cm$^{-1}$, chloroalkanes at 561.61 cm$^{-1}$, and Iodoalkanes at 482.16 cm$^{-1}$ and 428.20 cm$^{-1}$ wavelengths. These characteristics absorption peaks and their functional groups also presented in Table 2.

![Figure 2. SEM image of Fe doped SnO$_2$ sample for (a) (500 nm) and (b) (2 µm).](image)

![Figure 3. FTIR Spectra of Fe doped SnO$_2$ nanoparticles.](image)

| Name          | Functional group          | Adsorption |
|---------------|---------------------------|------------|
| Tin Oxide     | Alcohol/Phenol O-H stretch| 3389.86    |
|               | Aromatic C=C bending      | 1631.56    |
|               | Alkyl methyl              | 1400.75    |
|               | Monosubstituted alkenes   | 899.69     |
|               | Chloroalkanes             | 561.61     |
|               | Iodoalkanes               | 482.16     |
|               | Iodoalkanes               | 428.20     |

The size of particles such as spherical and different sizes like clusters are may be influenced the additional parameters of IR bands, the position, and their relative intensity. Ie, different size of particle is due to different nature of agglomeration [11, 15].
UV-Visible absorption spectra are recorded in the range of 200 nm to 600 nm is shown in Figure 4. The estimation of bandgap values for pure SnO2 is 4.1 eV, but for doped with Fe ions the bandgap values is 3.87 eV. So, the decreasing band gap value is due to the more accumulation of donor energy levels of TM ions by Fe than the band gap of Sn. And this is evident that the Fe ions enhancing the conduction behavior and also having more absorption further indicating the more optical response [16-17].

5. Conclusions

Fe doped SnO2 nanoparticles were synthesized by using sol-gel method. The tetragonal structure identified through XRD analysis. From Scherrer method using XRD datas and the SEM micrographs confirmed the particles are in nanophase. The FTIR spectra of SnO2 show different peaks at different wave number. The presence of Fe ions enhancing the optical behavior and decreasing band gap is suitable for functional/active devices.

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6. References

[1] F. Gu, S. F. Wang, M. K. Lu1, G. J. Zhou, D. Xu, and D. R. Yuan. Photoluminescence Properties of SnO2 Nanoparticles Synthesized by Sol–Gel Method. J. Phys. Chem. B. 2004;108: 8119-8123.
[2] I. A. Rahman,; P. Vejayakumaran, C. S. Sipaut, J. Ismail, M. Abu Bakar, R. Adnan, C.K. Chee. Effect of anion electrolytes on the formation of silica nanoparticles via the sol–gel process. Ceram. Int. 2006;32:691-699.
[3] Y. Ren, G. Zhao, Y. Chen. Fabrication of textured SnO : F thin films by spray pyrolysis. Appl. Surf. Sci. 2011;258:914–918.
[4] David D. Awschalom and Michael E. Flatté. Challenges for semiconductor spintronics. Nat. Phys. 2007;3: 153.
[5] J. Robertson. Electronic structure of SnO2, GeO2, PbO2, TeO2, and MgF2. J Phys C: Solid State Physics. 1979;12: 4767-4777.
[6] Takahiro Ohno, Toshio Kawahara, Hidekazu Tanaka, Tomoji Kawai, Masaoki Oku, Koichi Okada and Shigemi Kohiki. Ferromagnetism in Transparent Thin Films of Fe-Doped Indium Tin Oxide. *Jpn. J. Appl. Phys.* 2006;45(2): 33-36.
[7] Y. Ziad, Banyamin, Peter J. Kelly, Glen West and Jeffery Boardman. Electrical and Optical Properties of Fluorine Doped Tin Oxide Thin Films Prepared by Magnetron Sputtering. Coatings. 2014: 732-746.
[8] S. Fujihara, T. Maeda, H. Ohgi, E. Hosono, H. Imai, S.-H. Kim. Hydrothermal Routes to Prepare Nanocrystalline Mesoporous SnO2 Having High Thermal Stability. J Chem. Soc. 2004;20: 6476-6481.
[9] H. Kim, R.C.Y. Auyeung, A. Piqué. Transparent conducting F-doped SnO2 thin films grown by pulsed laser deposition. Thin Solid Films. 2008;516: 5052–5056.
[10] P.M. Gorley, V.V. Khomyak, S.V.Bilichuk, I.G.Oreitsky, P.P. Horley, V.O. Grechko. SnO2 films: formation, electrical and optical properties. Mater. Sci. Eng. B. 2005;118: 160–163.
[11] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. V. Molnar, M. L. Roukes, A. Y. Chichelow, J. N. Daughton, S. V. Molnar, M. L. Roukes, A. Y. Chichelonova and D. M. Treger. Spintronics: a spin-based electronics vision for the future. Science. 2001;294:1488-1495.

[12] K. Anandan, S. Gnanam, J. Gajendiran, and V. Rajendran. Size controlled synthesis of SnO2 nanoparticles: facile solvothermal process. J Non-oxide Glasses. 2010;2: 83-89.

[13] H. Rath, P. Das, T. Som, P.V. Satyam, U. P. Singh, P. K. Kularia, D. Kanjilal, D. K. Avasthi, and N. C. Mishra. Structural evolution of TiO2 nanocrystalline thin films by thermal annealing and swift heavy ion irradiation. J. Apl. Phys. 2009;105 (7): 074311.

[14] D.S. Koktysh, J.R. McBride and S.J. Rosenthal. Synthesis of SnS nanocrystals by the solvothermal decomposition of a single source precursor. Nanoscale Res. Lett. 2007;2:144-148.

[15] E. Elangovan, M.P. Singh, K. Ramamurthi. Studies on structural and electrical properties of spray deposited SnO2:F thin films as a function of film thickness. Mater. Sci. Eng. B. 2004;113:143–148.

[16] A. Punnoose, J. Hays, A. Thurber, M. H. Engelhard, R. K. Kukkadapu, C. Wang, V. Shutterthandann, and S. Thevuthasan. Development of high-temperature ferromagnetism in SnO2 and paramagnetism in SnO by Fe doping. Phys. Rev. B. 2005; 72 (5): 054402.

[17] C. Ming Wang, J. Feng Wang, W. Bin Su. Microstructural Morphology and Electrical Properties of Copper- and Niobium-Doped Tin Dioxide Polycrystalline Varistors. J Amer Cera Soc. 2006;89 (8):2502–2508.

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