Study of structural and optical properties of SnO$_2$ nanoparticles developed by sol-gel route

Vijay Garg*, **Harsh Sharma**

Department of Physics, Multanimal Modi College, Modinagar-201204 (U.P.) India
Corresponding Author. E-mail:drvgarg78@gmail.com

ABSTRACT

In this work, SnO$_2$ nanoparticles calcinated at 500 ºC were prepared by the sol-gel route. The structural and optical properties of the prepared sample were studied by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive x-ray spectroscopy (EDX), UV-Visible spectroscopy, Photoluminescence spectra (PL) and Fourier transformed infrared spectrum (FTIR). The XRD reveals the rutile tetragonal structure of the prepared sample. The mean crystallites size of developed SnO$_2$ nanoparticles was found to be 35.74 nm. The fine arrangement of spherical, circular grains along with some nanostructures obtained, and it is well supported by SEM images. The EDX spectra support the existence of the tin and oxygen elements. The 55% transmission was confirmed by UV-Visible spectroscopy. PL spectra confirmed the presence of one strong peak. FTIR confirms the presence of chemical bonding and functional groups.

Keywords: SnO$_2$, nanoparticles, sol-gel.

INTRODUCTION

The nano scale size of particles, particularly of oxide materials (TiO$_2$, SnO$_2$, ZnO etc.) has made the field of material science more applied and fascinating area of research due to their versatile applications such as optoelectronics, lithium battery technologies, photo-solar cell and so on. Researchers have noted so many peculiar properties of these metal oxide nanoparticles (below 100 nm) to those bulky materials. Out of these metallic oxide nanoparticles SnO$_2$ nanoparticles offer a wide range of applications in photo catalysis materials [1], transparent conducting electrodes & transistors [2], lithium-ion batteries [3], dye-sensitized solar cells i.e., DSSCs [4] and gas sensors [5] because of its good electron mobility, optical, gas-sensing and electrochemical properties [6].

The technological interest of tin oxide for electrodes of the solar cell, gas sensors, transparent conducting electrodes, and catalyst supports arise because of its fine chemical and mechanical stability [7]. Generally tin oxide is found in two states stannic (SnO$_2$; Sn has valency equal to +4) and stannous (SnO; Sn has valency equal to +2) with the rare existence of two other forms such as Sn$_3$O$_4$ and Sn$_2$O$_3$. SnO behaves like an insulator in the visible spectrum while SnO$_2$ used as a transparent conductor due to

its low resistivity and good optical transparency. At room temperature the energy band gap (E_g) of SnO (p-type) lies between 2.2 and 3.0 eV and for n-type SnO_2 it is equal to 3.5 eV [7-8].

Various synthesis methods are used by different researchers for preparing SnO_2 nanoparticles, which includes chemical vapour deposition, sono-chemical method, thermal evaporation, dc-plasma reaction, sol-gel, molecular beam epitaxy, sputtering, spray pyrolysis, and solution-derived synthesis [9-16].

Li et al., [17] obtained tin oxide (SnO_2) nanocrystals by two-step solid-state reactions. These nanocrystals have an irregular ball shape with grain size equal to 20 nm, and they can be used as selective gas-sensing materials to EtOH. Sun et al., [18] developed SnO_2 nanorods by the oriented accumulation of single SnO nanoparticles via solid state reaction method.

Aziz et al., [19] synthesized SnO_2 nanoparticle in the range of 22–31 nm size via a sol-gel method by using polyethylene glycol at calcination temperature of 450 ^{0}C and found that the average particle size increases with the rise of the calcination temperature. By employing same sol-gel route Gnanam and Rajendran [20] fabricated tin oxide (SnO_2) nanoparticles with crystal sizes 3.9, 4.5 & 5 nm by the reaction of $SnCl_4.5H_2O$ in water, ethanol and methanol, and they revealed that the solvents played crucial role in the crystallite size effect of nano-crystalline SnO_2.

The sol-gel method has been chosen in current work for the development of SnO_2 nanoparticles over the other methods because of various advantages like: lower processing temperature, good similitude, regulated stoichiometry, cost effectiveness, and flexibility of forming nanoparticles.

EXPERIMENTAL METHOD

Sol-gel route for the formation of SnO$_2$ nanoparticles

The standard sol-gel route was used for the development of tin oxide nanoparticles. The tin (II) chloride dehydrates, ethylene glycol and mono ethanol amine (all of AR grades) were used for

the synthesis of SnO_2 nanoparticles. Initially, 10 gm of tin (II) chloride dehydrate was dissolved in 15 ml of ethylene glycol with the constant stirring and after 1 hour, 10 ml of monoethanolamine was added drop by drop in the solution with constant stirring. The crystal clear solution was got after 1 hour of the constant stirring. The final solution was then heated at 120 ⁰C on a magnetic stirrer for 8 hrs. After 8 hrs, a crystal clear gel was formed and then gel left for 30 minutes. After 30 minutes, the final gel was calcinated at 500 ⁰C for 3 hrs. After 3 hrs of calcination, final nano sized tin oxide powder was formed which is further used for different characterization tools to analyze its structural and optical properties.

Characterizations

The structural properties of the synthesized sample were studied in scanning range of 2θ from 20 ºC to 70 ºC by X-ray diffractometer (Rigaku ULTIMA-IV). The SEM, Model: Zeiss EVOMA and EDAX Model: Oxford INCA 250 was used for the study of surface morphology and elemental composition of prepared tin oxide nanoparticles. The optical transmission spectra of the prepared sample was analyzed by U-3900, Model No. 2116-010 in the wavelength range 300-800 nm and luminescence property was studied by Edinberg Luminescence Spectrophotometer. Perkin Elmer, spectrum two models were used for the study of FTIR of the prepared sample (wave number range from 4000 cm^{-1} to 400 cm^{-1}).

RESULTS AND DISCUSSION

X-ray diffraction (XRD)

The phase analysis of prepared tin oxide nanoparticles was analyzed by X-ray diffraction technique. Fig. 1 depicts the x-ray diffraction for the prepared sample.
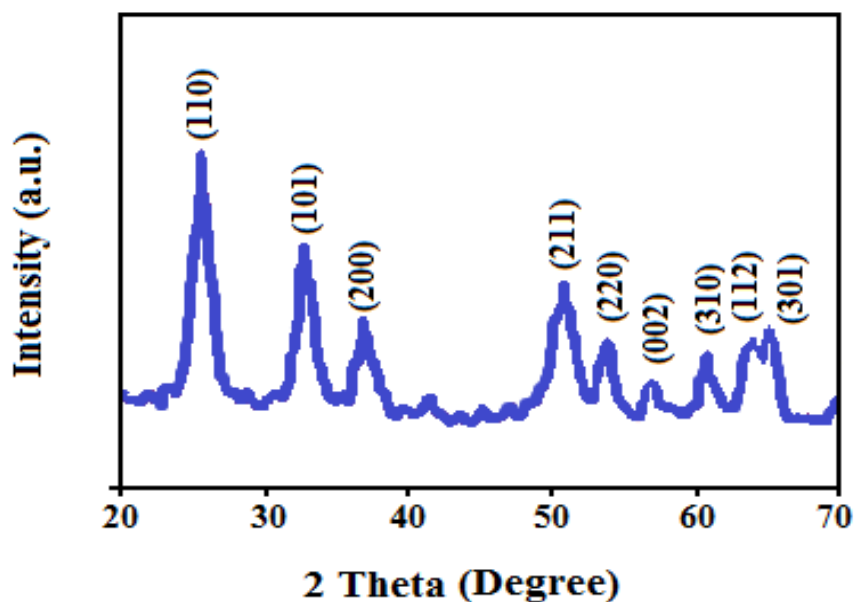

Figure.1 X-ray diffraction of SnO₂ nanoparticles prepared by sol-gel route

The rutile tetragonal structure of tin oxide nanoparticles was supported by x-ray pattern and it is well matched with JCPDS card no. 41-1445 [21]. Many peaks are observed along (110), (101), (200), (211), (220), (002), (310), (112) and (301) planes. The high intensity peak is observed along the plane (110). The mean crystallites size of the prepared tin oxide nanoparticles was measured by Scherrer's relation [22].

$$D = \frac{0.9\lambda}{\beta \, Cos\theta}$$

(1)

Where λ is the wavelength (A°) used in x-ray diffractometer, β is the full angular width at half maximum in radians (FWHM), D is the average crystallites size and θ is the diffraction angle which is calculated from Bragg's equation as [23]:

$$2d\sin\theta = n\lambda \tag{2}$$

Where d is defined as the interplanar distance (n=1) and it is calculated from the equation as [23]:

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

Where h, k, l are the lattice plane index, (a) and (c) are lattice constants. The calculated structural parameters for prepared tin oxide nanoparticles are as follows: Lattice constants (a=b) = 4.7412 A° and c = 3.1901A°, average

crystallites size (D nm) = 35.74 nm, average interplanar distance = 1.8237A°.

Scanning electron microscopy (SEM)

To examine the morphology of tin oxide nanoparticles we have used scanning electron microscopy. Fig. 2 depicts the presence of spherical, circular grains along with some nanostructures.
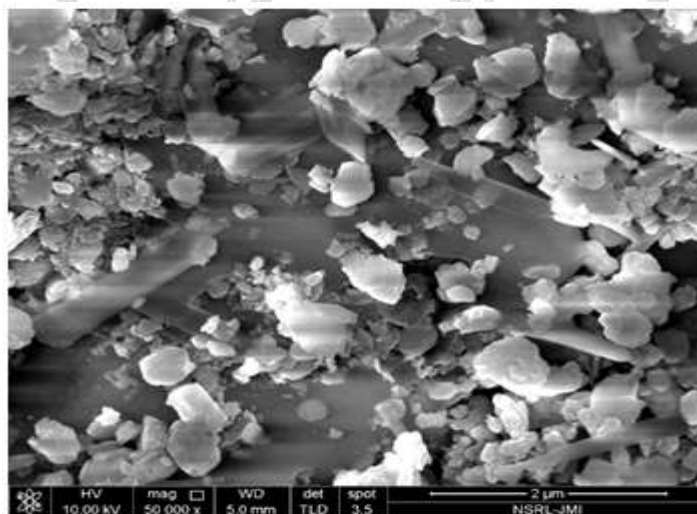

Figure. 2 SEM image of SnO₂ nanoparticles prepared by sol-gel route

But there is some non-uniformity in the shape of developed nanostructure and the porosity also exists. Agglomeration of some spherical grains is also observed because of low calcination temperature.

Energy dispersive x-ray spectroscopy (EDX)

The chemical characterization of the prepared sample of tin oxide nanoparticles is inspected by EDX spectrum. The EDX image of the prepared sample is shown in Fig. 3. The existence of the tin and oxygen elements is confirmed by EDX spectrum. The oxygen component (atomic percentage) in the developed sample is found to be almost double that of tin, hence confirming the chemical composition to be SnO_2.
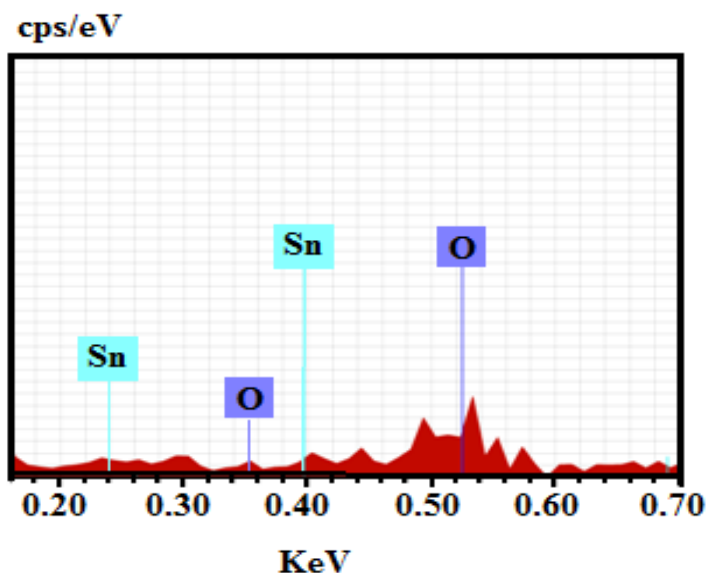
Figure. 3 EDX spectrum of SnO₂ nanoparticles prepared by sol-gel route

Optical properties

The transmittance spectrum of prepared tin oxide nanoparticles is plotted in the wavelength (λ) range from 300 nm to 800 nm as shown in Fig.4. The optical band gap of prepared tin oxide nanoparticles is calculated from the transmission spectrum. The transparency of the prepared sample was found to be 55%, which lies in the visible range. Suresh et al. reported the transmission of 57% for SnO_2 nanoparticles developed by a co-precipitation technique [24]. The well-known and most used relation by different researchers which is known as Tauc's relation is applied for measuring the band gap (E_g) [23].

$$\alpha h\nu = A(h\nu - E_g)^n$$

$$\text{(4)}$$

Where α is the absorption coefficient, A is constant which is energy independent, n is a constant & its value depends upon the type of transition and E_g is the energy band gap of the sample.
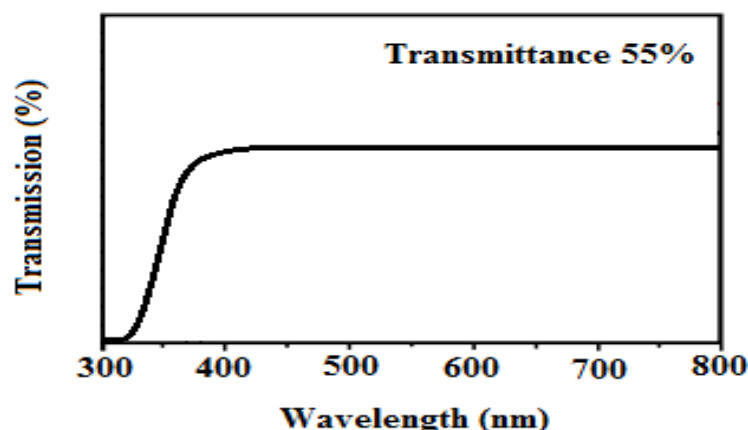
Figure. 4 UV-Visible transmission spectrum of SnO₂ nanoparticles prepared by sol-gel route

The optical band gap of the developed sample is calculated from the extrapolation of plot between $(\alpha h\nu)^2$ (a.u) and $h\nu$ (eV). The Tauc's plot of the prepared sample is depicted in Fig. 5. The optical band gap (E_g) for the developed tin oxide nanoparticle is found to be 3.26 eV.
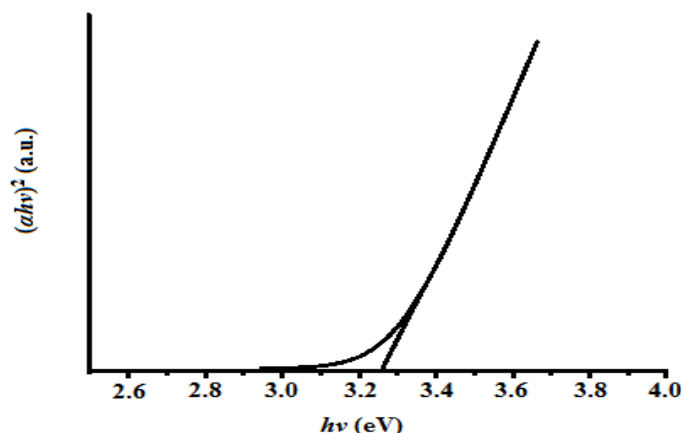

Figure. 5 Tauc's plot for SnO₂ nanoparticles prepared by sol-gel route

Photoluminescence (PL) analysis

It is a good technique to analyze the optical properties and crystalline quality of the prepared sample. The photoluminescence spectra for tin oxide nanoparticles are shown in the Fig. 6 at an excitation wavelength of 280 nm. The photoluminescence spectra show one strong peak at 501 nm. The visible state emission at 501 nm arises due to the reunion of electron-hole pairs from localized states [25].
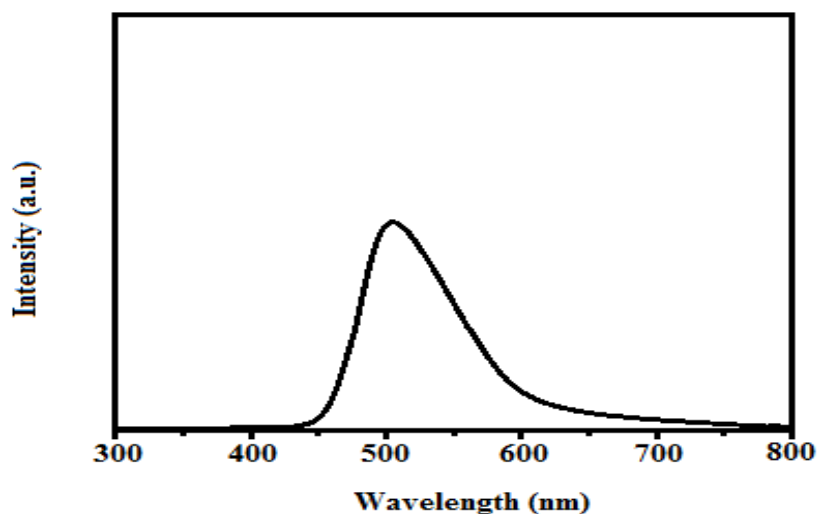
Figure. 6 PL spectra for tin oxide nanoparticle prepared by sol-gel route

Fourier transformed infrared spectrum (FTIR) analysis

To study the chemical bond nature and structure in prepared tin oxide nanoparticles we used the FTIR technique. Fig. 7 depicts the FTIR spectrum reported in the wave number range 4000 - 400 cm^{-1}. It exhibits the H-O-H band at 1628.50 cm^{-1} which is related to the water molecule presents in the surrounding. The absorption peak detected at 623.11 cm^{-1} corresponds to the stretching vibration of O-Sn-O band [26]. Hence, a preparation tin oxide nanoparticle is further confirmed by FTIR analysis.
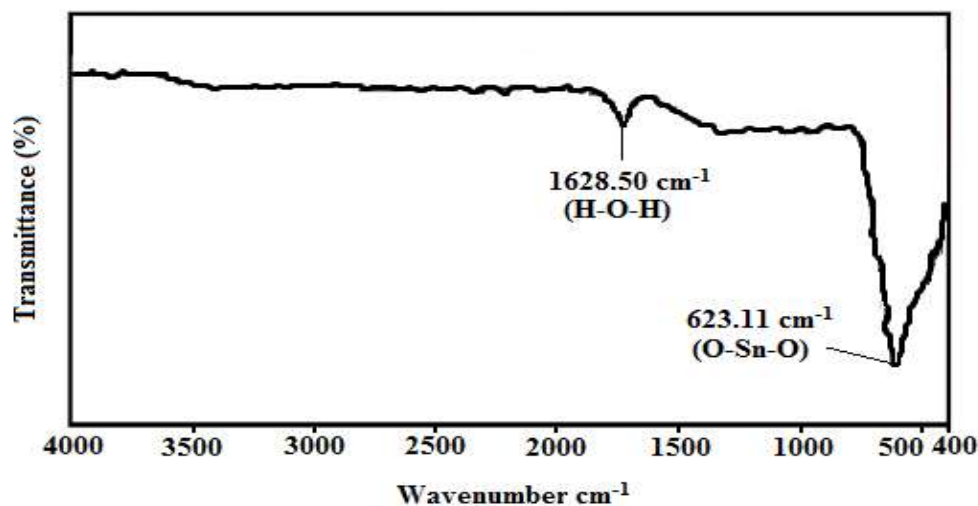

Figure. 7 FTIR spectrum of SnO$_2$ nanoparticles prepared by sol-gel route

CONCLUSION

Tin oxide nanoparticles were developed by sol-gel route at 500 ºC calcination temperature. The x-ray diffraction pattern reveals the rutile tetragonal structure for the prepared tin oxide nanoparticles. Agglomeration of some grains was observed in the SEM image due to good crystallinity of prepared sample. The energy band gap of tin oxide nanoparticles was found to be 3.26 eV. The photoluminescence emission spectra of tin oxide nanoparticles exhibit emission at 501 nm. FTIR spectra support the production of tin oxide nanoparticles.

ACKNOWLEDGMENT

REFERENCES

1. M. Aslam, M. Tariq Qamar, Shahid Ali, Ateeq Ur Rehman, M.T. Soomro, Ikram Ahmed, I.M.I. Ismail, A. Hameed. "Evaluation of SnO_2 for sunlight photocatalytic decontamination of water". Journal of Environmental Management, **217,** 805-814 (2018). doi: 10.1016/j.jenvman.2018.04.042.

2. Xianzhe Liu, Honglong Ning, Weifeng Chen, Zhiqiang Fang, Rihui Yao, Xiaofeng Wang, Yuxi Deng, Weijian Yuan, Weijing Wu, and Junbiao Peng. "Effect of Source / Drain Electrodes on the Electrical Properties of Silicon-Tin Oxide Thin-Film Transistors". Nanomaterials, **8**, 293–300 (2018). doi: 10.3390/nano8050293.

3. Kangning Zhao, Lei Zhang, Rui Xia, Yifan Dong, Wangwang Xu, Chaojiang Niu, Liang He, Mengyu Yan , Longbin Qu, and Liqiang Mai. "SnO 2 Quantum Dots@Graphene Oxide as a High-Rate and Long-Life Anode Material for Lithium-Ion Batteries". Small, **2**, 588–594 (2016). doi: 10.1002/smll.201502183.

4. Anders Hagfeldt, Gerrit Boschloo, Licheng Sun, Lars Kloo, and Henrik Pettersson. "Dye- sensitized solar cells". Chemical Reviews, **110**, 6595–6663 (2010). doi: 10.1021/cr900356p.

5. M. Narjinary, P. Rana, A. Sen and M. Pal. "Enhanced and selective acetone sensing properties of SnO 2 -MWCNT nanocomposites: Promising materials for diabetes sensor". Material Design, **115**, 158–164 (2017). doi: 10.1016/j.matdes.2016.11.042.

6. Min Hu, Zhenwei Zhang, Chenkun Luo and Xiuqing Qiao. "One-pot green synthesis of Ag-corated SnO_2 microsphere: an efficient andreusable catalyst for reduction of 4- nitrophenol". Nanoscale Research Letters, **12 (1)**, 435 (2017). Doi:10.1186/s11671-017-2204-8

7. D. Calestani, M. Zha, A. Zappettini, L. Lazzarini, G. Salviati, L. Zanotti, and G. Sberveglieri. "Structural and optical study of SnO2 nanobelts and nanowires". Materials Science and Engineering C **25**, 625-630 (2005). doi.org/10.1016/j.msec.2005.07.014

8. K. Vijayarangamuthu and S. Rath, **"**Nanoparticle size, oxidation state, and sensing response of tin oxide nanopowders using Raman spectroscopy". Journal of Alloys and Compounds, **610,**706-712 (2014). doi.org/10.1016/j.jallcom.2014.04.187

9. T. Thurn-Albrecht, J. Schotter, C. A. Kastle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen and T. P. Russell. "Ultrahigh-Density Nanowire Arrays Grown in Self-Assembled Diblock Copolymer Templates". Science, **290**, 2126–2129 (2000). DOI: 10.1126/science.290.5499.2126.

10. P. Davide. Cozzoli, Andreas Kornowski and Horst Weller, "Low-Temperature Synthesis of Soluble and Processable Organic-Capped Anatase TiO_2 Nanorods". Journal of the American Chemical Society, 125 (47), 14539–14548 (2003). doi.org/10.1021/ja036505h

11. Dan Li and Younan Xia. "Fabrication of Titania Nanofibers by Electrospinning". Nano Letters, 3 (4), 555–560 (2003).

12. Xiaochen Sun, Hongzhou Zhang, Jun Xu, Qing Zhao, Rongming Wang, Dapeng Yu. **"**Shape controllable synthesis of ZnO nanorod arrays via vapor phase growth**".** Solid State Communications, **129 (12),** 803–807 (2004). doi.org/10.1016/j.ssc.2003.11.051

13. M. Wang, C. H. Ye, Y. Zhang, G. M. Hua, H. X. Wang, M. G. Kong and L. D. Zhang, "Synthesis of well-aligned ZnO nanorod arrays with high optical property via a low-temperature solution method". Journal of Crystal Growth, **291**, 334–339 (2006). doi.10.1016/j.jcrysgro.2006.03.033

14. Cheng-Fang Lin, Chung-Hsin Wu, Zong-Nan Onn. "Degradation of 4-chlorophenol in TiO_2, WO_3, SnO_2, TiO_2 /WO_3 and TiO_2 /SnO_2 systems". Journal of Hazardous Material, **154 (1-3),** 1033–1039 (2008). doi.org/10.1016/j.jhazmat.2007.11.010

15. Ziyong Yu, Shenmin Zhu, Yao Li, Qinglei Liu, Chuanliang Feng, Di Zhang. "Synthesis of SnO2 nanoparticles inside mesoporous carbon via a sonochemical method for highly reversible lithium batteries". Material Letters, **65 (19-20),** 3072–3075 (2011). doi.org/10.1016/j.matlet.2011.06.053

16. Shamima Begum, Th. Babita Devi and M. Ahmaruzzaman. "Surfactant mediated facile fabrication of SnO 2 quantum dots and their degradation behavior of humic acid". Material Letters, **185**, 123–126 (2016). doi.org/10.1016/j.matlet.2016.07.028

17. Feng Li, Liying Chen, Zhiqiang Chen, Jiaqiang Xu, Jianmin Zhu and Xinquan Xin. "Two-step solid-state synthesis of tin oxide and its gas-sensing property". Materials Chemistry & Physics, **73 (2-3),** 335–338 (2002). doi.org/10.1016/S0254-0584(01)00357-1

18. Jin Q. Sun, Ji S. Wang, Xiu C. Wu, Guo S. Zhang, Jun Y. Wei, Shu Q. Zhang, H. Li and Dai R. Chen. "Novel Method for High-Yield Synthesis of Rutile SnO_2 Nanorods by Oriented Aggregation". Crystal Growth & Design, **6(7),** 1584-1587 (2006). doi.org/10.1021/cg050574l

19. Madzlan Aziz, Saad Saber Abbas, Wan Rosemaria Wan Baharom, Wan Zuraidah Wan Mahmud. "Structure of SnO 2 nanoparticles by sol–gel method". Materials Letters, **74**, 62–64 (2012). doi.org/10.1016/j.matlet.2012.01.073

20. S. Gnanam and V. Rajendran. "Synthesis of tin oxide nanoparticles by sol–gel process: effect of solvents on the optical properties". Journal of Sol-Gel Science and Technology, **53**, 555–559 (2010). doi:10.1007/s10971-009-2131-y

21. K. Sujatha, T. Seethalakshmi and O.L. Shanmugasundaram. "Synthesis, Charaterization of nano tin oxide co-precipitatiom method". Nanotechnology Research and Practice, **11(3),** 98-105 (2016). doi: 10.13187/nrp.2016.11.98

22. Suresh Sagadevan and Jiban Podder, "Investigation on structural, surface morphological and dielectric properties of Zn-doped SnO_2 nanoparticles". Material Research, **19(2),** 420-425 (2016). doi: http://dx.doi.org/10.1590/1980-5373-MR-2015-0657

23. K. Sujatha, T. Seethalakshmi, A. P. Sudha, O. L. Shanmugasundaram. "Photocatalytic activity of pure, Zn doped and surfactants assisted Zn doped SnO_2 nanoparticles for degradation of cationic dye". Nano-structures and Nano-objects, **18**, 100305 (2019). doi.org/10.1016/j.nanoso.2019.100305

24. Suresh Gopal, Sathishkumar Rajagemberam, Baskaran Iruson, Sathyaseelan Balaraman, Senthilnathan, Krishnmoorthy, Manikandan Elayaperumal, Study on structural, luminescence properties and Hall effect of SnO_2 nanoparticles obtained by a co-precipitaion technique, International Journal of Nano Dimension, **10(3)** 242-251 (2019).

25. M.V. Arularasu, M. Anbarasu, S. Poovaragan, R. Sundaram, K. Kanimozhi, C. Maria Magdalane, K. Kaviyarasu, F.T. Thema, D. Letsholathebe, Genene T. Mola and M. Maaza, "Structural, optical, morphological and microbial studies on SnO_2 nanoparticles prepared by co-precipitation method". Journal of Nanoscience and nanotechnology, **18 (5)**, 3511-3517 (2018). doi.org/10.1166/jnn.2018.14658

26. Masoud Salavati-Niasari, Noshin Mir, Fatemeh Davar, "Synthesis, characterization and optical properties of tin oxide nanoclusters prepared from a novel precursor via thermal decomposition route". Inorganica Chimica Acta, **363 (8),** 1719-1726 (2010). https://doi.org/10.1016/j.ica.2010.03.024