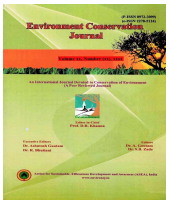
Environment Conservation Journal 24 (3):305--310, 2023

Journal homepage: https://www.environcj.in/

Environment Conservation Journal

ISSN 0972-3099 (Print) 2278-5124 (Online)



Influence of heat treatment on the properties of tin oxide nanoparticles: A potential material for environmental remediation applications

Manmeet Kaur
Department of Physics, MM Engineering College, Maharishi Markandeshwar, Mullana-Ambala, Haryana, India
Dixit Prasher
Department of Physics, MM Engineering College, Maharishi Markandeshwar, Mullana-Ambala, Haryana, India
Ranjana Sharma ✉
Department of Physics, MM Engineering College, Maharishi Markandeshwar, Mullana-Ambala, Haryana, India

ARTICLE INFO

Received : 05 December 2022
Revised : 26 February 2023
Accepted : 20 March 2023

Available online: 27 June 2023

Key Words:
Band gap
EDAX
Metal oxides
SEM
XRD

ABSTRACT

Metal oxides have gained a growing interest in the field of material science owing to their size and shape dependent physiochemical properties. Tin oxide (SnO_2) is considered as a multifaceted material with its widespread applications such as oxidation catalysis, energy harvesting, bio-imaging, gas sensing, storage devices and many more. This study reports the synthesis of SnO_2 nanoparticles derived via sol-gel route. To observe the effect of thermal treatment on the grown material, the samples were subjected to calcination at different temperature ranging from 350 °C to 550 °Cfor about 4 hrs. The structural, compositional, morphological and optical properties of Tin oxide were studied by XRD, EDAX, FESEM, and UV-Vis spectroscopic analysis respectively. The XRD pattern consists only SnO_2 peaks with preferred orientation along (110) plane. The crystallite size increases with higher calcination temperature and is found in the range of 3-15 nm. All the peaks corresponding to SnO_2 matches with the standard data indicating the growth of good quality single phase material. Compositional data reveals that that grown material manifested in required stoichiometric ratio of SnO. Scanning electron micrographs show uniform growth of SnO_2 nanoparticles with particle size ranging from 10-20 nm. The energy band gap of the SnO_2 calculated by optical studies was 3.1eV and 3.0 eV for 450 °Cand 550 °Crespectively. The calculated band gap lies in the visible region of the solar spectrum which could be beneficial for the enhanced photocatalytic performance of the SnO_2 nanoparticles.

Introduction

Metal oxides nanostructures are known for exhibiting unique and excellent physiochemical and optical properties as compared to their bulk counterparts due to their ability to show quantum confinement at nanoscale. Among various literature reported metal oxide semiconductors, particularly, Tin oxide (SnO_2) has gained considerable interest of scientific community due to its multifaceted applications in different sectors such as oxidation catalysis, energy harvesting, sensors and storage devices etc (Kaur *et al.,*2022). SnO_2, being n-type semiconducting oxide known to have wide bandgap energy of nearly 3.4-3.6 eV and also demonstrates strong thermal ability and magnificent transparency in the visible range (Lin *et al.,* 2016). The size dependent properties play a pivotal role in modifying SnO_2 nanostructures performance which provides the pathway for various applications. It is very important to control the particle size during the synthesis process (Mohana Priya *et al.,* 2016) as it directly correlates with the optical band gap which plays a crucial role in the photocatalytic performance of the metal oxides Several wet chemical synthesis route such sol-gel, hydrothermal, co-precipitation, spray pyrolysis and microwave method have been adopted by various

Corresponding author E-mail: *ranjanadixit2417@gmail.com*
Doi: https://doi.org/10.36953/ECJ.16482524

researchers to fabricate SnO_2 nanoparticles with different size and distributions. Among all of them, we employed sol-gel approach owing to its numerous benefits such as room temperature synthesis, cost effectiveness, and it possesses better homogeneity in results. Due to its simplicity and flexible nature nanocomposites can synthesized at an affordable price (Parashar *et al.,* 2020; Pawar *et al.,* 2012). Different operating features for instance reaction time, pH value and concentration of catalysts enhance functionality of synthesized SnO_2 nanoparticles. Also, the precise control on the annealing temperature helps in modifying the structure, morphology and band gap of tin oxide nanoparticles (Habte *et al.,* 2020; Rasheed *et al.,* 2016). Diallo *et al.* (2016) reported the calcination of cassiterite SnO_2 nanoparticles at elevated temperatures from 400 to 900 °C. Nehru *et al.* (2012) reported spherical SnO_2 nanoparticles using precipitation route. They showed that size of crystallite increases with the increment in temperature. It is evidently revealed that the crystallinity, size and phase of synthesized samples can effectively tuned the nanostructures by the process of controlled thermal treatment. In this present research work, efforts have been made to synthesize the SnO_2 nanoparticles via sol-gel approach. The main approach of the work was to study the impact of calcinating temperature on the structure, morphology and optical behavior of the prepared tin oxide nano powder.

Material and Methods

Tin (II) chloride dihydrate ($SnCl_2.2H_2O$), ammonia hydroxide (NH_4OH) and ethanol (C_2H_5OH) were procured from Sigma Aldrich. In this work sol-gel methodology was adopted to synthesize tin oxide (SnO_2) nanoparticles (Patel *et al.,* 2021). Initially, a sol was prepared by taking 0.3M Stannous chloride dihydrate ($SnCl_2.2H_2O$) as a precursor and dissolved completely in ethanol (50ml) subjected to constant stirring. To the stirred solution, freshly prepared ammonia drops (3.0 M) were added to sustain the pH 10.. At room temperature, the obtained gel was allowed to age for 10 hours. The so formed gel was then centrifuged and washed 3-4 times with distilled water to wipe out excess Cl^- ions. A schematic flowchart of the experimental procedure is shown in Figure 1. The structural and morphological analysis of the synthesized material was performed using X-ray diffractometer with Cu Kα-1 radiation (1.5406Å) and scanning electron microscope with EDS respectively. The UV-VIS absorption studies of prepared SnO_2 samples were done using UV-VIS Spectra Max iD3 spectrophotometer in the range 200-800 nm.

The mechanism involved during chemical reaction between $SnCl_2.2H_2O$ and NH_4OH is given below:

$$\mathbf{SnCl_2 \cdot 2H_2O + 2NH_4OH \rightarrow Sn(OH)_2 + 2NH_4CI + 2H_2O}$$

$$\mathbf{Sn(OH)_2 \rightarrow SnO + H_2O}$$

$$\mathbf{SnO + 1/2\ O_2 \rightarrow SnO_2}$$

The overall reaction is:

$$\mathbf{SnCl_2 \cdot 2H_2O + 2NH_4OH + 1/2O_2 \rightarrow SnO_2 + 2NH_4Cl + 3H_2O}$$

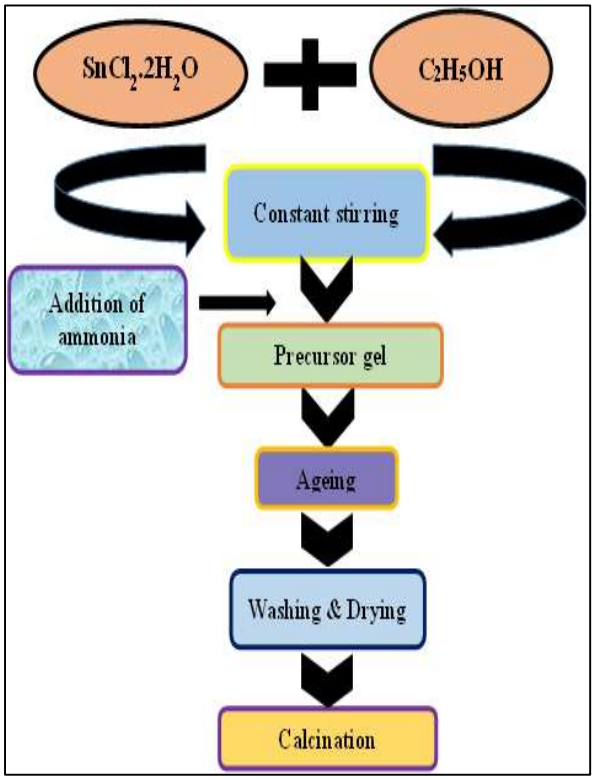


Figure 1: Flowchart of experimental procedure

Results and Discussion

Figure 2 reflects the XRD peaks of the prepared SnO_2 and the observed peaks indicating planes (110), (101), (200), (211), (220), (002), (310), (112), (301), (202), (321) are matched with the JCPDS No: 41-1445, a=4.738Å and c=3.178Å

which confirms the tetragonal rutile structure of the nanoparticles and the diffracted peaks of the prepared samples agrees very well with the lattice parameters. Fig 2 clearly demonstrates a correlation between the calcinating temperature and sharpness, height and narrowness of the emerged XRD predominant peaks revealing the formation of nanocrystallites with elevated temperature. The size of crystallites of SnO_2 particles was derived by applying Debye Scherer formula (Kundu *et al.,* 2013; Gaber *et al.,* 2014):

$$D = 0.94\,\lambda / \beta \cos\theta \quad \text{.....(i)}$$

In equation (i), D is the crystallite size, wavelength of X-rays is 'λ' , β is full width - half maximum (in radian) and θ is the diffracting angle.

The calculated crystallite size was found in the range of 3-15 nm. The results obtained clearly show that the crystallinity of the sample increases on increasing calcination temperature because defect concentration decreases at elevated temperature. Our results corroborated the previous findings reported by the various researchers (Al-Hada, N.M. *et al.,* 2018; Khaenamkaew *et al.,* 2020).The obtained crystallite dimension of the SnO_2 nanoparticles with increasing calcination temperature is shown in the table 1.

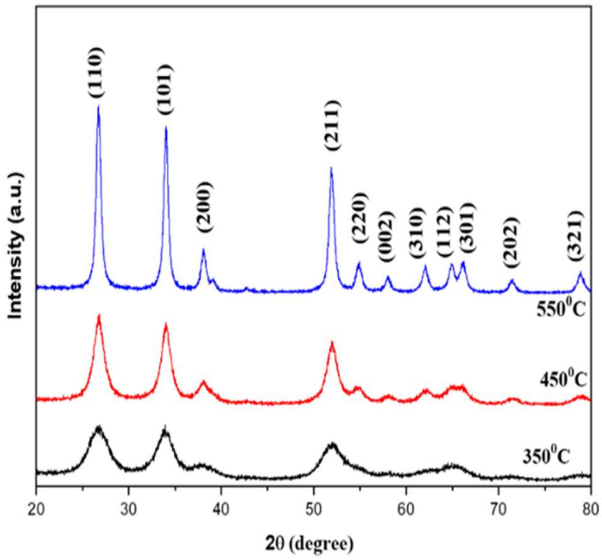


Figure 2: XRD peaks of SnO_2 nanoparticles calcined at different calcination temperatures

Table 1: Influence of calcination temperature on crystallite size

Calcination Temperature (^{0}C)	Crystallite size (nm)
350	2.85
450	7.1
550	13.4

The atomic composition of the required elements and morphology of the prepared material was also studied by using scanning electron microscopy with EDS attachment. The SEM pictures of the SnO_2 particles are presented in the Figure 3. Generally, the size of grains depends on the nucleation rate and growth process of the nanostructures. The FESEM images indicated that the formation of spherical tin oxide nano particles and was found to be in 10-20 nm range. It is clear from the micrographs that after thermal treatment ranging from 350 °C– 550 °C, the particle size gradually increased due to higher nucleation rate which further resulted in the lower bandgap energy. These findings are consistent with the past reported literature (Tazikeh, S *et al.,* 2014).

EDAX analysis was also conducted to analyze the composition of SnO_2 nanoparticles at different calcination temperature and the results are presented in the Figure 4, which confirm that tin and oxygen element exist in well stoichiometric ratio in the samples. Figure 4(a) shows that at temperature 350 ^{0}C, the Sn and O atomic percentage is around 43.06, 56.94 respectively. In this case the grown material is Sn rich which signifies its oxygen-deficient state which means that there are more O vacancies or Sn interstitial sites. Generally, increase in calcination temperature results in decreasing the Sn content, while O content increases, which means that Sn interstitial or O vacancies were reduced into matrix. This fact can be seen in figure 4(b) where Sn:O molar ratio is perfectly near to stoichiometry. Hence, at higher temperature large particle size causes decrement in surface defects (Zulfiqar *et al.,* 2017).

The optical study of the synthesized samples was conducted from 300-800 nm wavelength. The

energy band gap of the samples was evaluated from Tauc's formula:

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

Where, α is known as absorption coefficient, A is absorbance, hν stands for energy of incident photon and optical energy band gap is E_g (Ahmed *et al.,* 2012). The energy band gap of the SnO_2 grown at different calcinating temperatures was also determined. A Tauc plot of the samples can be plotted off $(\alpha h\nu)^2$ vs hν as shown in the Fig. 5 and the calculated band gap was 3.1eV and 3.0 eV for 450^0C and 550^0C respectively. As the calcination temperature raised, the optical band gap moved towards lower energy range (visible region). Similar behaviour was also reported by Baco*et al.* 2012). The red-shift occurred due to the increment in particle size, decrease in grain boundaries and defect densities. These results states that the grown

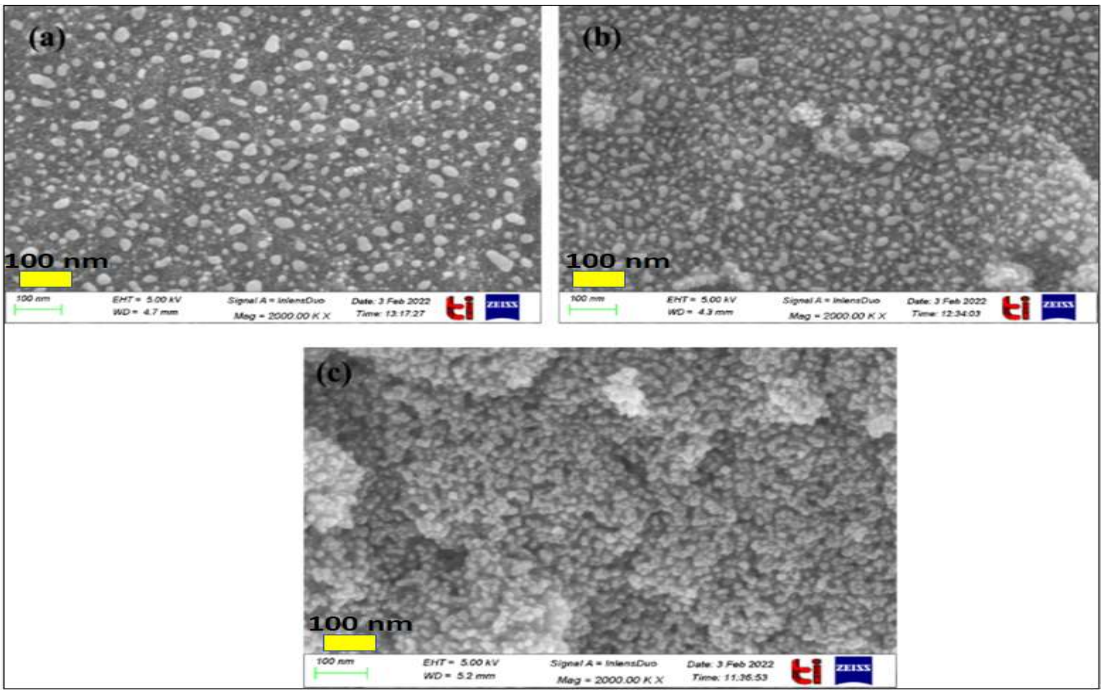


Figure 3: SEM micrographs of SnO_2 calcined at (a) 350 °C, (b) 450 °C and (c) 550 °C

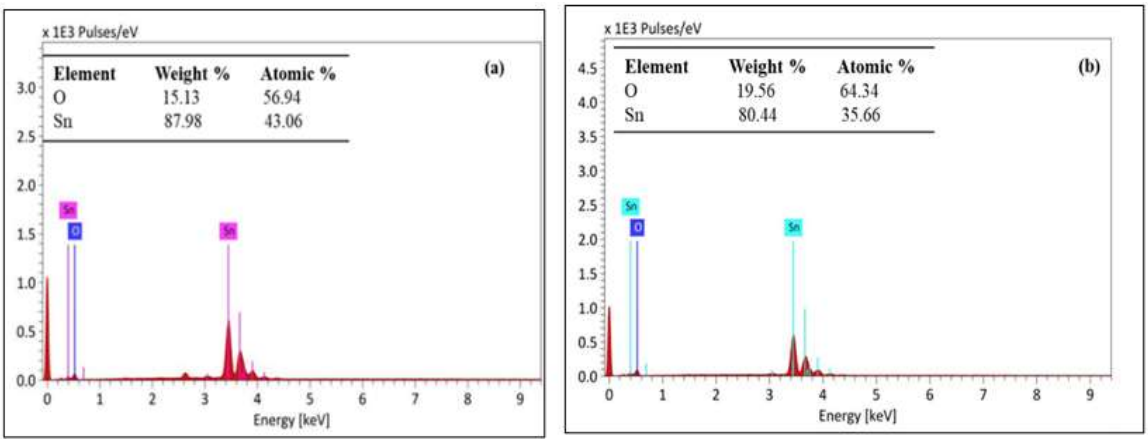


Figure 4: The composition analysis (EDAX) of SnO_2 NPs calcined at (a) 350 °C, (b) 550°C

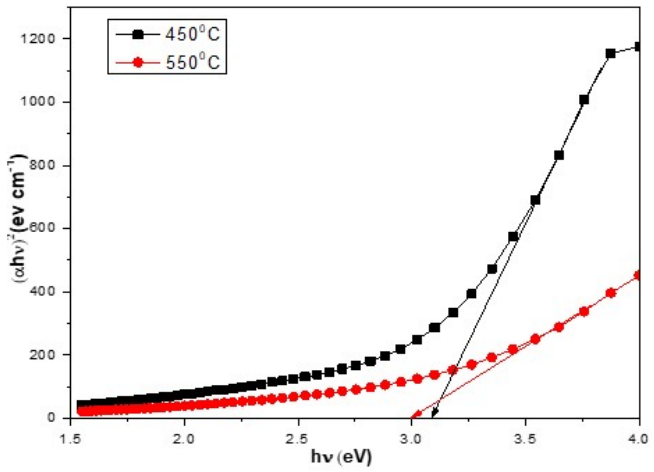


Figure 5: $(\alpha h\nu)^2$ versus hν plot shows the variation in the band gap energy at different calcinating temperature

SnO_2 nanoparticles can be used as highly promising material for solar optoelectronic devices and environment remediation applications especially for the natural sunlight driven photocatalytic dye degradation (Vidhya *et al.,* 2020)

Conclusion

In this present report, sol-gel technique was successfully employed to derive tin oxide (SnO_2) nanoparticles and the influence of calcinating temperature on its structure, morphology and band gap is investigated. The XRD results confirms the tetragonal geometry of the grown samples and shows that on increasing the temperature the crystallite size of the samples increases from 2.85 to 13.4 nm. The FESEM studies reveal the particle size of the tin oxide ranging between 10-20 nm. The band gap value of the prepared nanoparticles marginally changed from 3.1 to 3.0 eV at elevated temperature from 450°Cto 550°C.

Acknowledgement

One of the author, Ms. Manmeet Kaur acknowledges the MM (DU), Mullana for the financial assistance as a Ph.D Research fellowship. The authors are grateful to Prof. N. K. Batra, HOD Mechanical Engineering, MM (DU) for providing the calcination facility. We are also thankful to XRD lab, SAIF, PU Chandigarh, SAI Lab, TIET Patiala and Central R&D cell MM (DU) for the characterizations of the samples.

Conflict of interest

The authors declare that they have no conflict of interest.

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