Impact of Sintering Temperature on Crystallite size and Optical Properties of SnO$_2$ Nanoparticles

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Abstract. Tin oxide (SnO$_2$) nanoparticles synthesized by hydrothermal method and kept at sintering temperatures (800-1200 °C). The tin (II) chloride dehydrate (SnCl$_2$.2H$_2$O) used to prepared the SnO$_2$ precursor solution. The Tin oxide nanoparticles have been characterized by X-ray diffraction (XRD), Field emission scanning electronic spectroscopy (FESEM), and UV-Visible spectroscopy. The nanoparticles size of SnO$_2$ depends on the degree of sintering temperature, it found crystallite size (22.12,27.34 , 36.11 and 42.02) nm of the SnO$_2$ at800, 900, 1000 and1200°C, respectively. XRD shows a pure tetragonal rutile crystalline structure for SnO$_2$ nanoparticles. FESEM images revealed the particles size increased with increasing sintering temperature. The transmittance and absorption are affected by an increased degree of sintering temperature. The band gap of SnO$_2$ nanoparticles decreased with increasing sintering temperature (2.6 to 2.4) eV when temperature raised from 800 to 1200 °C, which belongs to the effect of particle size

Keywords: Tin oxide, sintering temperature, tin (II) chloride, tetragonal rutile.

1. Introduction
Nanomaterials or Nanometer-sized materials have more attracted toa new application. Nanotechnology is considered the most important in the last decade and occupies the forefront field in engineering, chemistry, physics and biology [1,2]. The particle size effects on electric, optical, magnetic and catalytic for semiconductor nanoparticles.

One of the essential semiconductors is Tin oxide (SnO$_2$), which has unique properties such as transparent, highly conducting and sensitive to gases with a direct band gap of 3.6 eV[3,4]. Tin dioxide (SnO$_2$) has type of crystal structure named the mineral Cassiterite. The crystal structure of SnO$_2$ semiconductor possesses tetragonal rutile structural phase with (P42/mmm and point group D4h14) a=b=4.72 Å, c= 3.1864 Å as depict in Figure 1 [4]. The unit cell SnO$_2$ is formed from four threefold coordinated oxygen ions and two six-fold coordinated tin. The position of atoms can be described as Sn$^{4+}$ cations are located at (0,0,0) and (1/2.1/2,1/2), the anions (O$^{2-}$) at (x,x,0) ±(½+x, ½-x,½) with x=0.307[2,5].
The hydrothermal method is one of the essential and new methods to prepare oxides powders and crystalline ceramics, which have the property of low-temperature. The hydrothermal synthesis was carried out under autogenous pressure at 145, 165 and 225 °C over 24 h, an alternative to the traditional methods that need high temperatures to synthesis oxide powders [6]. High purity, multi-component metal oxides and fine particles powders produced by hydrothermal process. Some of the conditions such as reaction time, reaction temperature and solute concentration are controlled to produce the desired size and shape of particles [7]. The hydrothermal method is useful for the grain, no aggregation, good dispersivity, moderate reaction conditions [6,7].

The sintering temperature affects on density of SnO$_2$, which in turn leads to modification of surface [8]. It has been observed that the sintering temperature affects the surface and grain boundaries of SnO$_2$, sintering temperature at 1200 ºC leads to high densities powders and pellets [9].

SnO$_2$ nanoparticles used in gas sensors, solar cells, transistors, etc. It offers many technological applications such as solid state gas sensors, optical devices and oxidation of organics [10].

The object of this study was to prepare SnO$_2$ nanoparticles to study the sintering temperature effect on nanostructure and nanoparticles and energy gap of SnO$_2$ powders synthesized by the hydrothermal method. And, it focused on the effect of high sintering temperature on density.

2. Theoretical part
Debye-Scherrer equation (Eq. 1) was used to determine the grain size of the SnO$_2$ samples by using XRD date

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

Where, $K$ is a constant (0.9)  $\lambda$ is the wavelength(0.1546nm), $D$ is the crystalline size, $\beta$ is the(FWHM), $\theta$ is the Bragg Diffraction angle.

The lattice parameters calculated by Eq. 2 because this structure has tetragonal phase

$$\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (2)

Where (a) and (c) are lattice parameters, $(hkl)$ is the lattice plane index.

The parameters of density ($\rho$) for sintering samples play an important role. The density for all sintered samples was estimated according to geometrical density, and calculated according to the following equation.

$$\rho = \frac{W}{\text{thickness} \times \text{area}} \frac{w}{V}$$  \hspace{1cm} (3)
Where $\rho$ = density (g/cm$^3$), $W$ = mass of the sample (g), $V$ = volume of the sample (cm$^3$).

Where $V$ = thickness $\times$ area for the SnO$_2$ discs.

The Tauc relation was used to estimate the optical band gap (Eg).

$$\alpha h\nu = A(h\nu/E_g)^{1/2}$$

(4)

2.1. Experimental details

The desired concentrations of SnCl$_4$.5H$_2$O (0.1 M) mixed with distilled water and ethanol at ratio (1:1). The solution stirred by magnetic stirrer for 10 minutes. The PH value adjusted until reach 13 by added NaOH slowly for sake to make the white solution. "Next, absolute ethanol was added slowly into the solution (Similar to the amount of NaOH that had been added before)".

The mixed solution is heated with a temperature of 100-160 °C after was sealed by the Teflon-lined stainless steel autoclave of 50 ml capacity for different period (12-24 hours) and then cooled to RT. The magnetic stirrer is used to mix the solution well to obtain perfect homogeneity after stirred 60 min and kept in microwave oven "(M/OS20MW-CG) operation at 2.45GHz was used as the device ". "The microwaveovenwasoperatedat1min/cycleandcooledinbetweentheecycles". The solution is heated by Microwave until the solvent released and the solution dried up completely.

![Figure 2](image_url)

Figure 2. The shape of pellets press at diameter (120 mm) and (2.5-3 mm) thickness.

Acetone and double distilled water used to cool or wash the content to remove any undesired organic impurities. The final product SnO$_2$ was taken out in the powder form. The dried powder has been ground in a mortar and pestle to get finally fine powder, it was compacted in a cylindrical steel model have (120 nm) internal diameter and (2.5-3 mm) thickness. The process used to press the powder (150-200 Mpa) into a pellet shape to reduce the vacancies and porosity between and shrinkage the size by packing the particles to each other as Figure 2. The sample was kept at different temperatures 800°C, 900°C, 1000°C and 1200°C in a muffle furnace."The formation of SnO nano powders was characterized using x-ray diffraction spectroscopy (XRD), Field Emission Scanning Electron Spectroscopy (FESEM) and UV-Visible Spectroscopy".

3. Results and discussions

Figure 3 shows the XRD patterns of SnO$_2$ nanostructures at different sintering temperature (800°C, 900°C, 1000°C and 1200°C). The intensities increase with increasing of the sintering temperature, but the degree of crystallinity does not change at 800 and 900 °C representing fully crystalline SnO$_2$ nano-powder."It is seen that among all XRD patterns, the XRD pattern at 1000 and 1200 °C show better crystallinity. The diffraction peaks located are angles (26.564, 33.784, 38.645, 51.853, 54.343, 56.678, 62.267, 66.762) with planes (110, 101, 200, 211,220, 002, 310, 301)". The produced phase is
mainly a cassiterite type of SnO$_2$, and the diffraction peaks appeared matching with SnO$_2$ tetragonal rutile structure (JCPDS file 00-041-1455). The results agree with Ref. [7].

**Figure 3.** The XRD patterns of SnO$_2$ nanostructures at different sintering temperatures.

Table 1. shows the lattice parameter sand crystallite size( 22.12,27.12, 36.113 and 42.02 nm of the SnO$_2$ particleat 800,900,1000 and 1200°C, it calculated by (Eq. 1) and (Eq. 2).

| Temp. ºC | Crystallite size nm | a (Å) | c (Å) | Unit Volume (Å³) |
|----------|---------------------|-------|-------|------------------|
| 800      | 22.12               | 4.795 | 3.22  | 74.04            |
| 900      | 27.34               | 4.709 | 3.24  | 71.84            |
| 1000     | 36.113              | 4.734 | 3.21  | 71.89            |
| 1200     | 42.02               | 4.743 | 3.19  | 71.62            |

The density of SnO$_2$ affected by sintering temperature increased with increasing as shown in Figure 4. At high sintering temperature leads to high crystallinity and the properties improved such as the density and stability, which turn change in electrical and optical properties of samples.

The parameters a, c are calculated by the same based on all crystal plane. A large number of local lattice disorder and vacant lattice sites affected the reduction in XRD intensity of the corresponding lattice plane. There are a large number of local lattice disorders, vacancy clusters and vacancies of oxygen which lead to an increase in (c) and decrease in (a) and the unit cell volume. Table. 2 shows the experimental density or geometrical density by (Eq. 3).
Table 2. values of geometrical density with different temperature.

| Sintering temperature | Density (g/cm³) |
|-----------------------|-----------------|
| 800 C                 | 6.867           |
| 900 C                 | 6.9467          |
| 1000 C                | 7.0456          |
| 1200 C                | 7.178           |

Figure 4. Crystalline size and density of SnO₂ as function sintering temperature

As we can be seen from FESEM image of samples in Figure 5, the sintering of the SnO₂ powder at 800 and 900 °C showed very grain size with spherical particles. All samples showed homogenous and spherical particles with similar morphology with finer particles, but agglomeration began to appear in some location. As results, the particles size of powders exhibited by FESEM morphology surface, particles size increased due to sintering temperature increasing. The results for surface images compatible with XRD analysis and Scherrer's formula calculations. The results match with Ref. [11].

All images indicate that the particles have non-uniform size with high degree of agglomeration. They are amassed into bigger particles parting some pores between which make them best for various uses. Besides, the changes in the morphology of SnO₂ nanoparticles strongly depends on the sintering temperatures. The samples exhibit a spherical shape with a high degree of agglomeration among fine particles. Therefore, one cannot measure the particles size at higher temperature. The FESEM examinations reveal that when the sintering temperature increases the agglomeration of non-uniform particles increases.
Figure 5. FESEM images of SnO$_2$ nanostructure at different temperature

Figure 6. Shows the transmittance increased with increasing sintering temperature because an increasing sintering temperature leads to increase density. The absorption decreased with increasing sintering temperature due to increase surface area of materials and reduction of oxygen vacancies.

Figure 6. Absorption and Transmittance of SnO$_2$ vs wavelength at 800 ºC and 1200 ºC.

Tauc’s plot of the samples was shown in Figure 7. The intercept values on the energy axis are 2.6 and 2.4eV for 800ºC and 1200ºC, respectively. It observed that the optical band gap energy is decreased when the sintering temperature is increased. The reason for this hypothesis belongs to the effect of particle size that was shown by increasing sintering temperature of SnO$_2$ nanoparticles. The results agree with Ref. [11].
Figure 7. Band gap energies of SnO$_2$ nanostructures at different sintering temperature

4. Conclusion

In conclusion, the successful synthesis of high purity, SnO$_2$ nanoparticles has been achieved via the hydrothermal method at different sintering temperature from 800 to 1200 ºC. The crystalline size was calculated from the Debye-Scherrer’s formula. The crystallite size is sintering temperature-dependent. The crystallite size of the samples increased with raised sintering temperature. The FESEM examinations reveal that when the sintering temperature increases the agglomeration of non-uniform particles increases.

The sample of SnO$_2$ sintered at 1200 ºC showed high density and its better degree for SnO$_2$ nanoparticles, and it observed that relation between the morphology surface and density.

The density increased with increasing sintering temperature due to sharking volume because of high densification at 1200 ºC. Optical studies have been carried out, using optical absorbance. The optical band gap energy is decreased when the temperature is increased due to influence of particles size.

Conflict of interest: The authors declare no competing financial interest.

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