

A study on the role of Ethylene Glycol /Alcohol ratio on synthesise of nano Size SnO₂

M. Barati Moghadam¹, S. M. Zebarjad^{2*}, J. Shakhs Emampour¹

¹Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad,
Mashhad, Iran

²Department of Materials Science & Engineering, Engineering Faculty, Ferdowsi University of
Mashhad, Mashhad, Iran

Abstract

Nano size SnO₂ particles have been synthesized using sol gel method. For this purpose SnCl₄.5H₂O, citric acid and ethylene glycol are used as initial materials. The obtained tin oxide powder at different Ethylene Glycol /Alcohol (Et.G / Et) ratios has been characterized using powder X-ray diffraction (XRD) and Transmission electron microscopic (TEM) techniques. The results show that their structures depend strongly on Et.G / Et ratio. The XRD patterns show SnO₂-cassiterite phase in the nano structured situation and the preferred orientation of the powder along (101) prevails up to Et.G / Et = 1 ratio, which shifts to (110) for Et.G / Et = 2 ratio. TEM investigation reveals that the average particle size is in the range of 80-160 nm and homogeneous atomization of Sn cations in xerogel depends strongly on the presence of ethylene glycol.

Key word: Oxides, sol-gel growth, nano-structured materials, X-ray diffraction

* Corresponding Author (Seyed Mojtaba Zebarjad, E-mail: Zebarjad@um.ac.ir, Tel,Fax:+985118763305)

1. Introduction

Tin oxide (SnO_2) is non-stoichiometric structure and has a typical wide band gap n-type semiconductor (3.8 eV) [1]. It is one of the most widely used semiconductor oxides due to its chemical and mechanical stabilities. Owing to their unique electronic, magnetic and optical properties, semiconductor SnO_2 nano-particles may find wide applications in various fields, such as microelectronics, photo-catalysis, nonlinear optics, photoelectron-chemistry, imaging science, and electro-optics [2].

Tin oxide as a key functional material has multifaceted technological applications including catalytic CO oxidation [3], gas sensors [4], oxidative dehydrogenations [5], heat mirrors [6], varistors [7], transparent electrodes for solar cells [8], glass melting electrodes [9], selective catalytic reduction of NO_x by hydrocarbons [10] and anodes for lithium ion batteries [11]. In some applications such as lithium ion battery, the best performance depends strongly on tin oxide particle size and a decrease in particle size leads to promote the capacity. This is why the synthesis of nano-scale tin oxide particles has been under attention during last decade.

According to literature survey done by the authors there are many methods to fabricate SnO_2 [12-15]. In fact the tin dioxide was prepared by various synthesis methods such as precipitation [16], two-step solid state synthesis [17], micro-emulsion [18], sol gel [19], spray pyrolysis [20], hydrothermal synthesis [21], solvothermal [22], polymerized complex [23] and amorphous citrate [24].

In some of them, there are difficulties to control specific surface area of the particle as temperature increases. For example, Nicolas et al. synthesized high surface area SnO_2 nano particles by direct oxidation of Sn in HNO_3 , but the specific surface area decreased sharply to only about $24 \text{ m}^2\text{g}^{-1}$ when heated at 600°C [25]. In some of them, corrosive media made a limitation. For example transparent tin dioxide films prepared by spray pyrolysis techniques were used as a protective coating in glass industry. The main difficulties associated with this technique were the presence of corrosive gas species and the necessity of a rather processing temperature greater than 400°C [26]. Or the gel-combustion method needed a large amount of organics and produced large volume of gases such as NO_x and CO_2 during the combustion reaction [27].

Because of mentioned limitations, in the last decade, the attention of researchers is focused on the sol gel method for the synthesis of various metal oxides. The sol gel method is a

versatile solution technique used to obtain ultrafine, homogenous powders of a variety of glass and ceramic materials at low temperature and in short time through the growth of metal OXO-polymers in a solvent [27]. This method can be used for the production of (a) metal oxides at relatively low processing temperatures, (b) metal oxides free from foreign ions, (c) metal oxides with precise control of the doping level, and (d) metal oxides with the particles in the nano size range [28]. Sol gel technique has many advantages over other methods, such as the large surface area can be obtained on both films and powders that will enhance the sensing properties [29], simple and low-cost processing, ability to coat large and complex shapes, a porous structure desirable for gas sensor application [30] and has a remarkable possibility to control a particle size of the SnO₂ thin film because molecular reactions of the raw materials could promote in the precursor solutions [31-36]. Song and Kim [37] synthesized SnO₂ powders with surface area of 86 m²g⁻¹ through a water-in-oil microemulsion method. Chen and Gao [38] obtained SnO₂ nanoparticles with high-specific area of 107-169 m²g⁻¹ and particle size of 3 nm via a water in-oil microemulsion-assisted hydrothermal process. SnO₂ thin films were prepared [39, 40] by sol gel route using an alcoholic solution of Sn(OC₂H₅)₄.2C₂H₅OH as the precursor. Subsequently these films were heated and annealed between 500 and 700⁰C and the sensitivity of these films to relative humidity was measured. Based on literature survey done by the authors role of both ethylene glycol and alcohol on synthesis of tin dioxide has not been under attention. Thus in the present work it is tried to investigate the synthesis of tin oxide nano crystallites in various Et.G / Et ratios by sol gel method from SnCl₄.5H₂O and citric acid.

2. Experimental procedure

2.1. Sol gel synthesis

Nano size SnO₂ particles have been synthesized using sol gel method. The flow chart of the synthesis is depicted in Fig. 1. In order to clarify the role Et. G/Et ratio on synthesise of nano Size SnO₂ three samples coded 1, 2 and 3 with different Et. G/Et were produced (Table 1)

Then, citric acid and ethylene glycol subsequently were added, and the mixture was stirred for 20 min at 40⁰C until dissolving all components. The solution was refluxed at 120⁰C for 3h. During refluxing the solution was turned into a metal-citrate homogeneous complex with light yellow color [40]. After ward cooling down, the solute was kept at 150⁰C by direct heating

on the hot plate for different times until drying (Table 1). The achieved product production was a black-brown porous gel as an aerogel. The precursor powder (xerogel), which has been prepared by grinding aerogel, was annealed at 550⁰C for 1h and under atmospheric condition in an electric box furnace and then cooled down to room temperature to achieve SnO₂ particles.

2.2. Characterization

The synthesized materials were characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). X-ray powder diffraction patterns were taken using an automatic diffractometer (CuK α) with 2 Θ in the range 20-70⁰. For transmission electron microscopy (TEM), the samples were dispersed in ethanol as a media. A drop of this dispersed suspension was put onto 200 mesh carbon coated Cu grid and then dried in vacuum.

3. Results and discussion

Fig.2 shows TEM micrographs of the produced SnO₂ nano-powders in samples 1 and 3. As seen the particle size of produced SnO₂ depends strongly on Et G /Et ratio and the particle size reduces with an increase in Et.G / Et ratio from 1/2 to 2. This is because ethylene glycol plays like a polymerizing agent in sol gel process. In summary the TEM micrographs prove that the presence of ethylene glycol is so effective for homogeneous atomization of Sn cations in xerogel or prevent from the agglomeration and grain growth of SnO₂ particles.

In order to clarify the role of Et.G / Et ratio on sol gel of tin dioxide particles, the results of X-ray diffraction (XRD) technique can be useful. Fig. 3 demonstrates XRD patterns of the samples before and after calcinations at 550⁰C for 1h. It is clear that the powders annealed at T=550⁰ C are completely crystallized. The crystallized powders exhibit single SnO₂ phase in tetragonal cassitrite structure. The XRD patterns at all annealing temperatures show that the intensities of three basic peaks of the (110), (101) and (211) planes are more than of other peaks. However, the number of peaks and their orientations are changed with Et.G / Et ratio used for the preparation of nano-powders.

At the lowest Et.G / Et = 1/2 ratio, the major orientation is (101) plane, with attention that the intensity of major orientation is (211) plane that is the same intensity as all samples. By increasing ratio to Et.G / Et = 1, slight improvement in the crystallinity is observed. It is

interesting to note that, the orientation (which is along (101) plane) of the sample preparation with Et.G / Et = 2 ratio shifts along (110) plane, which is assigned to tetragonal SnO₂.

The three different stages of growth of SnO₂ powder are: (1) nucleation; (2) crystal growth; and (3) further crystal growth with preferred orientation. At lower Et.G / Et = 1/2 ratio, large number of small nuclei might have formed. The growth of each nucleus has taken place separately with different orientations and finally the crystal growth along (101) plane is dominant. With increasing Et.G / Et = 1 ratio, initially formed large number of small nuclei might have agglomerated and relatively small number of large nuclei might have formed, and growth along (101) plane is further dominated. At Et.G / Et = 2 ratio preferred orientation is changed and lies along (110) plane. This might be due to saturation of growth of nuclei and crystallites, which enforces gradual incorporation of Sn atoms at the interstitial sites [41].

In summary in the present study it is demonstrated that the SnO₂ powder can be grown along (101) or (110) plane merely by adjusting the Et.G / Et ratio. This result is opposite to what proposed by Bruneaux *et al.* [42] who believed that the preferred orientation was along (110) [42]. Perhaps the difference in the result can be attributed to the nature of the precursor. As Patil [41] reported the preferred orientation for organotin compound, dibutyltin diacetate (DBTDA) was (200) , whereas for tetra-n-butyltin (TBT), (110) plane was predominant [41].

4. Conclusions

In the current study it is tried to elucidate the role of Et.G / Et ratio on growth condition of nano size SnO₂ produced by sol-gel method. The results are remarked as bellow:

- Ethylene glycol plays like a polymerizing agent in the synthesis of SnO₂ nano particles.
- Homogeneous atomization of Sn cations in xerogel depends strongly on the presence of ethylene glycol.
- The produced SnO₂ nanoparticles has a particle size in the range of 80-160 nm.
- Preferred orientation of crystal growth changes as Et.G / Et ratio increases.

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Table 1: The used material

Sample	SnCl₄.5H₂O (g)	Ethylene glycol (ml)	Citric Acid (g)	Ethanol (ml)	H₂O (ml)	Heating time (h)
1	10	5	10	10	10	0.45
2	10	10	10	10	101	1.5
3	10	20	10	10	10	3

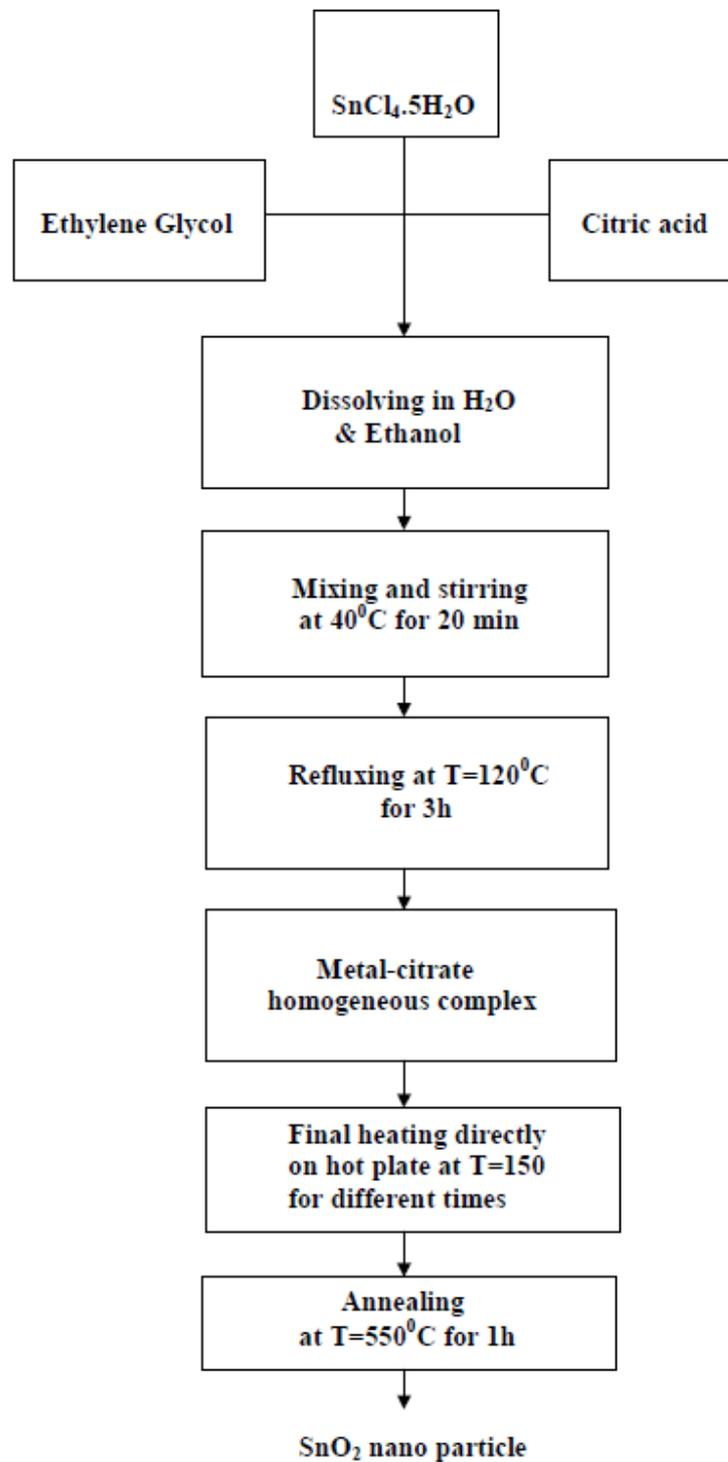


Figure 1: The flow chart of preparation of SnO₂ particles

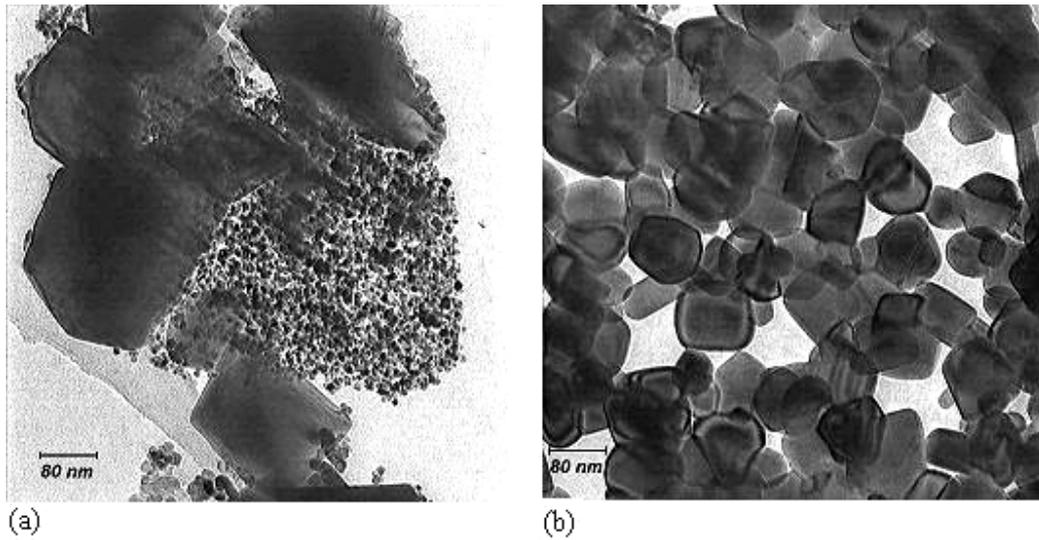


Fig. 2. The TEM images of SnO nano-particles annealed at different Et.G / Et ratios, (a) Et.G /Et = 1/2 (b) Et.G /Et = 2 ratio.

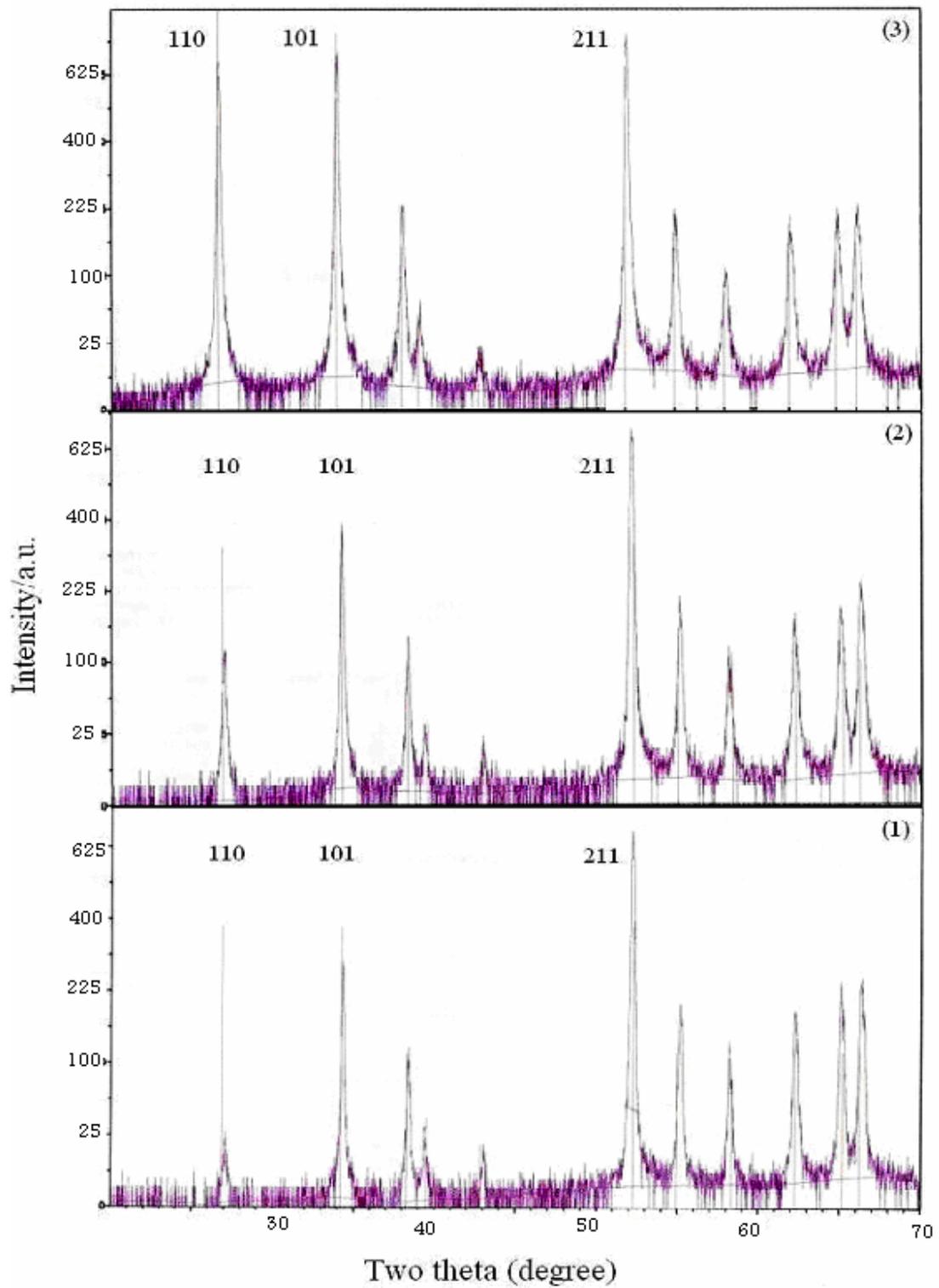


Figure 3: The XRD patterns of samples after calcinations at $T=550^{\circ}\text{C}$, 1h

