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A Study on the Role of Ethylene Glycol/Alcohol Ratio on Synthesis of Nano-Size SnO_2

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Nano-sized SnO_2 particles have been synthesized using sol-gel method. For this purpose, hydro-alcoholic solution consisting of $SnCl_4 \cdot 5H_2O$, citric acid, and ethylene glycol (Et.G) are used as initial materials. The tin oxide powder obtained at different Et.G/Et ratios is characterized using powder x-ray diffraction (XRD) and transmission electron microscope (TEM) spectroscopic techniques. The results show that their structural depend strongly on Et.G/Et ratio. The XRD patterns show SnO_2-cassiterite phase in the nanopowders and the preferred orientation of the powder along (101) plane prevails upto Et.G/Et = 1 ratio, which shifts to (110) plane for Et.G/Et = 2 ratio. TEM investigation revealed that the average particle size is in the range of 20 to 32 nm. Electron diffraction pattern of nanopowders obtained at different Et.G/Et ratios shows that distribution of spherical particles increase and crystallite size those reduces with an increase in Et.G/Et ratio from .5to 2 due to the effect of ethylene glycol as polymerizing agent in sol-gel process. The possible explanation for this is given in the present investigation.

Keywords: Ethylene glycol, nano-size SnO_2, sol-gel, synthesize

1. Introduction

SnO_2 is non-stoichiometric structure and has a typical wide band gap n-type semiconductor (3.8 eV) (Xi et al. 2008). 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 nanoparticles have many applications in various fields, such as microelectronics, photo-catalysis, nonlinear optics, photoelectron-chemistry, imaging science, and electro-optics (Gu et al. 2004).

Tin oxide as a key functional material has multifaceted technological applications, including catalytic CO oxidation (Fuller and Warwick 1973), gas sensors (Wang et al. 2006), oxidative dehydrogenations (Shen et al. 1994), heat mirrors (Kojima et al. 2001), varistors (Wang et al. 2002), transparent electrodes for solar cells (Moustafid et al. 2002), glass melting electrodes (Kim et al. 2002), selective catalytic reduction of NO_x by hydrocarbons (Teraoka et al. 1993), and anodes for lithium ion batteries (Bose et al. 2002). 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. Thus, synthesis nanoscale tin oxide particles have been given much attention during the last decade.

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According to a literature survey done by the authors, there are many methods to fabricate SnO_2 (Baik et al. 2000; Deng et al. 2002; Leite, Gomez, et al. 2002; Leite, Maicel, et al. 2002). Infact, the tin dioxide was prepared by various synthesis methods such as precipitation (Song and Kang 2000), two-step solid state synthesis (Chen et al. 2001), microemulsion (Song and Kim 1999), sol gel (Petrov et al. 2008), spray pyrolysis (Luyo et al. 2007), hydrothermal synthesis (Baik et al. 2000), solvothermal (Lili et al. 2006), polymerized complex (Udawatte et al. 2000), and amorphous citrate (Bhagwat et al. 2003).

In some of them, there are difficulties to control specific surface area of the particle as temperature increases. For example, Nicolas et al. (as discussed in Sergent et al. 2002) synthesized high surface area SnO_2 nanoparticles by direct oxidation of Sn in HNO_3, but the specific surface area decreased sharply to only about 24 m^2g^{-1} when heated at 600°C. In some of them, corrosive media made a limitation. For example, transparent tin oxide films prepared by spray pyrolysis techniques were used as a protective coating in glass industry. Themain difficulties associated with this technique were the presence of corrosive gas species and the necessity of a rather processing temperature >400°C (Rizzato et al. 2001). Orthe gel-combustion method needed a large amount of organics and produces large volume of gases such as NO_x and CO_2 during the combustion reaction (Zhang and Gao 2004).

Because of mentioned limitations, in the last decade, the research attentionhas beenfocused 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 (Zhang and Gao 2004). 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 (Risti et al. 2002). 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 (Rella et al. 1997), simple and low-cost processing, ability to coat large and complex shapes, a porous structure desirable for gas sensor application (Racheva and Critchlow 1997), and has a remarkable possibility to control a particle size of the SnO_2 thin film because molecular reactions of the raw materials could promote in the precursor solutions (Shoyama and Hashimoto 2003).

One disadvantage of this sol-gel method is that its process has a high cost and cannot be used on a large scale of Snalkoxides. Another drawback of metal alkoxides is that they are particulary moisture sensitive, such that they have to be processed under a dry and inert atmosphere, and the resulting OXO-polymers that constitute the sols and gels are generally poly dispersed in size and composition (Broussous et al. 2002). Zhang et al. (as discussed in Pena et al. 2001) have overcome this problem by using the cheap and easy to perform commercially available Sn precursor, $SnCl_4$ but the chlorine ions are very difficult to remove and the residual chlorine ions often affect the surface and electrical properties, introducing a random n-type doping in the material.

Many procedures for the production of fine powders and thinfilms of various metal oxides were described in the literature. For example, work reported by Seiyama et al. (1962), semi-conductive materials have been particular gas sensor materials, and huge researches on SnO_2 have been made by using various methods until now (Sakai et al. 2001). Song and Kim (Song and Kim 2000) synthesized SnO_2 powders with surface area of $86\,m^2g^{-1}$ through a water-in-oil microemulsion method. Chen and Gao (2004) obtained SnO_2 nanoparticles with high-specific area of $107–169\,m^2g^{-1}$ and particle size of 3 nm via a water in-oil microemulsion-assisted hydrothermal process. SnO_2 thin films were prepared (Shoyama and Hashimoto 2003) by sol-gel route using an alcoholic solution of $Sn(OC_2H_5)_4 \cdot 2C_2H_5OH$ as the precursor. Subsequently these films were heated and annealed between 500 and 700°C and the sensitivity of these films to relative humidity was measured.

In the present work, we investigate the synthesis of tin oxide nano-crystallites in various Et.G/Et ratios by sol-gel method from $SnCl_4 \cdot 5H_2O$ and citric acid. The obtained SnO_2 particles are in nanometer scale by particles size determined from transmission electron microscope (TEM). Also it is demonstrated that the SnO_2 powder can be grown along (101) or (110) plane merely by adjusting the Et.G/Et ratio. The particles have been characterized by mean of x-ray diffreaction (XRD) and TEM.

2. Experimental Procedure

2.1 Sol-Gelsynthesis

Nano-size SnO_2 particles have been synthesized using sol-gel method. The flow chart of the synthesis is depicted in Figure 1. For this purpose, hydro-alcoholic solution consisting $SnCl_4 \cdot 5H_2O$, H_2O and ethanol with according to Table 1 was prepared. Then, citric acid and ethylene glycol subsequently added to this solution, and the resulting mixture was stirred and dissolved at 40°C for 20 min until all the components were dissolved. The solution was refluxed at 120°C for 3 h. During refluxing the solution was turned into a metal-citrate homogeneous complex with light yellow color (Bagheri-Mohagheghi et al. 2008). Afterward, to cool down, the solute was kept at 150°C by direct heating on the hot plate for different times until drying (Table 1). The resultant production was a black-brown porous gel. The precursor powders (3 samples), was annealed at 550°C for 1 h and under atmospheric condition in an electric box furnace and then cooled down to room temperature to achieve SnO_2 particles.

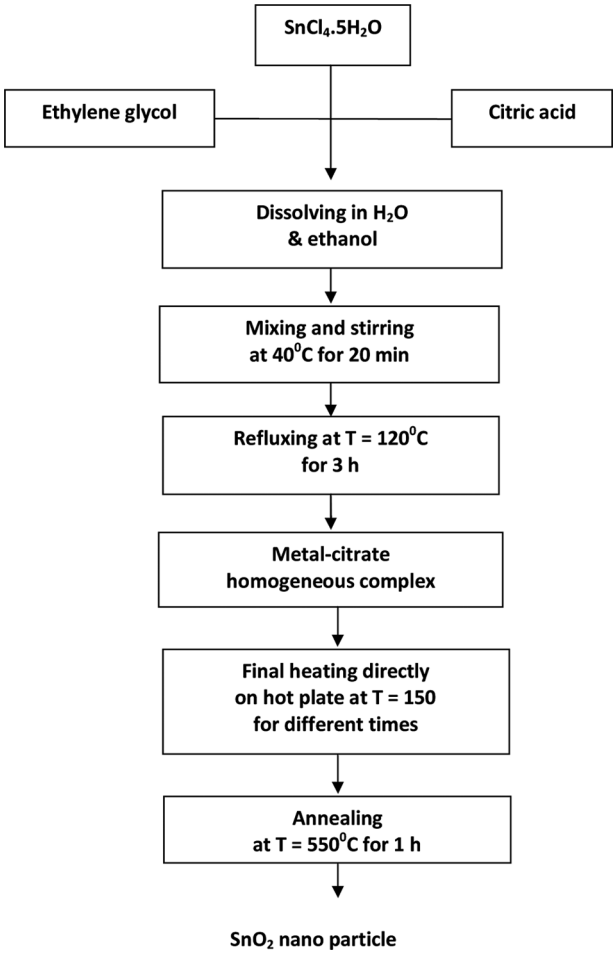


Fig. 1. The flow chart of preparation of SnO_2 nanoparticles by sol-gel process.

Table 1. SnO_2 by modified sol-gel method

$SnCl_4 \cdot 5H_2O$ [g]	Ethylene glycol [ml]	Citric acid [g]	Ethanol [ml]	H_2O [ml]	Direct heating time [h]
(1) 10	5	10	10	10	0.45
(2) 10	10	10	10	10	1.5
(3) 10	20	10	10	10	3

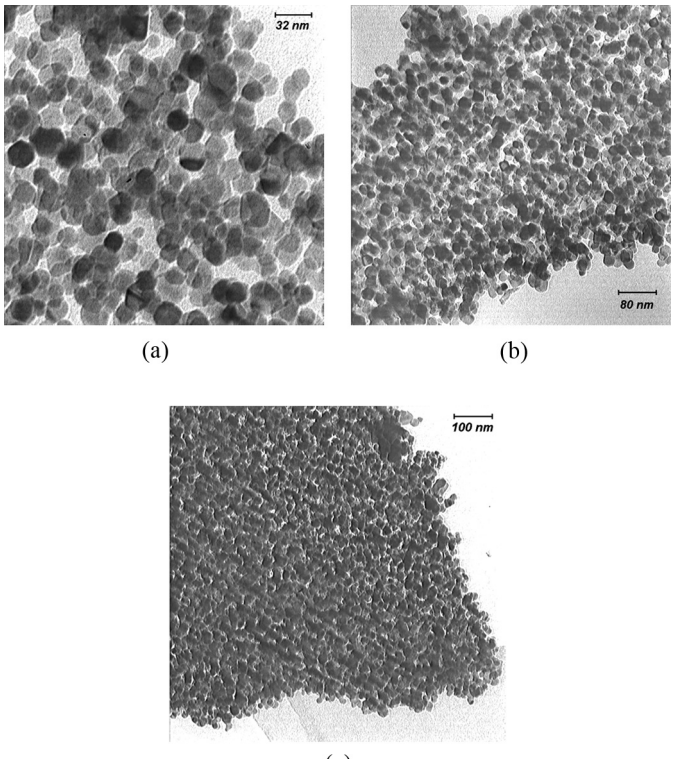
2.2 Structure and Morphology Studies

The synthesized materials were characterized for their structure and morphology by powder XRD and TEM, respectively. X-ray powder diffraction patterns were taken using an automatic diffractometer (CuKα) with 2Θ in the range 20–70°. For TEM, the samples were dispersed in ethanol using an ultrasound bath. A drop of this dispersed suspension was put onto 200- mesh carboncoated Cu grid and then dried in vacuum.

3. Results and Discussion

3.1 Effect of Different Et.G/Et Ratios on TEM

Figure 2 shows TEM images of the SnO_2 nanopowders in samples which shows an average particle size in the range of 20 to 32 nm. It also shows the particle size reduces with an increase in Et.G/Et ratio from .5 to 2 due to the effect of ethylene glycol as polymerizing agent in sol-gel process (Bagheri-Mohagheghi et al. 2008). These results indicate that ethylene glycol works as a barrier, hindering agglomeration of nanoparticles, and, thus, avoiding their growth.



(a) (b)

(c)

Fig. 2. TEM images of SnO_2 nanoparticles annealed at different Et.G/Et ratio: a) Et.G/Et = 1/2, b) Et.G/Et = 1, c) Et.G/Et = 2.

3.2 Effect of Different Et.G/Et Ratios on Powder XRD

In order to understand the effect of Et.G/Et ratio on sol gel of tin dioxide particles, the XRD technique were studied (Table 2). Figure 3 demonstrates XRD patterns of the samples before and after calcinations at 550°C for 1 h. It is clear that the powders annealed at T = 550°C are completely crystallized.

The crystallized powders exhibit single SnO_2 phase (in tetragonal cassiterite structure). The XRD patterns at all annealing samples show that the intensities of three basic peaks of the (110), (101), and (211) planes are more than of other peaks. However, the orientations peaks are changed with Et.G/Et ratio used for the preparation nanopowders. Indeed at the lowest Et.G/Et = 1/2 ratio, we have lower degree of polymerization and the major orientation is (101) plane, with attention that the intensity of major orientation is (211) plane that is the same intensity for 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 in higher degree of polymerization, shifted along (110) plane, which is assigned to tetragonal SnO_2. This result is almost similar to what proposed in previous work which believed that ethylene glycol plays as polymerizing agent (Lee and Choi 2005).

Formation of SnO_2 thin film from $SnCl_4 \cdot 5H_2O$ precursor by sol-gel technique is well known. The existence of preferred orientations of SnO_2 thin films by sol gel are briefly discussed here for comparison.

Bruneaux et al. (1991) have reported that the films prepared from concentrated stannic chloride solution showed preferred orientation, along (110) plane and those prepared from diluted stannic chloride solution presented different orientations.

The growth of SnO_2 thin film along preferred direction was also found to depend on nature of the precursor, e.g., for organotin compound, dibutyltindiacetate (DBTDA), (200) plane was dominant, whereas for tetra-n-butyltin (TBT), (110) plane was predominant (Murakami et al. 2005).

In the present study, it is demonstrated that the SnO_2 powder can be grown along (101) or (110) plane merely by adjusting the Et.G/Et ratio.

Table 2. Summary of the different Et.G/Et ratio in this study

Ratio of ethylene glycol/ethanol [ml/ml]	Ratio of citric acid/$SnCl_4$ [g/g]
(1) 0.5	1
(2) 1	1
(3) 2	1

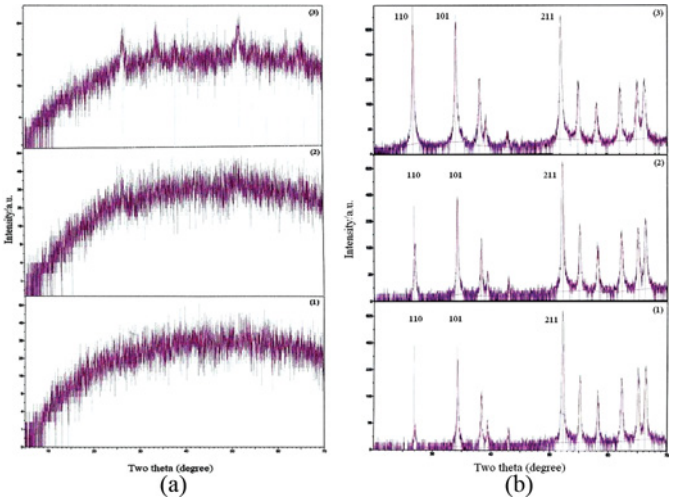


Fig. 3. XRD patterns of the samples a) before calcinations and b) after calcinations at 550°C for 1 h. (Figure available in color online.)

4. Conclusions

SnO_2 nanoparticles having particle size in the range of 20 to 32 nm supported by TEM results are prepared by sol gel of $SnCl_4 \cdot 5H_2O$ in air flow. The direct use of $SnCl_4$ reduces the cost of particles preparation. Addition of ethylene glycol as polymerizing agent in the synthesis of SnO_2 nanoparticles prevents from the agglomeration and grain growth of SnO_2 particles. Structural characterization indicates that tetragonal SnO_2 particles have cassitrite structure and preferred orientation of the powder along (101) plane for prevailing up to (1) ratio, which changes to (110) for (2) ratio due to the effect of ethylene glycol as polymerizing agent in sol-gel process. Generally, in sol-gel processes the synthesis processes are very simple and this method can also be utilized to synthesize many other doped tin oxide nanocrystallites.

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