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A Study on the Role of Ethylene Glycol/Alcohol Ratio on Synthesis of Nano-Size SnO₂

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Nano-sized SnO₂ particles have been synthesized using sol-gel method. For this purpose, hydro-alcoholic solution consisting of SnCl₂·5H₂O, 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 dependence strongly on Et.G/Et ratio. The XRD patterns show SnO₂-casiterite phase in the nanopowders and the preferred orientation of the powder along (101) plane prevails up to 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 increases and crystallite size those reduces with an increase in Et.G/Et ratio from 1 to 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 SnO₂, sol-gel, synthesize

1. Introduction

SnO₂ 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 SnO₂ nanoparticles have many applications in various fields, such as microelectronics, photo-catalysis, nonlinear optics, photo-electron-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 NOₓ 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.

According to a literature survey done by the authors, there are many methods to fabricate SnO₂ (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 SnO₂ nanoparticles by direct oxidation of Sn in HNO₃, but the specific surface area decreased sharply to only about 24 m²/g 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 NOₓ and CO₂ during the combustion reaction (Zhang and Gao 2004).

Because of mentioned limitations, in the last decade, the research attentionhas been 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 ultra-
fin\-e, 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\textit{ 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\textsubscript{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 Snalk-
oxides. Another drawback of metal alkoxides is that they are
particulary moisture sensitive, such that they have to be pro-
cessed 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 \textit{et al.} 2002).
Zhang et al. (as discussed in Pena \textit{et al.} 2001) have
overcome this problem by using the cheap and easy to per-
form commercially available Sn precursor, SnCl\textsubscript{4} but the
chlorine ions are very difficult to remove and the residual
chlorine ions often affect the surface and electrical proper-
ties, 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 litera-
ture. For example, work reported by Seiyama \textit{et al.} (1962),
semi-conductive materials have been particular gas sensor
materials, and huge researches on SnO\textsubscript{2} have been made
by using various methods until now (Sakai \textit{et al.} 2001). Song
and Kim (Song and Kim 2000) synthesized SnO\textsubscript{2} powders
with surface area of 86 m\textsuperscript{2}g\textsuperscript{-1} through a water-in-oil micro-
emulsion method. Chen and Gao (2004) obtained SnO\textsubscript{2}
nanoparticles with high-specific area of 107–169 m\textsuperscript{2}g\textsuperscript{-1} and
particle size of 3 nm via a water in-oil microemulsion-
asisted hydrothermal process. SnO\textsubscript{2} thin films were pre-
pared (Shoyama and Hashimoto 2003) by sol-gel route using
an alcoholic solution of Sn(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} \cdot 2C\textsubscript{2}H\textsubscript{5}OH as the pre-
cursor. Subsequently these films were heated and annealed
between 500 and 700\textdegree 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\textsubscript{4} \cdot 5H\textsubscript{2}O and citric acid. The obtained
SnO\textsubscript{2} particles are in nanometer scale by particles size deter-
mined from transmission electron microscope (TEM). Also
it is demonstrated that the SnO\textsubscript{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
diffraction (XRD) and TEM.

\section*{2. Experimental Procedure}

\subsection*{2.1 Sol-Gel\textsubscript{synthesis}}

Nano-size SnO\textsubscript{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 consist-
ing SnCl\textsubscript{4} \cdot 5H\textsubscript{2}O, H\textsubscript{2}O and ethanol with according to Table 1
was prepared. Then, citric acid and ethylene glycol subse-
tively added to this solution, and the resulting mixture
was stirred and dissolved at 40\textdegree C for 20 min until all the
components were dissolved. The solution was refluxed at
120\textdegree C for 3 h. During refluxing the solution was turned into
a metal-citrate homogeneous complex with light yellow color
(Bagheri-Mohagheghi \textit{et al.} 2008). Afterward, to cool down,
the solute was kept at 150\textdegree 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\textdegree C for 1 h and
under atmospheric condition in an electric box furnace and
then cooled down to room temperature to achieve SnO\textsubscript{2} particles.

\begin{align*}
\text{SnCl}_4\cdot 5\text{H}_2\text{O} & \xrightarrow{\text{Ethylene glycol}} \text{Citric acid} \\
\text{Dissolving in H}_2\text{O} & \text{& ethanol} \\
\text{Mixing and stirring} & \text{at 40\textdegree C for 20 min} \\
\text{Refluxing at T = 120\textdegree C} & \text{for 3 h} \\
\text{Metal-citrate} & \text{homogeneous complex} \\
\text{Final heating directly} & \text{on hot plate at T = 150} \\
& \text{for different times} \\
\text{Annealing} & \text{at T = 550\textdegree C for 1 h} \\
\text{SnO}_2 \text{ nano particle} & \\
\end{align*}

\text{Fig. 1. The flow chart of preparation of SnO}_2 \text{ nanoparticles by sol-gel process.}
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 carbon-coated 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 SnO₂ nanoparticles 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.

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 SnO₂ 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 SnO₂. 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 SnO₂ thin film from SnCl₄ · 5H₂O precursor by sol-gel technique is well known. The existence of preferred orientations of SnO₂ 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 SnO₂ 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 SnO₂ powder can be grown along (101) or (110) plane merely by adjusting the Et.G/Et ratio.

Table 1. SnO₂ by modified sol-gel method

<table>
<thead>
<tr>
<th>SnCl₄ · 5H₂O [g]</th>
<th>Ethylene glycol [ml]</th>
<th>Citric acid [g]</th>
<th>Ethanol [ml]</th>
<th>H₂O [ml]</th>
<th>Direct heating time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 10</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td>(2) 10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Ratio of ethylene glycol/ethanol [ml/ml]</th>
<th>Ratio of citric acid/SnCl₄[g/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 0.5</td>
<td>1</td>
</tr>
<tr>
<td>(2) 1</td>
<td>1</td>
</tr>
<tr>
<td>(3) 2</td>
<td>1</td>
</tr>
</tbody>
</table>
Ethylene Glycol/Alcohol Ratio on Synthesis of Nano-Size SnO₂

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

SnO₂ nanoparticles having particle size in the range of 20 to 32 nm supported by TEM results are prepared by sol gel of SnCl₄·5H₂O in air flow. The direct use of SnCl₄ reduces the cost of particles preparation. Addition of ethylene glycol as polymerizing agent in the synthesis of SnO₂ nanoparticles prevents from the agglomeration and grain growth of SnO₂ particles. Structural characterization indicates that tetragonal SnO₂ particles have c-axisite 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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