Microwave-assisted hydrothermal synthesis of nanocrystalline SnO powders

F.I. Pires, E. Joanni, R. Savu *, M.A. Zaghe te, E. Longo, J.A. Varela

LIEC, UNESP, Instituto de Química de Araraquara, Rua Francisco Degni s/n, 14800-900 Araraquara, SP, Brazil

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Abstract

Tin oxide (SnO) powders were obtained by the microwave-assisted hydrothermal synthesis technique using SnCl₂·2H₂O as a precursor. By changing the hydrothermal processing time, temperature, the type of mineralizing agent (NaOH, KOH or NH₄OH) and its concentration, SnO crystals having different sizes and morphologies could be achieved. The powders were characterized by X-ray diffraction (X-ray), Field Emission Scanning Electron Microscopy (FE-SEM), High Resolution Transmission Electron Microscopy (HR-TEM) and Selected Area Electron Diffraction (SAED). The results showed that plate-like form is the characteristic morphology of growth and the TEM analyses indicate the growth direction as (200).
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1. Introduction

Semiconducting oxides (SnO₂, ZnO, In₂O₃, etc.) have been intensively studied due to their wide applications ranging from liquid crystals displays, photovoltaic cells, transparent electrodes, lasers and sensors. The methods reported for obtaining semiconducting oxide nanoparticles include colloidal growth, hydrothermal synthesis, chemical vapor condensation, spray pyrolysis, sputtering and laser ablation in liquids and gases [1–4].

Among the chemical methods, hydrothermal synthesis is often used due to its simplicity, allowing the control of grain size, morphology and degree of crystallinity by easy changes in the experimental procedure. A variation of this method, microwave-assisted hydrothermal synthesis, has the advantage of a smaller processing time and a uniform nucleation of the powders in suspension [4,5]. The control of the size uniformity, dimensionality, growth direction and dopant distribution within the nanostructure are crucial factors, due to the fact that their functionality will be based on these structural parameters [5]. Recently, research for obtaining various nanostructures of tin dioxide (SnO₂) was intensively developed [6–13]. In the chemical methods reported in the literature the most common precursor used was SnCl₄·5H₂O with the oxidation state IV of tin in solution leading to the formation of SnO₂ nanocrystals [10–13].

A continual challenge for the researchers is to fabricate metal oxide materials by controlling the oxidation state of multivalent metal ions in solution. Although many morphological studies have been conducted, the control of the oxidation state of metal ions in an aqueous solution has hardly been investigated [14]. Due to the fact that Sn(II) is easily oxidized to Sn(IV), the preparation of SnO is relatively difficult. For this reason, very few articles on the synthesis of tin monoxide (SnO) have been reported [14–16].

For the first time we report in this work the fabrication of tin monoxide (SnO) nanocrystals, with oxidation state II of tin in solution, by microwave-assisted hydrothermal synthesis. Pow ders with different morphologies and crystal sizes were obtained using SnCl₂·2H₂O as precursor and three different mineralizing agents. Due to their high volume to surface ratio, these nanostructures have very good potential for applications in gas sensors, photo-catalysis and photo-electrochemical cells.

2. Experimental procedure

Tin oxide powders were obtained by first preparing aqueous solutions of SnCl₂·2H₂O and mineralizing agents
(NaOH, KOH or NH₄OH). The concentration of tin chloride was kept constant at 0.25 M and the basic solutions were added, under constant stirring at room temperature, until their concentration was two or three times the amount of tin in solution. Microwave-assisted hydrothermal treatment (CEM Corporation, MARS 5) was performed using Teflon flasks (CEM, XP 1500) with 50 ml of each of the starting solutions. The process was carried out at 120 °C or 180 °C for 2 or 6 h. The complete set of conditions studied is shown in Table 1. After synthesis, the powders were cooled, washed several times with ethanol and dried at room temperature. Some of the powders were heat-treated in air at 800 °C for 2 h. The samples were characterized by X-ray diffraction, SEM, TEM and SAED techniques.

3. Results and discussion

Fig. 1 shows typical X-ray diffraction patterns for the obtained powders before and after calcination. Fig. 1a shows that the powders were composed only by SnO crystals, the only exception being the solution prepared with the highest NaOH concentration that exhibited a small amount of unidentified residual phases. The relative intensities of the peaks present in the diffraction pattern differ from the indexed pattern for SnO powder. This is due to the plate-like morphology of the powders as discussed later on the electron microscopy analyses (see Figs. 2 and 3). During sample preparation for X-ray diffraction, the plates have the tendency to align themselves parallel to the sample holder and in this way increasing the intensity of the (002) peak. After heat treatment in air at 800 °C for 2 h, all the powders were completely oxidized and the only phase present in the X-ray diffraction graphs was SnO₂ as shown in Fig. 1b.

The SEM analysis showed that by changing the synthesis parameters, grains with different morphologies and dimensions could be synthesized. Fig. 2 shows the SEM images of the different types of SnO powders that could be obtained by the microwave-assisted hydrothermal method. The characteristic form of growth for all the powders is the plate-like form as can be observed in the SEM images. Shorter syntheses times, with NaOH as mineralizing agent, led to big plates of about 2 μm thickness (Fig. 2a). Hydrothermal treatments of 6 h, under the same experimental parameters, formed smaller, very thin plates with approximately 30 nm thickness (Fig. 2b). Similar results were obtained by Uchiyama et al. [14] through a simple precipitation method at atmospheric pressure using the same mineralizing agent with longer times (more than one day) and lower temperatures (60 °C). These small plates are formed by a process of surface delamination of the big plates. This can be more clearly observed in the powders synthesized with KOH as mineralizing agent (Fig. 2c) where the kinetics of this process is slower. After the same reaction time as for the samples synthesized with NaOH (6 h), one can still notice the small plates forming on the surface of the original big structures. At the other extreme, with the use of a smaller concentration of a weaker base (NH₄OH), small plates are formed even with short reaction times and the crystals are more densely packed then the ones formed by the deconstruction of the bigger plates (Fig. 2d). By lowering the temperature for the hydrothermal process to 120 °C, a new kind of morphology of the powders was observed. Fig. 2e shows typical results obtained when a high base concentration (NH₄OH) and a short synthesis time are used. Under these conditions, the arrangement of the plates is not interpenetrating as before, forming instead a spherical ensemble of intermediate sized plates.

The precursor used in our experiments (SnCl₂·2H₂O) easy hydrolyzes in aqueous solution producing Sn(OH)₂, leading to the formation of SnO nanoplates, as shown in the following set of possible chemical reactions:

\[
\text{Sn}^{2+} + \text{OH}^- \rightarrow \text{Sn(OH)}_2^+ \quad (1)
\]

\[
\text{Sn(OH)}_2^- + \text{H}_2\text{O} \rightarrow \text{SnO} + \text{H}_3\text{O}^+ \quad (2)
\]

Parameters like pressure, temperature, time, concentration of metals and/or base deeply influence the morphologies, sizes and crystallinity of the final products. Jia et al. [16] report the formation of SnO nanowiskers using surfactant (CTAB) that helps in modifying the morphology by playing the role of a template during synthesis. The authors also report that when the surfactant is replaced or not used the morphology of the powders changes from nanowiskers to thin sheets. In our experiments the precursors were surfactant free allowing the growth of SnO nanoplates with different sizes, according to the type of base and its concentration.

Table 1
Concentrations and conditions of hydrothermal treatments applied to the starting solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base concentration (mol/l)</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na5182</td>
<td>NaOH 0.5</td>
<td>180</td>
<td>2</td>
</tr>
<tr>
<td>Na5186</td>
<td>NaOH 0.5</td>
<td>180</td>
<td>6</td>
</tr>
<tr>
<td>Na7182</td>
<td>NaOH 0.75</td>
<td>180</td>
<td>2</td>
</tr>
<tr>
<td>Na7186</td>
<td>NaOH 0.75</td>
<td>180</td>
<td>6</td>
</tr>
<tr>
<td>K5182</td>
<td>KOH 0.5</td>
<td>180</td>
<td>2</td>
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<tr>
<td>K5186</td>
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<tr>
<td>K7186</td>
<td>KOH 0.75</td>
<td>180</td>
<td>6</td>
</tr>
<tr>
<td>NH5122</td>
<td>NH₄OH 0.5</td>
<td>120</td>
<td>2</td>
</tr>
<tr>
<td>NH5126</td>
<td>NH₄OH 0.5</td>
<td>120</td>
<td>6</td>
</tr>
<tr>
<td>NH7122</td>
<td>NH₄OH 0.75</td>
<td>120</td>
<td>2</td>
</tr>
<tr>
<td>NH7126</td>
<td>NH₄OH 0.75</td>
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</table>
Further characterizations by TEM and SAED techniques were performed on thin plates taken from the sample synthesized at 180 °C with KOH. Fig. 3a shows that the plates are very thin and single crystalline. Their natural tendency to align themselves with the supporting surface was responsible for increasing the intensity of the (002) peaks in the X-ray diffractograms, since the (200) interplanar distance of approximately 2.5 Å, calculated from the SAED pattern and measured in the high resolution TEM image (Fig. 3b), indicates that the (002) planes make up the faces of the plates. The SAED pattern is consistent with the tetragonal structure.
of SnO with the unit cell parameters of $a=b=3.802\ \text{Å}$ and $c=4.836\ \text{Å}$.

4. Conclusions

We produced, for the first time, SnO powders with micrometric and nanometric dimensions by the microwave-assisted hydrothermal synthesis. By varying the processing time, temperature and mineralizing agents, nanocrystals having different sizes and morphologies could be obtained. The characteristic form of growth for all the powders is the plate-like shape, with crystal thicknesses varying from 30 nm to 2 $\mu$m. TEM and SAED analyses indicate that the growth direction of these nanoplates is (200), with approximately 2.5 Å interplanar distance, consistent with the indexed pattern for the tetragonal structure of SnO. The control over the oxidation state of Sn in solutions and the heat treatment performed led to the formation of SnO and SnO$_2$ nanocrystals. This is a clear indication that by an accurate control of the two processes, tin oxide nanocrystalline powders with different oxidation states can be obtained. Due to their high surface to volume ratio and variable oxidation states of tin, these nanostructures have a high potential for applications in gas sensors, photo-catalysis processes and photo-electrochemical cells.

Work is now in progress for studying other synthesis conditions as well as for the fabrication of nanostructures from oxide mixtures, including ZnO and In$_2$O$_3$.

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References