Formation of SnO$_2$ Nanoparticles from $\{\text{SnCl}_4 + \text{H}_2\text{O}\}$ Reactive System at 30 MPa and 415°C

Zhen Fang$^1$, Hassane Assaoudi$^1$, Ian S. Butler$^2$, Janusz A. Kozinski$^1$

$^1$Department of Metals & Materials Engineering, $^2$Department of Chemistry, McGill University Montreal, QC, Canada H3A 2B2, *E-mail: zhen.fang@elf.mcgill.ca

Introduction

Nanocrystalline SnO$_2$ is widely used for solid-state gas sensors and transparent electrodes$^{1-2}$. Many metal oxide crystals (e.g., AlOOH, $\alpha$-Fe$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$, NiO, ZrO$_2$ and TiO$_2$) were synthesized in water above its critical point (CP; 374 °C & 22.1 MPa) from $\{\text{salts} + \text{H}_2\text{O}\}$ systems$^3$. However, synthesis of SnO$_2$ was so far only reported to take place in subcritical water ($<\text{CP}$)$^2$. When both temperature and pressure are above the critical point (called supercritical water; SCW), synthesis reaction rate increases dramatically due to low dielectric constant of SCW$^4$. This work focused on synthesis of SnO$_2$ nanocrystals from $\{\text{SnCl}_4 + \text{H}_2\text{O}\}$ system at supercritical region (up to 415 °C and 30 MPa) in a tubular flow reactor.

Experimental

Aqueous SnCl$_4$ solutions (0.1 and 0.4 M) were made by adding double-distilled water to solid SnCl$_4$$\cdot$5H$_2$O (98% purity, Sigma-Aldrich). A flow reactor was used to synthesize SnO$_2$. The flow reactor was made of a 3/8” (9.19 mm) 316-SS tube (11.3 mL; length = 400 mm, wall thickness = 1.59 mm), which was heated by an electric tube furnace (F21100, Fisher, NJ) to 385-415 °C. A high-pressure liquid chromatography pump (Waters Associates, Inc., Milford, MA, Model 510; flow rate 0.1-9.9 mL/min) was used to feed the aqueous SnCl$_4$ solution in a 500-mL beaker. The solution was preheated to 300 °C at the end of a 1/16” 316-SS tube (2.19 mL, length = 5 m, o.d. = 1.53 mm, thickness = 0.39 mm) by a Samox heavy insulated heating tape (Omega, Stamford, Connecticut; STH051-80) and subsequently entered into the reactor. The reaction temperature (385-415 °C) was measured by a K-type thermocouple (Omega; TJ36-Cain-116G-12) inserted into the center of the reactor tube. The exit temperature at the end of the reactor and the preheated temperature outside the 1/16” (1.53 mm) tube were also measured by the same type of thermocouples. The pressure was controlled by a back pressure regulator (Tescom, MN, Model: 54-2162D26; pressure up to 40 MPa) at 30 MPa. After leaving the reactor, effluent is was rapidly quenched with a cooling water jacket to terminate the reaction. Solid particles were obtained by separating the effluent with a super-speed centrifuge (RC-5, Du pont Inst., Sorvall, Newtown, Conn.). The solid sample was analyzed by a scanning electron microscope (SEM; JEOL 840A, Tokyo), energy dispersive X-ray spectrometry (EDX; EDAX phoenix system, NJ), transmission electron microscopy (TEM; JEOL EM2011), Fourier transform infrared (FTIR)
microscopy (UMA 500, Bio-Rad, Cambridge, MA), Raman microscopy (Renishaw 3000, 514.5-nm Ar-ion laser, 50( objective, Gloucestershire, UK) and X-ray diffractometer (XRD; Rigaku Rotaflex RU-20B). These analyses were performed after the sample was calcination at 450 °C for 2 h or 600 °C for 10 h. Particle size was determined from SEM and TEM images directly or calculated by Scherrer equation using XRD pattern parameters according to5:

\[ D_c = K\left(\frac{\lambda}{\beta}\right)\cos\theta \]  

where \( D_c \) is the average crystal size, \( K (= 0.89) \) is the Scherrer constant, \( \lambda (= 15.406 \text{ nm}) \) is the X-ray wavelength, \( \beta \) is the full width at half-maximum (FWHM) and \( \theta \) is the diffraction angle. Tin concentration of the effluent was measured by an inductively coupled plasma spectrometry (ICP; PE40 emission spectrometer; Perkin-Elmer, UT) after filtration by a 25-nm filter paper (Millipore, Bedford, MA). The conversion rate was then calculated.

**Results and Discussion**

Table 1. Experimental conditions and results in supercritical water at 30 MPa (0.1 M SnCl\(_4\))

<table>
<thead>
<tr>
<th>Test 1a</th>
<th>Test 2</th>
<th>Test 3</th>
<th>Test 4</th>
<th>Test 5</th>
<th>Test 6</th>
<th>Test 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp (°C)</td>
<td>385</td>
<td>390</td>
<td>390</td>
<td>390</td>
<td>415</td>
<td>415</td>
</tr>
<tr>
<td>Reaction time (s)</td>
<td>85.8</td>
<td>106.2</td>
<td>79.7</td>
<td>63.7</td>
<td>53.1</td>
<td>50.6</td>
</tr>
<tr>
<td>Conversion rate (%)</td>
<td>73.6</td>
<td>53.2</td>
<td>64.5</td>
<td>70.0</td>
<td>53.1</td>
<td>75.0</td>
</tr>
<tr>
<td>Size (nm)b</td>
<td>4 (3–6)</td>
<td>4 (3–6)</td>
<td>4 (3–6)</td>
<td>4 (3–6)</td>
<td>4 (3–6)</td>
<td>4 (3–6)</td>
</tr>
<tr>
<td>Size (nm)c</td>
<td>8.5</td>
<td>8.5</td>
<td>8.9</td>
<td>7.6</td>
<td>7.3</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Note: a Using 0.4 M SnCl\(_4\); b Measured by TEM after incineration at 450 °C for 2 h;

\(^c\) Calculated by Scherrer equation after incineration at 600 °C for 10 h.

Seven series of experiments were conducted in the flow reactor for \{SnCl\(_4\) + H\(_2\)O\} at 30 MPa, 385-415 °C and 38-106.2 s. Table 1 summarizes the experimental conditions and results. Figures 1-2 show EDX spectra and EDX maps (Sn and O for test 7) after calcination at 450 °C for 2 h. Figure 3 shows TEM images and electron diffraction patterns (test 3) without and with calcination. FT-IR, XRD and Raman spectra are given in Figs. 4-6.

**Fig. 1 EDX spectra after calcination at 450 °C for 2 h**
The conversion rate to solid particles was 53-81% (table 1). The color of particles changed from green to red after calcination. The particle size was about 4 nm after incineration at 450 °C for 2 h but increased to 6-9 nm after incineration at 600 °C for 10 h. In Fig. 1, all particles have strong EDX peaks (keV) at 3.44 for Sn and at 0.52 for O. There are also several weak peaks for Sn at 3-4.5. The strong C peak at 0-0.5, two weak Au & Pd peaks at 2-3 came from carbon tape and coating. The other weak peaks of Si, Cr and Fe were from the corrosion of the reactor made of 316-stainless steel (65% Fe, 17% Cr, 12% Ni, 2.5% Mo, 2.0% Mn, 1.0% Si and other trace elements). The presence of Cl was related to the solution of effluent during separation process. This proves that the particles were mainly composed of Sn and O. Figure 2 shows that they were in the form of SnOx. After calcination at 600 °C for 10 h, the particle size not only increased from an average of 3.7 to 9 nm but also its size distribution varied from 3-5 to 4-14 nm (Fig. 3; a vs. b). However, all particles revealed the same structure due to similar electron patterns. Little change was found in the IR spectra with a band at 1628 cm⁻¹ for all particles after calcination (Fig. 4). But, three strong Raman peaks at 622, 714 and 843 cm⁻¹ (Fig. 5) were detected after calcination, which were attributed to higher crystallinity of the particles⁶. Therefore, Raman rather than IR
Spectrometry provides for better estimation of the degree of crystallinity. Strong XRD spectra (Fig. 6) confirmed high crystallinity of the particles after calcination. XRD spectra proved that all particles are SnO$_2$ tetragonal crystals. Calculation of the particle size using eq. (1) based on XRD data was confirmed by TEM images (e.g., test 3: 8.9 nm vs. 9 nm). SnO$_2$ nanocrystals were formed according to reactions (2) and (3):

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl$$ \hspace{1cm} (2)

$$Sn(OH)_4 = SnO_2 + 2H_2O$$ \hspace{1cm} (3)

**Fig. 5 Raman spectra with and without calcination**

**Fig. 6 XRD spectra with and without calcination**

**Conclusions**

Nanocrystalline SnO$_2$ was synthesized at 385-415 °C, 30 MPa and 38-106.2 s in a tubular flow reactor from \{SnCl$_4$ + H$_2$O\}. A high conversion rate of 53-81% was achieved. It was found that the average particle size was about 3.7 nm (390 °C and 79.7 s). The particle size increased to 9 nm revealing high crystallinity after calcination at 600 °C for 10 h. All SnO$_2$ particles had tetragonal crystalline structure.

**References**