



## Synthesis of High Surface Area Tin Oxide via Sol-gel Process Using Tin Glycolate Precursor

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### ABSTRACT

Synthesis of new metal alkoxide is of importance in metal oxide chemistry. Particularly, metal alkoxides having moisture stable property are remarkably useful for producing high surface area metal oxides via sol-gel process due to capability to control the hydrolysis and condensation rates. Thus, in this work, synthesis of high surface area tin oxide is focused due to its excellent properties, such as, high chemical and mechanical stabilities, high conductivity and low resistivity. To achieve the goal, moisture stable tin glycolate synthesized directly from commercially available tin oxide and ethylene glycol via the Oxide One Pot Synthesis (OOPS) process is used as the precursor via the sol-gel technique. The effects of  $H_2O$ /acid ratios, aging time/temperature, calcinations time/temperature are discussed. The obtained structure of tin oxide is characterized using TGA, XRD, FT-IR and BET.

**Keywords:** Sol-gel, Tin Glycolate, Tin oxide.

### 1. INTRODUCTION

Intense interest has been focused on the investigation of metal alkoxides owing to their use as precursors in the sol-gel synthesis of inorganic metal oxides. High surface area tin oxide has been a subject of great interest due to its excellent properties, such as, high chemical and mechanical stabilities, high conductivity and low resistivity [1]. The sol-gel process is a method preferably used to prepare high surface area tin oxide because of a possibility to control its microstructure and homogeneity. More importantly, the process is easier to prepare three dimensional network metal oxides than other techniques at low temperature [2]. Zhanget et al. [1] synthesized nanocrystalline tin oxide via the sol-gel process using granulated tin dissolving in  $HNO_3$  and citric acid to slow down the hydrolysis and condensation. Wang et al. [3]

synthesized mesostructured tin oxide using a cationic surfactant (cetyltrimethyl ammonium bromide, CTAB) as the organic supramolecular template and hydrous tin chloride ( $SnCl_4 \cdot 5H_2O$ ) in  $NH_4OH$  as the inorganic precursor and counter ion, respectively, under acidic conditions at room temperature.

Recently, Wongkasemjit and coworkers have synthesized several metal alkoxides having moisture stable property, for example, titanium glycolate (Phonthammachai, 2003) [2, 4] directly synthesized via the Oxide One Pot Synthesis (OOPS) process from the reaction of commercially available titanium dioxide and ethylene glycol. In this work, tin alkoxide was thus synthesized via the OOPS process and used as precursor for preparation of high surface area tin oxide. Various sol-gel processing conditions were investigated to obtain the optimal condition, as well.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Tin Glycolate

#### Precursor

Tin Glycolate was synthesized directly via the OOPS method from  $\text{SnO}_2$  which was purchased from Sigma-Aldrich Laborchemikalien GmbH. Ethylene glycol (EG) was obtained from Malinkrodt Baker, Inc. and triethylenetetramine (TETA), acting as base catalyst, was purchased from Facai Polytech. Co. Ltd. The mixture was stirred vigorously and heated up to  $200^\circ\text{C}$  under nitrogen atmosphere for 24 h. The mixture solution was centrifuged to separate unreacted  $\text{SnO}_2$  and the solution was vacuum distilled to remove excess EG and TETA to precipitate off. The white solid product was washed with acetonitrile and dried in a vacuum desiccator.

### 2.2 Sol-gel Processing of Tin Glycolate

Tin glycolate precursor was dissolved in various ratios of  $x$  8M  $\text{HNO}_3$ ;  $y$   $\text{H}_2\text{O}$ , where  $x:y = 0.4, 0.5$  and  $0.75$ . The mixtures were magnetically stirred at room temperature until clear gel was obtained. The gels were calcined at  $300^\circ$ ,  $400^\circ$  and  $500^\circ\text{C}$  by varying calcinations time and heating rate. The structure of obtained tin oxide is characterized using TGA, XRD, FT-IR and BET.

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis of Tin Glycolate

Tin glycolate was successfully synthesized via the OOPS process under an inert atmosphere. The synthetic mixture was continuously removed water generated as by-product from the condensation reaction.

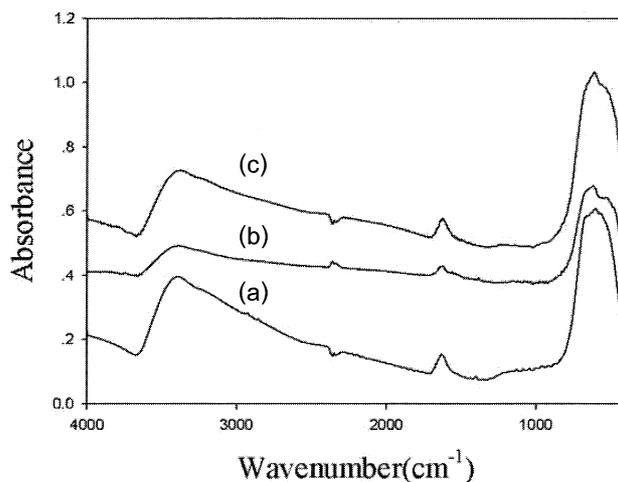
The synthesized and purified precursor was identified using TGA, FT-IR and  $^{13}\text{C}$ -NMR. The TGA thermogram was analyzed on a Perkin Elmer TG-DTA over  $30^\circ$ - $1000^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere, giving  $\sim 63.2\%$  ash yield at  $300^\circ$ - $400^\circ\text{C}$ , corresponding to organic ligand decomposition. The ash yield is closed to the theoretical value of  $63.1\%$ , belonging to the structure of  $\text{Sn}(\text{OCH}_2\text{CH}_2\text{O})$ . FT-IR was recorded on a Nicolet spectrometer with

spectral resolution of  $4\text{ cm}^{-1}$  to determine the functional groups of tin glycolate. The spectrum showed O-H stretching ( $3400$ - $3300\text{ cm}^{-1}$ ) from trace amount of ethylene glycol in the product, C-H stretching ( $2930$ - $2830\text{ cm}^{-1}$ ), C-O stretching ( $1077\text{ cm}^{-1}$ ), Sn-O-C stretching ( $900$ - $880\text{ cm}^{-1}$ ) and Sn-O stretching ( $600$ - $550\text{ cm}^{-1}$ ) of tin glycolate. Solid-state  $^{13}\text{C}$ -NMR spectrum was performed on Bruker 300 MHz spectrometer with cross polarization and magic angle spin (MAS) comparability. The spectrum clearly confirms the structure of tin glycolate at the chemical shift of  $62.5\text{ ppm}$  which is in a good agreement with a recent study on a solid-state NMR of C-O-Sn moiety located at  $\sim 61.5\text{ ppm}$  [5].

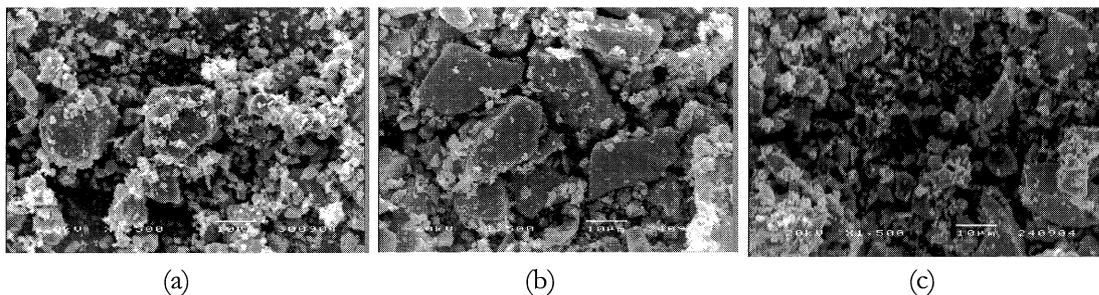
The glycolate was used further as precursor for preparing tin oxide via the sol-gel process. Figure 1 shows the FT-IR spectra analyzed after being calcined at various temperatures with the heating rate of  $0.5^\circ\text{C}/\text{min}$ . From the spectra the band at  $3500$  to  $2500\text{ cm}^{-1}$  indicates the presence of hydrogen bonds between O-H oscillators arising from adsorbed water and Sn-OH group, and the band at  $600$ - $500\text{ cm}^{-1}$  corresponded to Sn-O vibration of metal oxide.

Figure 2 shows the morphologies of the samples calcined at various temperatures. As can be seen, the lowest temperature resulted in some amorphous phase along with the crystalline phase, and when temperature increases, Figure 2 (b), more crystalline phase occurs. These results can be confirmed by XRD, as shown in Figure 3. The broadening peaks increase with increasing the calcinations temperatures from  $300^\circ$  to  $400^\circ$  and to  $500^\circ\text{C}$ . Nevertheless, surface areas of these products show the same trend of the increase in crystallinity giving decreasing value as increasing the calcinations temperature (as listed in Table 1).

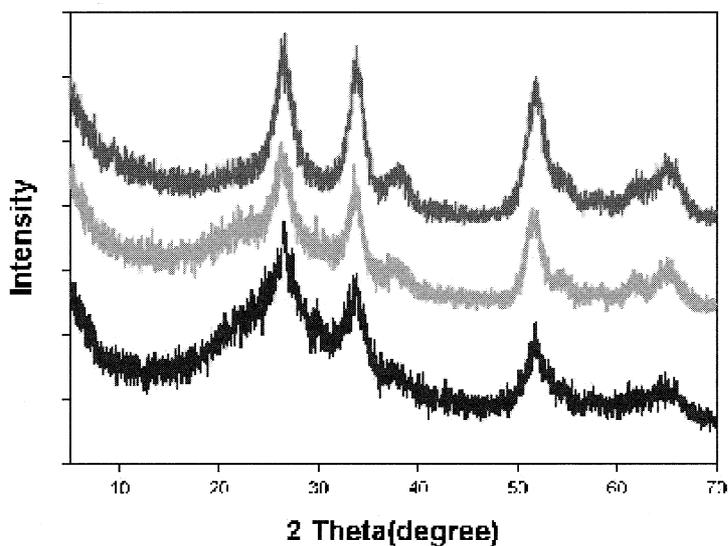
XRD patterns (Figure 4) and SEM micrographs (Figure 5) obtained from investigating the effect of  $\text{HNO}_3/\text{H}_2\text{O}$  ratio on the product formation show that when the  $\text{HNO}_3/\text{H}_2\text{O}$  ratio increases the XRD pattern becomes sharper. This is due to the



**Figure 1.** FT-IR spectra of SnO<sub>2</sub> gels at various temperatures with the heating rate of 0.5 °C/min; (a) 300°, (b) 400° and (c) 500°C



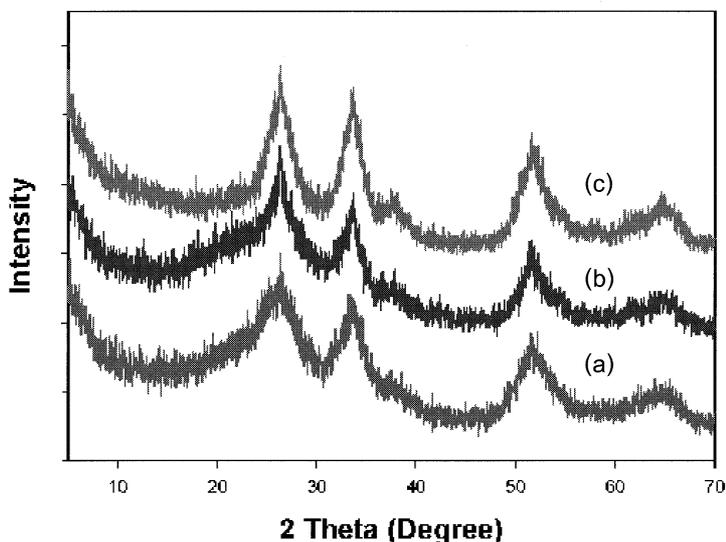
**Figure 2.** SEM images of the calcined SnO<sub>2</sub> at various temperatures with the heating rate of 0.5 °C/min; (a) 300°, (b) 400° and (c) 500°C



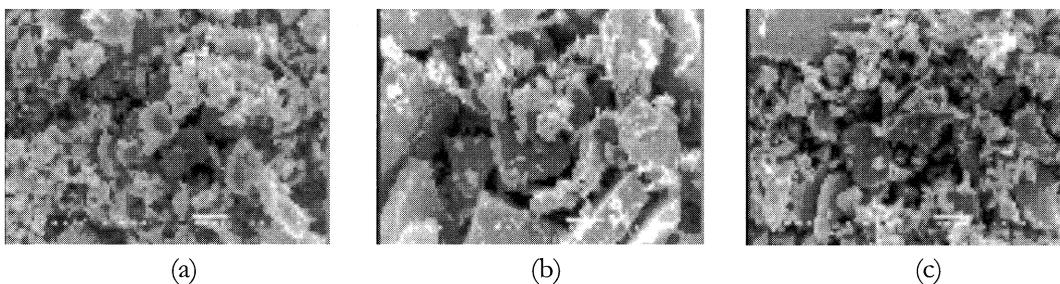
**Figure 3.** XRD patterns of tin oxide gels calcined at various temperatures with the heating rate of 0.5 °C/min; (a) 300°, (b) 400° and (c) 500°C.

**Table 1.** Specific surface area of the tin oxide synthesized by the sol-gel method at various calcinations temperatures.

Temperature (°C)	Specific surface area (m <sup>2</sup> /g)
300	152.19
400	74.56
500	52.14



**Figure 4.** XRD patterns of tin oxide gels calcined at 300°C using the HNO<sub>3</sub>/H<sub>2</sub>O ratio of (a) 0.4, (b) 0.5 and (c) 0.75



**Figure 5.** SEM images of the calcined SnO<sub>2</sub> at the 300°C calcinations temperature using the HNO<sub>3</sub>/H<sub>2</sub>O ratio of (a) 0.4, (b) 0.5 and (c) 0.75

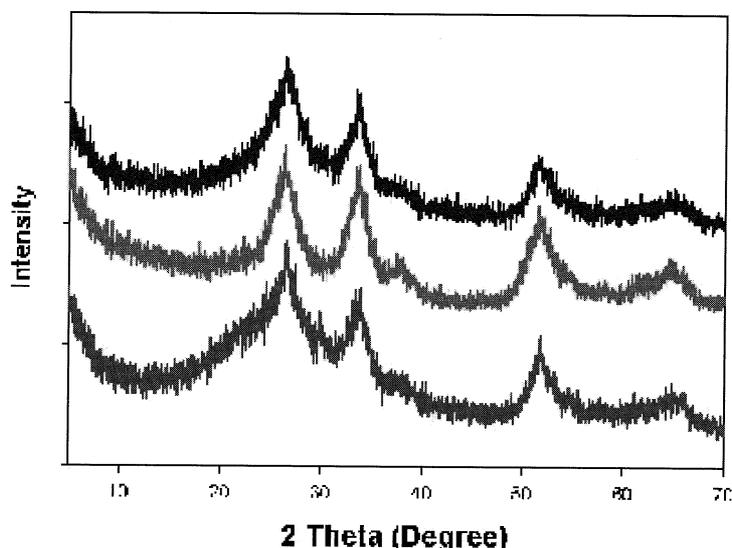
acid acting as a catalyst to hydrolyze the alkoxide ligands [6]. As the acid concentration increases, the hydrolysis and condensation rates of some molecules occur faster, causing precipitation, as a result, giving some amorphous, as can be confirmed by SEM results (Figure 5). When a suitable acid concentration is used, the hydrolysis and condensation rates are controllable and provide enough time for tin oxide molecules to arrange themselves better

to become tin oxide crystals. Table 2 indicates that the highest surface area was obtained at the 0.4 HNO<sub>3</sub>/H<sub>2</sub>O ratio.

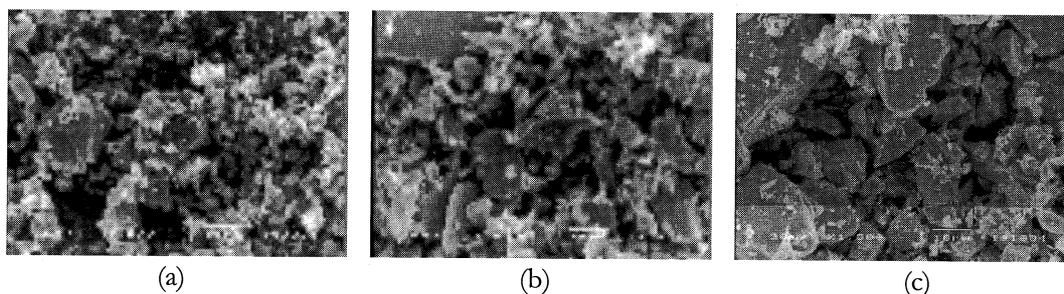
The effect of calcinations times on the tin oxide formation is shown in Figure 6-7 for XRD and SEM results, respectively. At 300°C it is shown that the longer calcinations time causes the more crystallinity. However, too long calcinations time resulted in the phase transformation of tin oxide and became

**Table 2.** Specific surface area of the tin oxide synthesized by the sol-gel method at various HNO<sub>3</sub>/H<sub>2</sub>O ratios.

8 M HNO <sub>3</sub> /H <sub>2</sub> O ratio	Specific surface area (m <sup>2</sup> /g)
0.40	491.18
0.50	205.40
0.75	145.75



**Figure 6.** XRD patterns of tin oxide gels calcined at 300°C for (a) 2 h, (b) 4 h and (c) 6 h



**Figure 7.** SEM images of SnO<sub>2</sub> gels using the heating rate of 0.5°C/min for (a) 2 h, (b) 4 h and (c) 6 h

amorphous again. This can be confirmed by BET analysis (Table 3) showing an increase in the surface area as increasing the calcinations time.

#### 4. CONCLUSIONS

High surface area tin oxide was successfully synthesized using tin glycolate as the

precursor via the sol-gel process. The gel can be formed at room temperature using 8 M HNO<sub>3</sub>. The acid/H<sub>2</sub>O ratio, calcinations time and calcinations temperature have affected the crystal structure of the resulted tin oxide. The highest surface area of ~490 m<sup>2</sup>/g can be obtained when using a suitable condition.

**Table 3.** Specific surface area of the tin oxide synthesized by the sol-gel method at various calcinations times.

Calcinations time (h)	Specific surface area (m <sup>2</sup> /g)
2	152.19
4	145.75
6	246.80

#### ACKNOWLEDGEMENTS

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