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Preparation of nanostructured tin oxide using a sol-gel process based on tin tetrachloride and ethylene glycol

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A sol-gel process starting with tin tetrachloride and ethylene glycol as precursors, has been successfully used to prepare nanostructured tin oxide powders. The molecular structure evolution during the process has been identified using infrared spectroscopy and the underlying reaction mechanisms of the sol-gel process are proposed. Results suggest that the -$OHCH_2CH_2OH$- prevent Cl^- ions from access to tin ions due to steric effect and hence increase the stability of the sol solution. Ethylene glycol functions not only as a complexion agent to form a polymer network but also as a spacer to modulate the distance between metal ions, preventing metal oxide particles from aggregation during earlier stages of organics removal. Further, conversion of xerogel to tin oxide are studied using thermogravimetric analysis, X-ray diffraction, and electron microscopy. It is found that cassiterite begins to form at a temperature as low as 250 °C when organics start to burn off. However, nanocrystalline tin oxide powders are formed only after the chemically bonded hydroxyl groups are completely removed at about 600 °C.

1. Introduction

Because of its unique electrical and catalytic properties, tin oxide has been widely used for various electrochemical and catalytic applications, such as solid state gas sensors for environmental monitoring [1] and active catalyst for partial oxidation and amino oxidation of olefins [2–4]. For these applications, small particle size or large specific surface area is essential to high performance. Among various chemical synthesis methods for preparation of metal oxides of large surface area, a sol-gel process offers several advantages over other methods, including lower processing temperature, better homogeneity, controlled stoichiometry, and flexibility of forming dense monoliths, thin films, or nanoparticles. Different precursors may be used as starting materials for preparation of tin oxides using a sol-gel process such as tin alkoxide [5] and tin tetrachloride [6–9]. However, tin alkoxides are not only expensive but also extremely sensitive to moisture, heat, and light, implying that the process is difficult to control and not cost-effective. The use of tin tetrachloride [10] as precursor and water as solvent overcomes the problems associated with alkoxides. In this process, $NH_4(OH)$ solution is added to an aqueous $SnCl_4$ solution to form tin hydroxide precipitate, which is then filtered and washed with distilled water to remove Cl^-. Then, aqueous NH_3 solution was added to the precipitate and, over a period of time, this mixture becomes clear sol and later turns to gel [9]. Nevertheless, there are two disadvantages associated with the process. First, it is difficult to control the stoichiometry of a doped tin oxide since NH_3 readily forms complexes with the metal ions to some extent, which are typically soluble and remain in the solution. Accordingly, repeated washing of the precipitate using distilled water could alter the stoichiometry of the intended metal oxides. Second, residual Cl^- ions not only affect the stability of the sol but also retard the kinetics of gelation. Goodman and Gregg [11] reported that a period of up to 30 days was required to turn the sol into a transparent bluish gel.

To prepare powders with large specific surface areas, an alcoholic solvent is preferred to water because of its lower surface tension so that a "loose" powder can be obtained from collapsing of gel structure. In addition, another advantage of the process using alcoholic solvent is that the sol solution is stable and gelation process is not susceptible to Cl^-. Hence it is not necessary to eliminate Cl^- from the sol solution, which would ensure the stoichiometry of the final doped metal oxide. Although Yamamoto *et al.* [12] prepared indium tin oxide thin films using thermal decomposition of ethylene glycol solution, little is known about the molecular structure change during the sol-gel process. The objective of this study is to gain an insight into the molecular structure change during the sol-gel process based on ethylene glycol and metal chlorides.

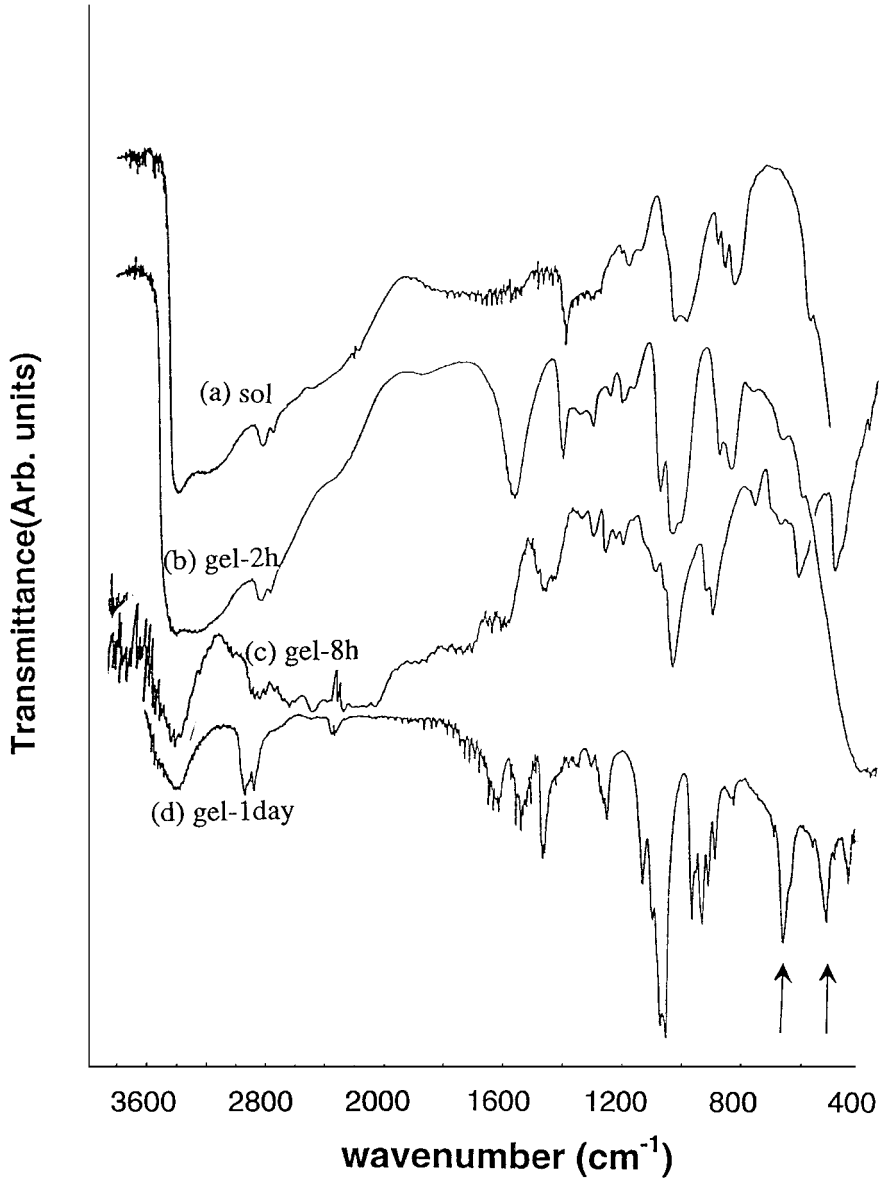


Figure 1 FTIR spectra of SnO_2 sol-gel transition: (a) a sol solution; (b) a gel dried at 150 °C for 2 h; (c) a gel dried at 150 °C for 8 h; and (d) a gel dried at 150 °C for 1 day.

2. Experimental

$SnCl_4$ (99%) and ethylene glycol (reagent grade) were obtained from Aldrich and Fisher, respectively, and used as received. A solution of 0.1 mol % $SnCl_4$ in ethylene glycol was prepared by dissolving appropriate amounts of $SnCl_4$ in ethylene glycol under vigorous stirring at 80 °C until colorless and transparent solution was obtained. The solution was then heated to 120 °C and kept at the temperature to evaporate water and hydrochloride. During evaporation, samples of the solution were periodically taken for FTIR analysis. When the solvent was completely removed, a dark brown gel was obtained. The gel was aged for 20 min and then dried at 150 °C for 24 h. Drying was essentially completed within the first 8 h. After drying xerogel was heat-treated at temperatures varied from 250 to 600 °C and nanosized tin oxide powders were obtained by heat-treatment at 600 °C for 2 h.

The evolution of the molecular structure of sol and gel as well as the microstructure of oxide throughout the sol-gel process was characterized using infrared spectroscopy (Nicolet 205 FTIR spectrometer), X-ray diffraction (Philips PW-1800 X-ray diffractometer), thermogravimetric analysis (Perkin-Elmer TG S-2), and electron microscopy (Hitachi HF-2000 Transmission Electron Microscope). The structural features of the xerogel were characterized using FTIR transmittance spectra acquired between 400 and 4000 cm^{-1} (the sample powder was diluted with KBr). Special attention was paid to the bands at 650 and 500 cm^{-1} due to vibration of O–Sn–O bridging bond and Sn–O terminal bond, respectively. Structural changes induced by subsequent heat-treatment was also investigated using FTIR in conjunction with XRD. TG curves were recorded for xerogel which was first dried at 200 °C for 2 h. Samples for TGA were placed in a Pt crucible in air and the temperature was swept at 10 °C/min to 700 °C.

3. Results and discussion

3.1. Stability of sol

When tin chloride was dissolved in ethylene glycol at 80 °C, colorless and transparent sol solution formed.

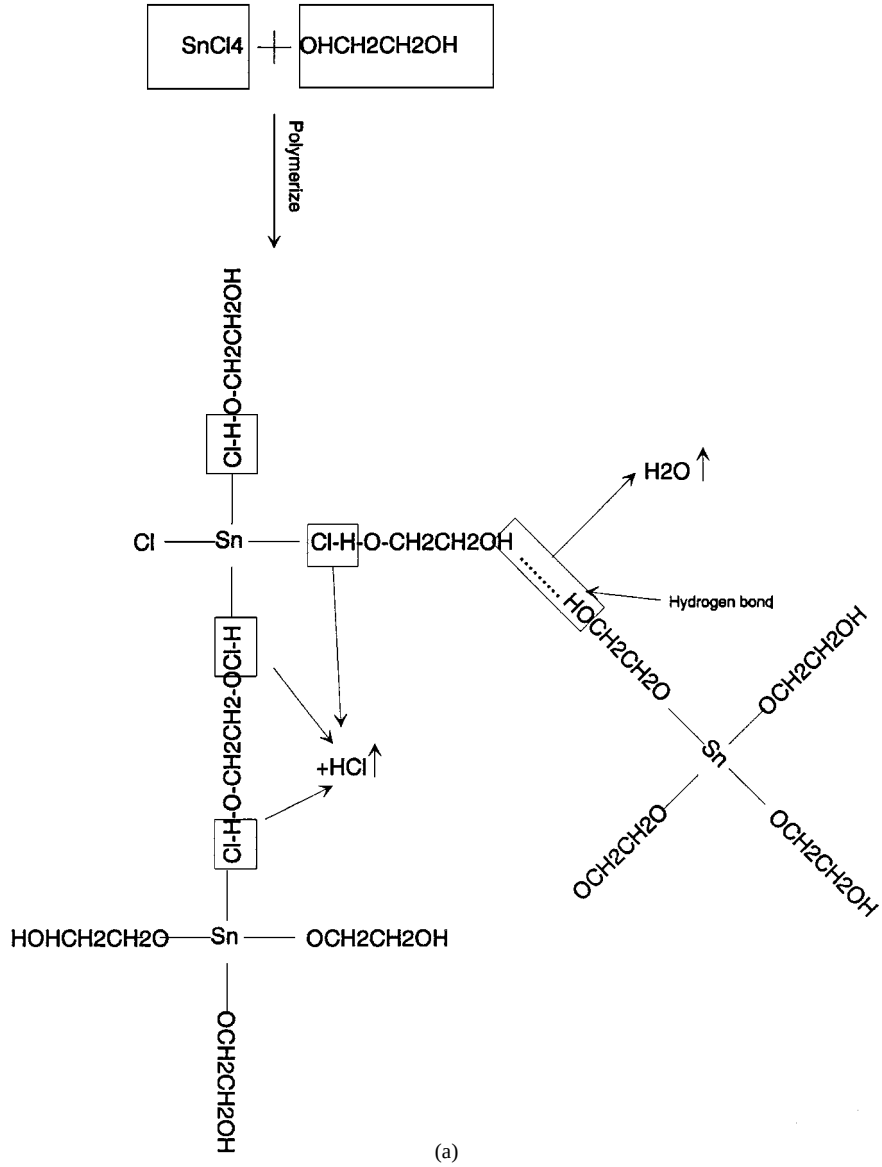
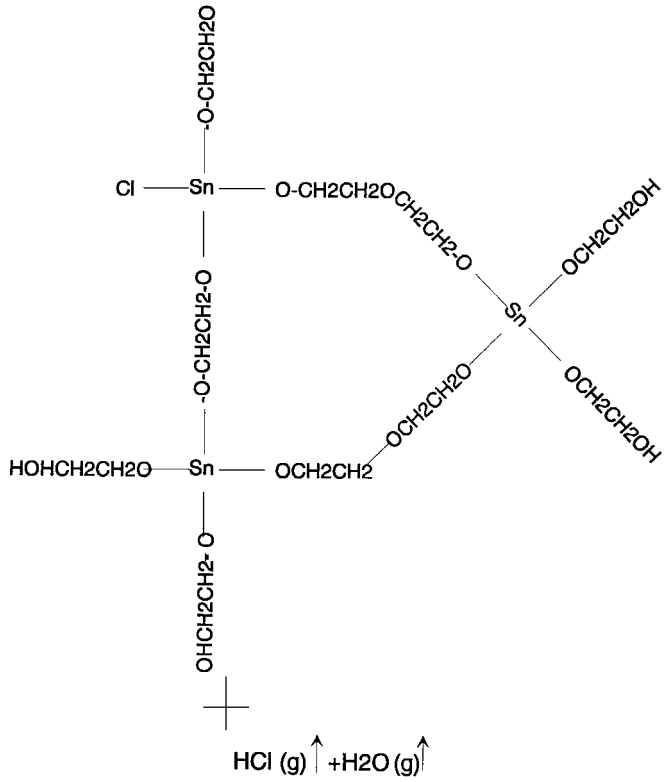


Figure 2 Proposed structural evolution during the sol-gel process: (a) reaction between ethylene glycol and tin chloride with release of HCl and H_2O; and (b) the resultant polymeric network of the gel. (*Continued*).

The pH of the solution was 1.5, indicating the release of HCl during dissolution of $SnCl_4$. Shown in Fig. 1 are several FTIR spectra of the solution and the gels dried at 150 °C for different periods of time. A typical broad band at 3400 cm^{-1} indicates that a strong hydrogen bond formed between hydroxyl groups from ethylene glycol. Further, the formation of some O–Sn–O bridging bond is confirmed by the small peak localized at 650 cm^{-1}. The characteristics of the O–Sn–O bridging mode and the terminal Sn–O mode were observed, respectively, at 650 and 500 cm^{-1}, in our study, rather than at 667 and 551 cm^{-1} as reported previously by Orel *et al.* [6]. This is because the precursors and solvents used in our system are different from those used in the previous study [6]. Another reason for this difference is that the valence state of tin ion is four in our system and two in the previous case [6]. As expected, the Sn–O terminal mode was not observed in the sol due to the existence of excess ethylene glycol.

The degree of aggregation of particles in sol solution plays an important role in colloidal stability, which may further influence the structure of derived gel and the morphology and microstructure of metal oxides during firing. Satoshi *et al.* [9] revealed that the presence of residual chloride ions decreased the colloidal stability of sols using water as solvent. A prolonged dialysis of a sol solution for 7 days to remove chloride ions resulted in a colloidal suspension that was stable only when the concentration of tin ions was less than 0.11 M. Washing with small amount of distilled water to remove the excess residual ions (chloride and ammonium) yielded stable sols only when the concentrations were less than 0.009 M. It is believed that the residual Cl^- may modify the physical and chemical characteristics of the solution and the interfacial properties of the colloidal particles in suspension, which would result in the formation of aggregate. In our study, it is found that the sol solution is not at all susceptible to the Cl^- and is quite stable even when the concentration of tin ions reaches 1 M. One possible explanation is that tin ions in the solution are surrounded by -OCH_2CH_2O-, whose molecular size is much bigger than that of hydroxyl group and, thus, prevent Cl^- from accessing to the tin ions. In addition, the large amount of protons released by the reaction



(b)

Figure 2 (*Continued*)

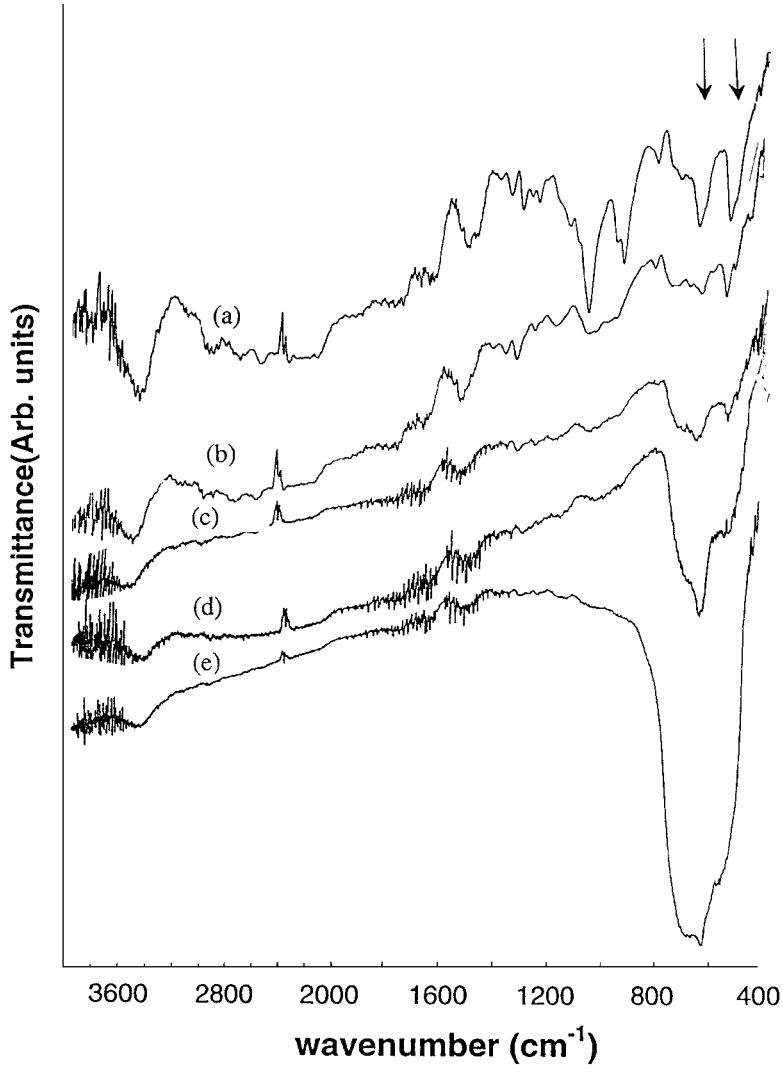


Figure 3 FTIR spectra of the xerogel heat-treated at different temperatures: (a) 200 °C; (b) 300 °C; (c) 400 °C; (d) 500 °C; and (e) 600 °C.

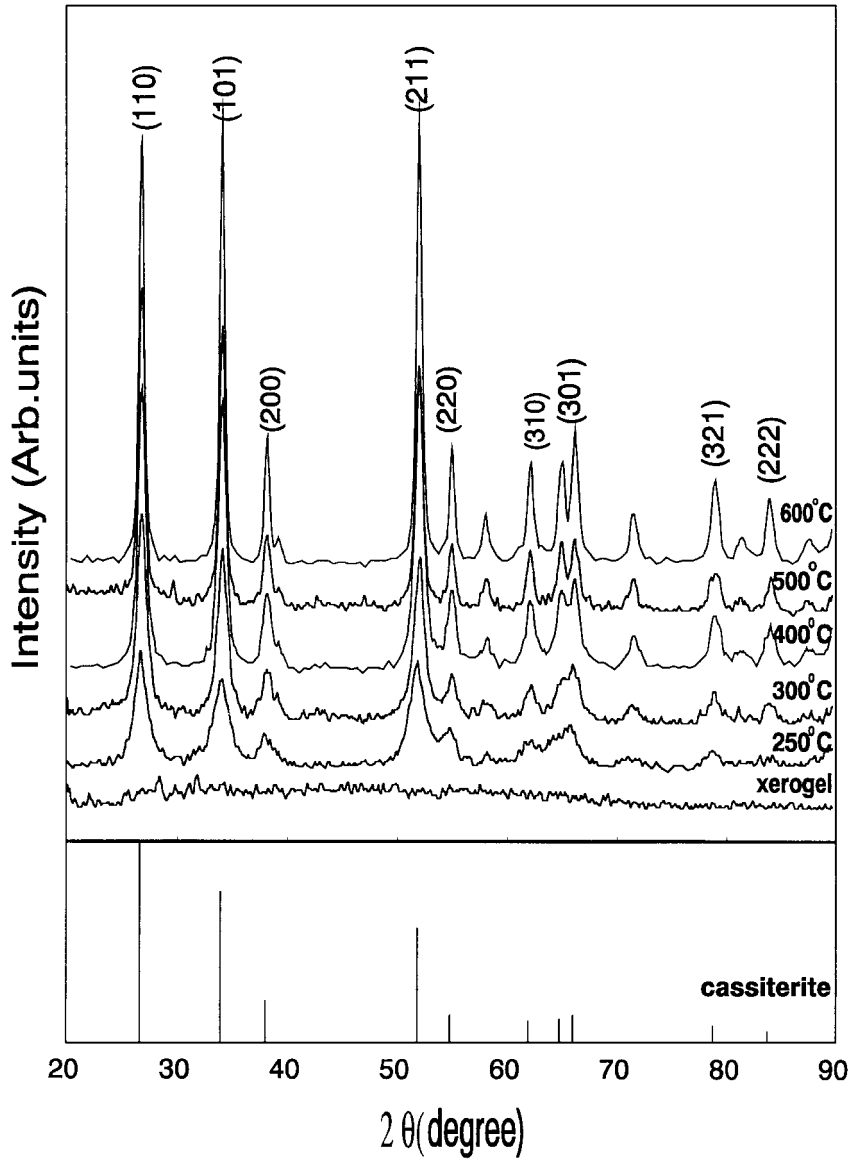


Figure 4 X-ray diffraction patterns of xerogels at different stage of transition to oxide. The temperature by each pattern represents the temperature at which the gel was heat-treated for 2 h.

will be adsorbed on the surface of the particles so that they are positively charged, which also improve the stability of sol solution through preventing particles from aggregation.

3.2. Transition to gel and xerogel

With evaporation of H_2O and HCl, the viscosity of the sol increased continuously and, eventually, a dark brown gel formed. It is noted from Fig. 1 that, during drying, the peak at 3400 cm^{-1} becomes smaller and sharper whereas the intensity of O–C–O mode at 1030 cm^{-1} gets stronger. These observations confirm that, at temperatures $\leq$150 °C, the hydrogen bond underwent dehydration and resulted in ester bridge O–C–O, which is one of the mechanisms of the formation of polymeric network. In addition, with the liberation of HCl and free ethylene glycol, the formation of O–Sn–O bonds also promote the interconnectivity of the system. Accordingly, the molecular evolution during drying can be schematically shown in Fig. 2. In the dried gel, most of the Sn ions are coordinated with four oxygen ions although the terminal tin ions are coordinated with less than four oxygen ions. It is also noted that neither C–Cl nor Sn–Cl bonds were detected in the structure; this explains why the process is not susceptible to Cl^- ions. Further, the observed little difference in FTIR spectra of the gel dried for more than 8 h indicates that the drying is essentially completed in 8 h. About 24 h later, a pulverized xerogel was obtained. Examination of the morphology of the gel using an SEM suggests that the xerogel is homogeneous and there are no apparent particles. These results agree well with the XRD patterns shown in Fig. 4; although most tin ions are bonded with oxygen in the xerogel, they are still in an amorphous state when dried at temperature below 250 °C.

3.3. Formation of crystalline tin oxide

The pulverized gels were then heat-treated at temperatures from 250 to 600 °C and the structural evolution of xerogels heat-treated at different temperatures was revealed using FTIR as shown in Fig. 3. Attention is paid to the ratio of the relative intensity for the bands of Sn–O terminal mode to that of O–Sn–O bridging

mode because this ratio could be correlated to different types of atomic rearrangement occurring during the heat treatments of SnO_2 xerogel and oxide [13]. The spectra shown in Fig. 3 indicate that the ratio remains unity over the temperature range up to 300 °C; implying no significant rearrangement occurs below 300 °C because the residual organic molecules prevent the rearrangement of O–Sn and O–Sn–O bonds. It is reported in a previous study [6], however, that rearrangements of these bonds do occur at much lower temperatures (25 °C) when water is used as solvent in the inorganic route. In our study, the ratio decreased dramatically at temperature above 400 °C, even faster than that via the inorganic route. This implies that the activity of the xerogel derived from ethylene glycol-based system is higher than that derived from water-based system.

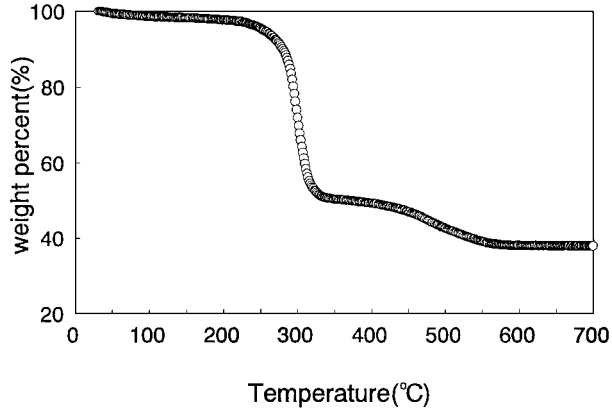


Figure 5 Thermogravimetric analysis of gel-oxide transition in the temperature range of 25 to 700 °C. The first dramatic weight loss (250–330 °C) corresponds to the removal of organics whereas the second one (430–550 °C) corresponds to the removal of chemically bonded OH groups.

Fig. 4 shows the XRD patterns of the gels heat-treated at different temperatures. The crystallization of tin oxide occurs at a temperature as low as 250 °C. Shown in Fig. 5 is a thermogravimetric curve of the xerogel in the temperature range from 200 to 700 °C. The first dramatic weight loss, beginning at about 250 °C and ending at about 320 °C, is assigned to the pyrolysis of organics. XRD and TG analysis seems to indicate that the crystallization of tin oxide starts as the organic groups are removed. The second significant decrease in weight is believed to be due to the desorption of chemically bonded hydroxyl groups from gel particles. This is confirmed by the disappearance of the characteristic hydroxyl peaks in the range from 3000 to 3600 cm^{-1} in the infrared spectra of samples heat-treated at temperatures above 400 °C (Fig. 3). At temperatures above 600 °C, no further weight loss was observed, indicating complete removal of organic and hydroxyl groups and formation of crystalline SnO_2. From the broadening effect of the X-ray (110) peaks, the crystallite sizes are estimated using the Scherrer's equation [14] to be about 2.6 (250 °C), 4.8 (300 °C), 5.4 (400 °C), 7.3 (500 °C), and 10.2 nm (600 °C), respectively.

Fig. 6 shows the morphology of tin oxide particles derived from a gel fired at 600 °C for 2 h. The average

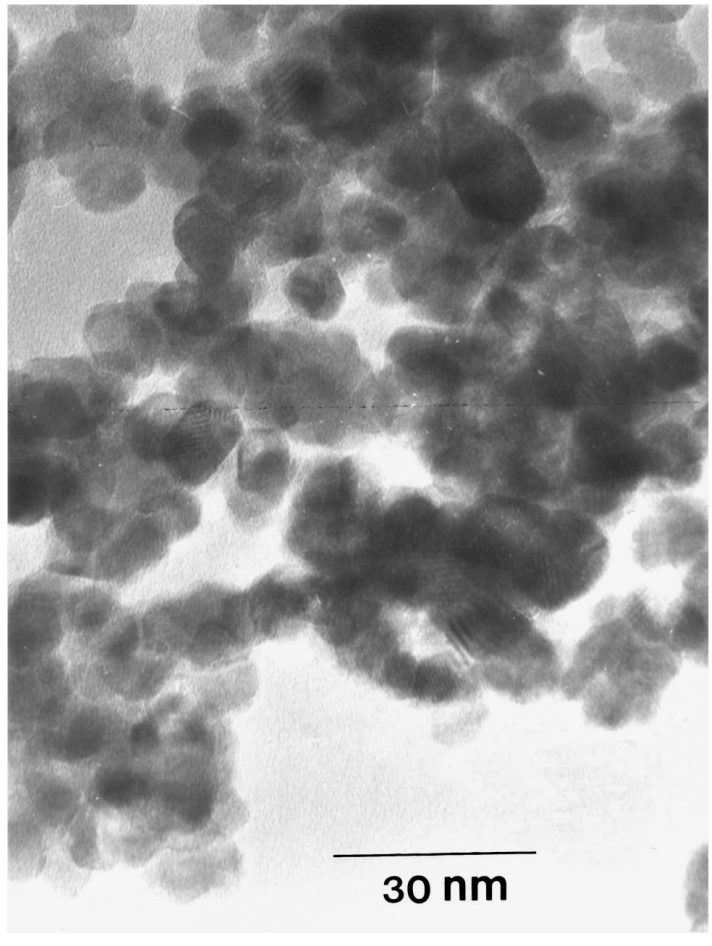


Figure 6 A TEM micrograph of the SnO_2 powder derived from a gel fired at 600 °C for 2 h.

particle size is about 12 nm. Most of the nanoparticles are well separated although some of them partially aggregated. This micrograph and the XRD data indicate that structural rearrangement on an atomistic scale (e.g., crystallization) occurs at a temperature as low as 250 °C, whereas particle size increased with the firing temperature due to continued grain growth. Accordingly, the fabrication of tin oxide nanoparticles are feasible only under appropriate thermal conditions.

Lim and Oh [8] also investigated Pd-doped SnO_2 powders prepared using water as solvent through three different impregnating processes to introduce dopant. The powders they obtained are highly aggregated. Since it is believed that gelation under basic condition leads to gels with large pore volumes and surface areas, Lim and Oh used NH_3 as precipitant and maintained the solution in an alkaline environment. In our study, however, acidic condition was chosen and well separated powders were obtained. Thus, acidity seems not to be a critical parameter in the process using ethylene glycol as solvent.

4. Conclusion

Nanostructured SnO_2 powders have been successfully prepared using a sol-gel process starting with tin tetrachloride and ethylene glycol. Compared to a sol-gel process using metal alkoxides as precursors, this process is not only cost-effective but also simple to control; the sol solution is extremely stable even in the presence of high concentration of hydrochloride and the kinetics of the gelation process is not susceptible to Cl^- ions. In this process, ethylene glycol functions not only as a complexion agent to form a polymeric network but also as a spacer to modulate the distance between metal ions, preventing metal oxides from aggregation during earlier stage of organic removal. Crystallization of tin oxide starts at about 250 °C, and growth continues at higher temperatures as the organics are removed. Fine powders with average particle size of 12 nm are obtained upon firing at 600 °C for 2 h.

Acknowledgements

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