Preparation of mesoporous tin oxide for electrochemical applications

Fanglin Chen and Meilin Liu*

*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA.
E-mail: meilin.liu@mse.gatech.edu*

Mesoporous tin oxide stable up to 500 °C has been prepared for the first time using both cationic and neutral surfactants.

Following the discovery of the MCM family of mesoporous silicates using the supramolecular templating approach,[1] mesoporous materials have attracted considerable attention because of their remarkably large surface areas and narrow pore size distributions, which make them ideal candidates for catalysts, molecular sieves, and as electrodes in solid-state ionic devices. A number of related synthetic strategies have been developed and a variety of materials, in terms of both composition and structure, have been prepared.[2–4]

Tin oxide is a wide-energy-gap semiconductor and has been widely used as a catalyst for oxidation of organic compounds, and for applications such as solid-state gas sensors, rechargeable Li-batteries, and optical electronic devices. The success in many of these applications relies critically on the preparation of crystalline SnO_2 with uniform nanosize pore structure. Consequently, the synthesis of thermally stable mesoporous SnO_2 is of great importance.

To date, several preparative approaches utilizing a supramolecular templating mechanism have been reported for the preparation of mesoporous tin oxide.[5–7] Upon removal of the surfactant, however, the mesoporous structures were destroyed; in other words, the preparation of mesoporous SnO_2 without the support of a surfactant has not yet been achieved. For example, upon hydrolysis of $SnCl_4$ in the presence of sodium dioctylsulfosuccinate (AOT, an anionic surfactant), Rao and Ulagappan[5] obtained a mesoporous SnO_2–AOT material with an average pore size of 3.2 nm. Attempts to remove the surfactant either by calcination at *ca.* 400 °C or by solvent extraction, however, resulted in collapse of the mesoporous structure. Similarly, upon hydrolysis of $SnCl_4$ in the presence of sodium dodecyl sulfonate (another anionic surfactant), Qi *et al.*[6] obtained mesoporous tin oxide with an average pore size of 4.1 nm. Again, the mesostructure collapsed when the surfactant was removed at 400 °C. Starting with tin isopropoxide and tetradecylamine (a neutral surfactant), Pinnavaia and coworkers[7] obtained mesoporous tin oxide with an average pore size of 5.6 nm. The mesoporous structure was stable up to 350 °C, but was destroyed upon calcination at 400 °C and the surface area was greatly reduced.

For electrochemical applications such as gas sensors, however, thermal stability of a mesoporous structure at high temperatures and without the support of a surfactant is critical for high catalytic reactivity, fast charge and mass transport, and long-term microstructural stability and durability. Thus, the objective of this study was to develop synthesis procedures for the preparation of mesoporous SnO_2, stable at high temperatures (> 400 °C), without the support of a surfactant. We have explored both neutral (S^0I^0) and electrostatic (S^+I^-) templating approaches to prepare mesoporous SnO_2.
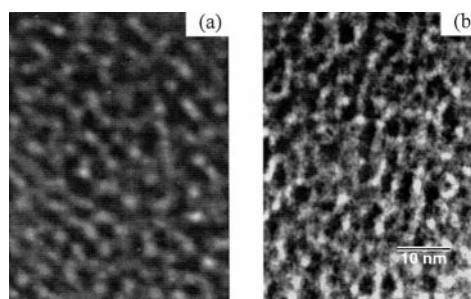
In the neutral templating approach,† tetradecylamine (a neutral primary amine) was used as the surfactant (S^0) or structure director and tin isopropoxide as the inorganic precursor (I^0). Fig. 1 shows X-ray diffraction (XRD) patterns of the as-synthesized product and the mesostructured SnO_2 after calcination at 500 °C for 2 h. While the as-synthesized product
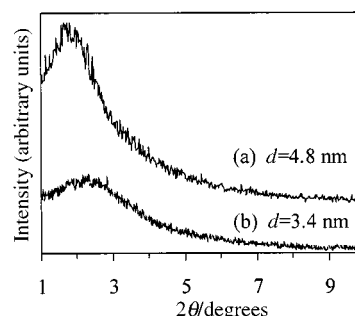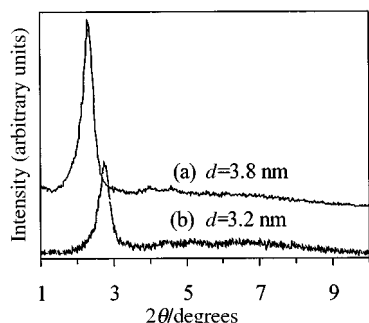

Fig. 1 XRD patterns of tin oxide synthesized *via* a neutral templating approach: (a) as-synthesized and (b) after calcination at 500 °C for 2 h.

showed a sharp diffraction peak at low angle (characteristic of a mesostructured material), the calcined sample displayed only a very broad diffraction peak. However, TEM analysis indicated that the calcined solid was indeed mesoporous; the short-range hexagonal order can be seen from the TEM images shown in Fig. 2. The average *d*-spacings of the as-synthesized and the as-calcined mesostructures are 4.8 and 3.4 nm, respectively, as calculated from the positions of the XRD peaks, which are also consistent with the pore sizes as determined from the TEM micrographs. Thermogravimetric analysis of the as-synthesized tin oxide mesoporous powder under N_2 flow indicated that the weight loss occurred between 200 and 500 °C, probably resulting from the decomposition of the surfactant and subsequent removal of the carbon residue. There was no detectable weight loss above 500 °C, indicating that the amine surfactant was completely removed from the mesoporous SnO_2 structure upon calcination at 500 °C for 2 h. Thus, we have obtained mesoporous SnO_2 (without the support of a surfactant) which is stable up to 500 °C.

In the electrostatic templating approach, cetyltrimethylammonium bromide (CTAB) was used as the structure director (S^+) and $[Sn(OH)_6]^{2-}$ used as the inorganic precursor (I^-).‡ This approach is similar to that employed by Suib and coworkers.[8]§ Fig. 3 shows the XRD patterns of the as-synthesized product and the mesostructured SnO_2 after calcination at 500 °C for 2 h. A sharp diffraction peak at small angle corresponding to the (100) diffraction was observed in both cases. Small peaks due to the (110) and (200) reflections are also observable before and after the removal of the surfactant.
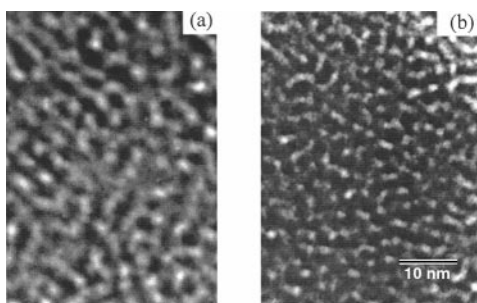

Fig. 2 Representative TEM micrographs of tin oxide synthesized *via* a neutral templating approach: (a) as-synthesized and (b) after calcination at 500 °C for 2 h.

Fig. 3 XRD patterns of tin oxide synthesized *via* an electrostatic templating approach: (a) as-synthesized and (b) after calcination at 500 °C for 2 h.

The average *d*-spacings of the (100) layers in the as-synthesized and calcined SnO_2 mesostructures are 3.8 and 3.2 nm, respectively, as determined from the peak positions in the XRD patterns. Thermogravimetric analysis of the as-synthesized tin mesoporous powder under an N_2 flow showed that most of the weight loss occurred below 500 °C, implying that the surfactant could be removed from the mesoporous SnO_2 structure upon calcination at 500 °C for 2 hours. Fig. 4 shows the TEM images of the mesoporous SnO_2 before and after surfactant removal.

Fig. 4 Representative TEM micrographs of tin oxide synthesized *via* an electrostatic templating approach: (a) as-synthesized and (b) after calcination at 500 °C for 2 h.

In both approaches, the (100) peak shifts to slightly larger angles after removal of the surfactant, indicating that the mesostructure (and hence the pore size) contracted slightly upon surfactant removal. After calcination at 500 °C for 2 h, the BET surface area of the mesoporous SnO_2 from the neutral templating approach is *ca.* 107 m^2 g^{-1} and that from the electrostatic templating approach is *ca.* 143 m^2 g^{-1}. The measured surface areas are much smaller than those for MCM-type materials (usually > 500 m^2 g^{-1}), implying that some of the pores are closed and are not accessible to BET measurement. It is clear, however, that the electrostatic templating approach is better than the neutral templating approach for the preparation of mesoporous SnO_2 with well organized structure (as revealed by XRD and TEM) and large surface area.

The major challenge in obtaining mesoporous oxides is to preserve the mesoporous structures while the surfactant is being removed. In order to avoid the collapse of the mesostructure, it is necessary to form a rigid three-dimensional inorganic framework based on Sn–O–Sn bonding before surfactant removal. In this study, it is believed that Sn–O–Sn bonds are formed during the aging process through water- or alcohol-condensation. Once a condensed 3-D mesoporous network is formed, its essential mesoporous features are likely to be preserved upon surfactant removal at 500 °C. Although there is no direct evidence to prove the formation of the Sn–O–Sn network during the aging process, we believe that this is a critical step to successful preservation of the mesoporous structure during surfactant removal. The detailed mechanism of formation of mesoporous SnO_2 structures which are stable at high temperatures is still under investigation.

Preliminary testing of a CO_2 gas sensor based on the mesoporous SnO_2 from the electrostatic templating approach showed a response time of 110 s when the gas was switched from CO_2 to air, which is seven times faster than CO_2 gas sensors based on nanosized SnO_2 powders derived from a sol–gel process (response time *ca.* 750 s[9]). Currently, the processing conditions are being further optimized to reduce the pore diameters or increase the surface area in an effort to enhance the sensitivity and speed of response of gas sensors based on mesoporous SnO_2. Further, the cycling behavior and reversible capacities of mesoporous SnO_2 used as an electrode in lithium batteries are still under investigation and will be reported in due course.

Notes and references:

† 3.0 g of tin isopropoxide and 0.36 g of 1-tetradecylamine were added to 80 ml of propan-2-ol and stirred to form a homogeneous solution. This solution was kept under water-saturated air at room temp. for 48 h prior to loading to an autoclave and being kept at 80 °C for 24 h. The precipitate was then filtered off, washed with water and ethanol and then refluxed in ethanol for 10 h. The dried product was crushed into a powder and calcined at 500 °C in static air for 2 h.

‡ 10 g of $SnCl_4$ was dissolved in 30 ml distilled deionized water (DDW) and heated to 75 °C. 6.2 g of NaOH dissolved in 15 ml DDW was added to the $SnCl_4$ solution under vigorous stirring to form $Sn(OH)_4$. The pH of the solution was maintained at *ca.* 10. Then 6.7 g of CTAB was dissolved in 45 ml DDW and this solution was added to the $Sn(OH)_4$ solution. The mixture was stirred at 75 °C for 30 min and then loaded in an autoclave kept at 75 °C for 24 h. It was then aged at 90 °C for 24 h. After cooling to room temperature, the precipitate was recovered by filtration on a Buchner funnel, washed with water and dried. The as-synthesized product was then calcined in air at 500 °C for 2 h.

§ Starting from $MnCl_2$ and CTAB, Suib and coworkers[8] synthesized mesoporous manganese oxide structures which were reported to be stable up to 1000 °C. They proposed that an electrostatic interaction was established between $[Mn(OH)_6]^{4-}$ and the positively charged surfactant head group (CTA$^+$). Owing to the similarity between $[Sn(OH)_6]^{2-}$ and $[Mn(OH)_6]^{4-}$, it was thought that this approach was applicable to the preparation of mesoporous SnO_2.

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