Supramolecular assembly of mesostructured tin oxide

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The first example of a mesostructured tin oxide that is stable to surfactant removal has been prepared by hydrolysis of tin isopropoxide in the presence of a neutral amine surfactant (tetradecylamine).

Since the discovery of mesoporous silica molecular sieves in 1992[1,2] several supramolecular assembly pathways have been reported and extended to the synthesis of a variety of mesoporous metal oxide compositions including alumina, titania, niobia and zirconia.[3] Other surfactant metal oxide mesostructures also have been reported, but they have not been stable with respect to surfactant removal. Among them is a tin oxide assembled by the hydrolysis of $SnCl_4$ in the presence of an anionic surfactant.[4] Tin oxide is particularly interesting because it has semiconductive properties and its performance in semiconductor gas sensor applications is highly dependent upon its structure and morphology.[5,6] The structure directing capabilities of a supramolecular assembly pathway may allow for the controlled optimization of a mesostructured form of SnO_2 for chemical sensing.

In this study we use a neutral S^0I^0 assembly pathway‡ to produce the first stable mesostructured tin oxide. The mesostructure is synthesized using a neutral primary amine surfactant as the structure director (S^0) and tin isopropoxide as the inorganic precursor (I^0). We have chosen this pathway because it tends to provide mesostructured materials with thick pore walls.[7] Materials with thick walls may be less susceptible to collapse upon surfactant removal.[8] We have successfully prepared stable mesostructured tin oxide using a range of primary amines including octylamine, dodecylamine, tetradecylamine and hexadecylamine.[9] We report here on mesostructured SnO_2 assembled from tetradecylamine and compare it to the oxide prepared in an analogous manner in the absence of surfactant.

The XRD patterns of the as-synthesized products prepared in the presence and absence of tetradecylamine and that of a commercial SnO_2 sample are presented in Fig. 1. The pattern of tin oxide assembled with tetradecylamine contains the low angle peak (*d*-spacing: ≈ 46 Å) characteristic of mesostructured materials,[1–4,7,8] whereas the tin oxide prepared in the absence of surfactant and the commercial oxide do not exhibit a low angle reflection. However, all three materials exhibit reflections of comparable integral intensity in the region 2θ 20–80° that are characteristic of cassiterite, signifying that the as synthesized materials are largely crystalline in nature. On the basis of the < 110 > line widths, the products obtained by hydrolysis in the presence or absence of surfactant have the same average domain size (15 Å). The hydrolysis and condensation processes are apparently similar in both reaction systems, except that SnO_2 crystallites are assembled into a mesostructure in the presence of tetradecylamine. The presence of a single low angle XRD reflection is consistent with a sponge-like or wormhole channel motif.[7]

XRD patterns of the mesostructured SnO_2 after calcination at different temperatures are shown in Fig. 2. It can be seen that the average *d*-spacing for the mesostructure is largely unchanged by calcination at 300 °C, which indicates that the surfactant has been removed without structural collapse. Also, the average

crystallite domain size has increased from 15 to 18 Å. Although low temperature sintering is commonly observed for tin oxide materials,[10] the mesostructured SnO_2 shows a lower tendency toward sintering than the tin oxide prepared in the absence of a surfactant. The domain size of the latter oxide after calcination at 300 °C is 27 Å. Thus, the surfactant acts not only as a structure director, but it also inhibits crystallite growth during calcination.

The mesostructured SnO_2 produced after calcination 300 °C has a BET surface area of 314 m^2 g^{-1} (Table 1), approximately twice that of the SnO_2 prepared in the absence of surfactant calcined at the same temperature (158 m^2 g^{-1}). In contrast the surface areas reported for SnO_2 gels obtained from aqueous $SnCl_4$ solutions and calcined at 300 °C are only 110–120
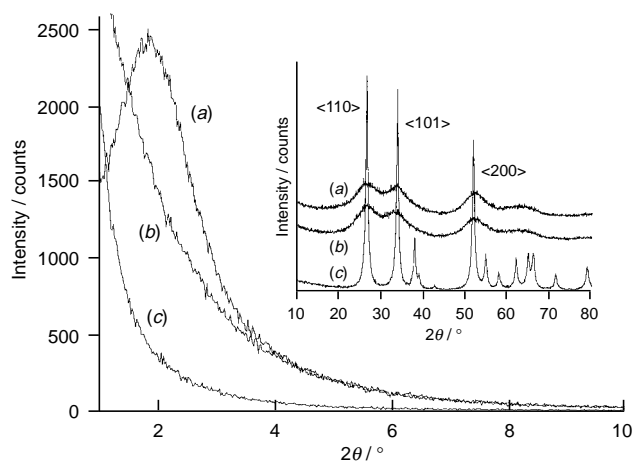

Fig. 1 XRD patterns of tin oxides: (*a*) as-synthesized product obtained by S^0I^0 assembly at ambient temperature, (*b*) as-synthesized product obtained by hydrolysis of tin isopropoxide in the absence of a surfactant, and (*c*) commercial sample of polycrystalline tin(IV) oxide
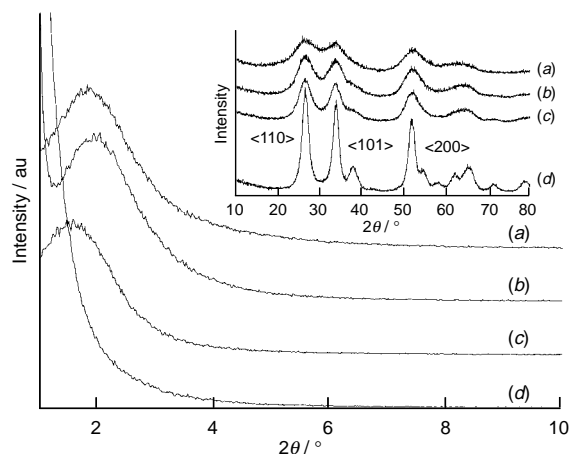

Fig. 2 XRD patterns of tin oxide assembled in the presence of tetradecylamine: (*a*) as-synthesized and after calcination at (*b*) 300, (*c*) 350 and (*d*) 400 °C

Table 1 Characterization of tin oxide prepared from tin isopropoxide in the presence of tetradecylamine surfactant

Calcination temp./°C	d-Spacing^a/Å	Crystallite domain size^b/Å	BET surface area/m^2 g^{-1}	Average pore diameter^c/Å
As made	46	15	—	—
300	46	18	314	14
350	56	24	300	18
400	None	44	99	43

^{a} As determined from 2θ of the low angle XRD peak. ^{b} As determined using Scherrer equation from the width of the $<110>$ peak at 26.5° (2θ) in the XRD pattern. ^{c} BJH adsorption average pore diameter.

m^2 g^{-1}.[11,12] Because the density of crystalline tin oxide is more than three times that of amorphous SiO$_2$, our mesostructured tin oxide has a surface to framework volume ratio comparable to that of mesoporous silicas.[7] No hysteresis is observed in the N$_2$ isotherms (Fig. 3). Therefore, the pores are relatively free of constrictions and of uniform diameter. The average pore diameter is 14 Å and the pore size distribution is relatively narrow in comparison to the pore distribution observed for the SnO$_2$ prepared in the absence of surfactant (Fig. 3 inset).
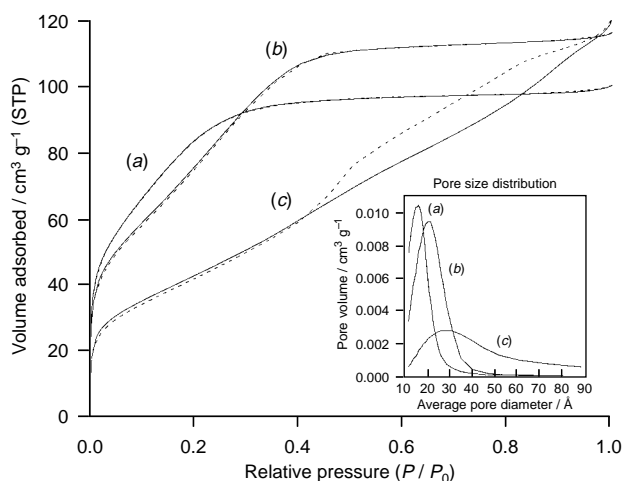

Fig. 3 N$_2$ adsorption–desorption isotherms of mesostructured SnO$_2$ synthesized in the presence of tetradecylamine and calcined at (a) 300 and (b) 350 °C, and (c) tin oxide prepared without surfactant and calcined at 300 °C. Inset shows pore size distributions for these materials as determined using the BJH model and the adsorption branch isotherm.

The low angle diffraction peak for the calcined product provides an estimate of the average distance between framework pores (46 Å). Since the average pore size is 14 Å, the pore walls are *ca.* 32 Å thick, almost twice the average crystallite domain size (Table 1). These values are in reasonable agreement with those inferred from TEM micrographs of the as-synthesized mesostructure. We may conclude, therefore, that the walls are comprised largely of aggregates of small crystallites, but we can not preclude the possibility of the crystallites being encapsulated in a matrix of amorphous SnO$_2$. Small crystalline domains surrounded by amorphous grain boundaries could account for the increase in crystallite domain size without a change in the d-spacing of the mesostructure upon calcination.

In contrast to the mesostructured SnO$_2$ calcined at 300 °C, SnO$_2$ prepared in the absence of surfactant has an average pore diameter of 28 Å, a value similar to its average crystallite size.

The pore size distribution is very broad [Fig. 3(c) inset] and consistent with a pore structure resulting from the irregular packing of small crystalline particles. Thus, the role of the surfactant in forming mesostructured SnO$_2$ is to organize the small oxide crystallites into a structure sufficiently ordered to generate regular pores and a low angle Bragg reflection.

Calcination of the mesostructured tin oxide at 350 °C lowers the BET surface area only slightly to 300 m^2 g^{-1}, but the average crystallite size (24 Å), pore diameter (18 Å), pore volume (0.15 cm^3 g^{-1}) and d-spacing (56 Å) are all significantly larger than those measured for the sample calcined at 300 °C (Table 1). As inferred from these measurements, the average pore wall thickness has also increased, to a value of 38 Å. Although more restructuring occurs at 350 °C than at the lower calcination temperature, the lack of hysteresis in the N$_2$ isotherms (Fig. 3) again indicates that the pore channels remain quite uniform, despite their increased diameters. This thermal dependence of pore size and wall thickness is not typical of a mesostructure formed by micellar assembly and further suggests a mechanism based on the packing of surfactant-decorated crystallites of uniform size.

Upon calcination at 400 °C the mesostructured framework collapses and the surface area is lowered to 99 m^2 g^{-1}. The low 2θ peak is no longer present (Fig. 2) in the XRD pattern and the average crystallite domain size increases to 44 Å (Table 1). In addition, the average pore size has increased to 43 Å, the pore size distribution has broadened and necking has developed in the channels (average diameter *ca.* 37 Å). These results are consistent with a material comprised entirely of cassiterite crystallites. TGA analysis[9] indicates that at this calcination temperature the surface hydroxyl groups condense, and this process may lead to extensive sintering.

Notes and References

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‡ *Experimental methods*: mesostructured SnO$_2$ was prepared quiescently from a 1 Sn(OPr^i)$_4$: 0.2 tetradecylamine : 60 Pr^{i}OH mixture under water-saturated air at RT. After 2 days the product was filtered and washed with water and ethanol. The surfactant was removed by a 2 h reflux in ethanol (*ca.* 80% remained) After filtration, the product was calcined (4 h) at the reported temperature (heating rate 1 °C min^{-1}).

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