

## Synthesis and Characterization of Mesoporous Indium Tin Oxide Possessing an Electronically Conductive Framework

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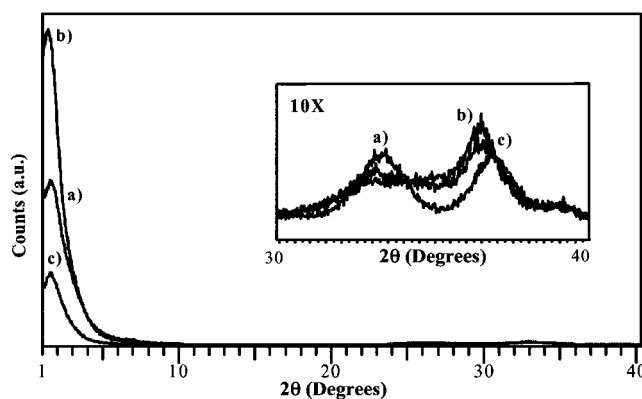
Received November 26, 2001

Transparent conductive oxides (TCOs) are important materials in the solid-state chemical and physics community. Along with challenging concepts of electron transport, they have found applications in electrochromic and electrochemical devices and as window coatings. Recently, they have become the focus of intensified study as possible components in solid-state optoelectronic devices.<sup>1,2</sup> These materials are typically dense thin films comprised of the well-known indium–tin-oxide (ITO);<sup>3,4,5,6</sup> or other related materials such as zinc–indium-oxide.<sup>7,8</sup> Highly crystalline thin films of n-type conductors such as ITO can exhibit conductivities above  $1 \times 10^2$  S/cm,<sup>3,4</sup> although typical values lie close to 1 S/cm.

Formation of these materials with accessible internal porosity, and restricted dimensions, together with high conductivity and transparency, would offer a host of new fascinating opportunities. The development of nanocrystalline-doped tin oxides shows, for example, that their sensing ability increases strongly with decreasing crystallite size.<sup>9</sup> Altered electronic properties are also expected due to quantum restraint relaxation of the electronic states.<sup>10</sup> One method of inducing regular mesopore order in a porous oxide is by nucleating its growth on the surface of organic surfactant arrays. First demonstrated for silica,<sup>11</sup> the surfactant template method has been extended to form mesoporous transition-metal oxides, TMOs (i.e., Nb, Ta, Ti, and Mn), that introduce redox activity as an additional component.<sup>10,12</sup> Nonetheless, these black materials all display weak hopping semiconductivity on the order of  $10^{-6}$ – $10^{-8}$  S/cm, owing to their highly localized electronic states. An ionic conductor ( $\sigma \approx 10^{-8}$  S/cm at 650 K) has also been reported.<sup>13</sup>

Reported herein is the first mesoporous transparent conducting oxide that combines both a high surface area and a regular pore order, while possessing an appreciably electronically conductive, stable ITO framework ( $\sigma > 1 \times 10^{-3}$  S/cm at 300 K). The possibility to deliver electrons to a large accessible pore allows for the creation of selective gas sensors<sup>3–8</sup> and micro-electrochemical reactor chambers for specific electrocatalytic transformations, while transparency provides the opportunity for tunable display devices.

The ITO frameworks were prepared by a variation of a ligand-assisted templating mechanism in conjunction with a positively charged assembly pathway. A prime impediment was achieving control of the competing hydrolysis and condensation reactions. This was achieved by employing atrane complexes, extensively characterized by Verkade,<sup>14</sup> and used in the production of highly doped silicates and alumina phosphates,<sup>15</sup> as precursors to slow the kinetics of hydrolysis. Our  $S^+I^-$  pathway used triethanolamine atrane complexes of indium and tin alkoxides as the inorganic precursors to the mesostructure. Materials were prepared by dissolving indium acetate and tin isopropoxide in an excess of triethanolamine, using cetyltrimethylammonium bromide (CTAB) as a surfactant.<sup>16</sup> Three different ratios of In:Sn were employed; 1:1; 3:1, and 5:1. Low-angle XRD measurements on the materials



**Figure 1.** XRD patterns of calcined ITO materials; In:Sn ratios of (a) 1:1,  $d$  spacing 54 Å, (b) 3:1,  $d$  spacing 50 Å, and (c) 5:1,  $d$  spacing 60 Å. (Insert) High-angle region ( $\times 10$  expansion).

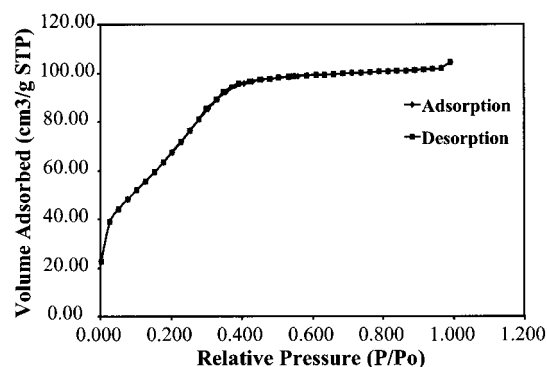
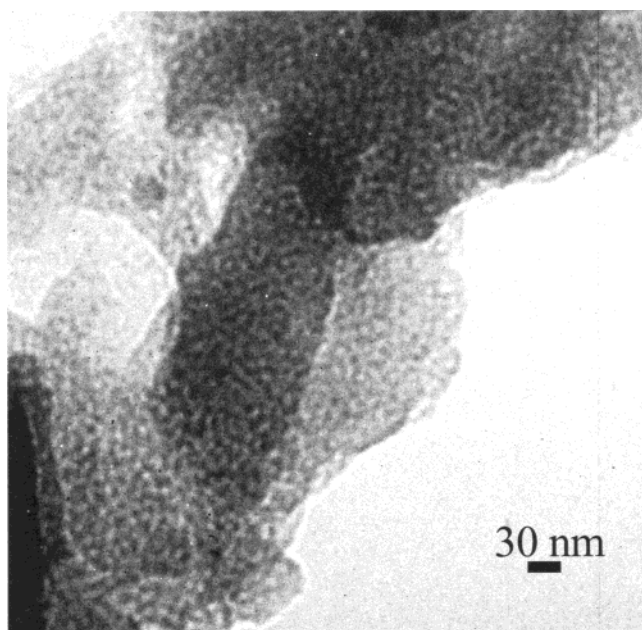
isolated after controlled hydrolysis confirmed the materials were mesostructured. They all displayed a well-defined loss of surfactant in their DTA–TGA curves between 300 and 380 °C (not shown). In accord, IR spectra of materials calcined at 400 °C showed the disappearance of the characteristic surfactant peaks at 2920, 2850, 2370, 2015, 1483, and 1359  $\text{cm}^{-1}$  and retention of features at 935, and 536  $\text{cm}^{-1}$  attributable to the ITO framework. The relative ratios of In, Sn, and residual C (less than 1%) determined by elemental analysis were close to expected.<sup>17</sup> The 5:1 In:Sn ratio approaches the 8–10% tin for optimal electrical conductance and sensing capabilities.<sup>7,4</sup> The calcined materials were pale yellow-white powders that appeared colorless and almost transparent in thin pressed pellets.

Powder X-ray diffraction patterns of the calcined products with varying indium-to-tin ratios are displayed in Figure 1. Each shows a strong reflection at low angle with  $d$  spacings ranging from 50 to 60 Å, characteristic of mesostructured compounds. The breadth of the reflection is consistent with that of the worm-hole channel pore motif.<sup>18</sup> A mesostructure is formed only in the presence of cetyltrimethylammonium bromide even though the hydrolysis and condensation processes are analogous in the absence of the structure-directing reagent. For all materials, the  $d$  spacing shifted slightly to lower angle on calcination along with a decrease in the width of the reflection, indicating that some reorganization of the pore structure occurs during template removal. The two extremely weak and broad reflections observed at high angle at about 34 and 37°  $2\theta$ , attributable to the (101) and (110) reflections of doped  $\text{In}_2\text{O}_3$ , indicate either the presence of nanocrystalline domains within the amorphous walls or very minor amounts of phase-separated precipitated oxides. The 1:1, 1:3, and 1:5 calcined materials show high BET surface areas up to 310  $\text{m}^2/\text{g}$  typical of mesoporous compounds (see (Table 1)).<sup>19</sup> The surface areas of the framework are comparable to those obtained for mesoporous siliceous com-

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**Table 1.** Characteristics of Mesoporous ITO Materials, In:Sn

sample	$d$ -spacing (Å)	surface area (m <sup>2</sup> /g)	pore diameter (Å)
1:1	54	273	18.9
3:1	50	280	30.2
5:1	60	312	40.3

**Figure 2.** Adsorption-desorption isotherm of the 1:1 In-Sn calcined mesoporous ITO. Total pore volume was 0.22 cm<sup>3</sup>/g.**Figure 3.** TEM image of the mesoporous structure of the 1:1 In:Sn ITO obtained after calcination to remove the surfactant.

posites after normalization for the difference in mass between Si and Sn/In (equivalent to  $\sim 750$  m<sup>2</sup>/g for Si). The values are particularly impressive when compared to their dense ITO counterparts and thin film gels with surface areas around 50 m<sup>2</sup>/g.<sup>20</sup> Barrett-Joyner-Halenda (BJH) analysis<sup>21</sup> indicates a narrow pore-size distribution with average diameters  $> \sim 20$  Å (Table 1). In accord, the adsorption-desorption isotherm displayed in Figure 2 for the 1:1 composition (pore volume of 0.22 cm<sup>3</sup>/g) shows lack of hysteresis, demonstrating the presence of primary mesopores of a highly regular structure. Other compositions also show little hysteresis.

The TEM images of the materials (Figure 3) indicate the presence of a worm-hole or sponge topology that has been observed previously in an ever expanding number of TMOs and metal oxides.<sup>18,22</sup> The high surface area therefore does not arise from a porous network of aggregated nanoparticles, but from a true framework mesostructure. Although phase separation of the In and Sn oxide on a nanoscale cannot be discounted, SEM EDX scans of the materials indicate a very high level of homogeneity with no

localized aggregation of elements. The lack of phase separation is further demonstrated by the conductivity measurements, as neither SnO<sub>2</sub> nor In<sub>2</sub>O<sub>3</sub> are conductive in their pristine states. The materials show promising electronic properties. Conductivity measurements taken on a water-free pressed pellet (1:1 ratio In:Sn) showed an average value of  $\sigma = 1.2 \times 10^{-3}$  S/cm at 300 K.<sup>23</sup> This value is about a factor of 10<sup>3</sup> times less than ITO thin film conductance measured at the same temperature and similar levels of tin.<sup>15</sup> However, residual organic components, grain-boundary effects in the powder and defects in the wall structure will all contribute to higher resistivity in the mesoporous material compared to sputtered dense thin films. Experiments to further stabilize the framework at high temperatures and increase the conductivity are in progress.

**Acknowledgment.** We thank the NSERC for financial support. We also thank: Dr. V. Pralong for her assistance with the SEM and conductivity measurements and Dr. J. Corbett and Kevin Yin for their TEM work.

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- (16) Reactions were performed under an inert nitrogen atmosphere. Solutions of the desired indium acetate/tin isopropoxide stoichiometry were prepared in a 10-fold molar excess of triethanolamine, and dry formamide (ca. 10 vol %) was added to lower the viscosity. After the solution was mixed for 4 h, cetyltrimethylammonium bromide (3.5:1 molar ratio with respect to the total metal concentration) was added, and the pH was adjusted to 8 with 4 M sodium hydroxide. The mixture was held at 80 °C for 96 h prior to filtering off the product.
- (17) For compositions **1:1**: Sn, 31.5%; In, 43.9%; C, 0.9%; **1:3**: Sn, 25.3%; In, 73.64%; C, 0.6%; **1:5**: Sn, 13.7%, Sn, 82.6%, C, <0.5% (Galbraith).
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- (19) Values are typical of those reported for mesoporous SnO<sub>2</sub> (314 m<sup>2</sup>/g; Pinnavaia, T. et al. *Chem. Commun.* **1998**, 1471), and 107–143 m<sup>2</sup>/g; Liu, M. et al. *Chem. Commun.* **1999**, 1829.
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- (23) Circular thin pellets of dimensions 0.14 cm  $\times$  1.0 cm were prepared from calcined powders oven-dried at 200 °C overnight. Pellets were prepared in a Carver press, dried again in a vacuum oven at 70 °C at 10<sup>-3</sup> Torr, and loaded into the conductivity apparatus in an argon-filled drybox. Measurements were performed by pressing two electrode surfaces across opposite faces of the pellet contained within a specially designed holder, and carrying out an  $I$ - $V$  measurement on a MacPile galvanostat/potentiostat with nanoampere resolution, imposing a current between 0 and 10 mA. Conductivity was calculated from  $\sigma = d/(RS)$ , where  $S$  is the surface area of the pellet in contact with the electrode,  $R$  is the resistance, and  $d$  is the thickness. Measurements were performed on three different pellets for consistency.

JA0125826