Transparent Conducting Films of Antimony-Doped Tin Oxide with Uniform Mesostructure Assembled from Preformed Nanocrystals

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ABSTRACT

Transparent conducting films of antimony-doped tin oxide (ATO) with a uniform 3D-mesostructure are prepared by self-assembly of crystalline ATO nanoparticles with various antimony content directed by commercially available Pluronic copolymers. The mesostructure of the films calcined at 300 - 500 °C exhibits periodicity of 14 nm, surface area of 200 - 300 m^2/cm^3 and a well-developed accessible porosity of 45 - 55 %. The high crystallinity of the nanoparticles serving as building blocks enables to obtain the fully crystalline inorganic frameworks with sufficient electric conductivity already at temperatures as low as 300 °C. Ferrocene molecules covalently immobilized in the conducting mesoporous matrix show significantly enhanced electrochemical response proportional to the electrode surface area. The high electric conductivity and the uniform accessible mesoporosity combined with a simple and generally applicable preparation procedure make the developed ATO films attractive as the nanostructured transparent electrodes for various optoelectronic applications.

Keywords: Transparent conducting materials, antimonydoped tin oxide, nanoparticles, mesoporous films

1 INTRODUCTION

The recent rapid progress in nanoscience and nanotechnology has lead to the development of completely new nanoscale materials. Novel morphologies in already known materials have substantially extended their application potential. Transparent conducting oxides are known as thin dense films, being indispensible for touch panel displays, OLEDs or non-silicon solar cells. However, other types of optoelectronic devices, especially those involving immobilized species or functional layers, require conducting networks rather than flat electrode interfaces. Such 3D-electrode architectures with very high interface area are suitable as conducting hosts accommodating functional guest species, which allows a substantially more efficient electron transfer and consequently increased efficiency of the devices.

Some years ago we reported the preparation of 3Dnetworks of indium tin oxide (ITO) and demonstrated their potential as efficient electrode systems [1, 2]. Of great interest is the extension of such architectures to other 3Dorganized transparent conductors replacing the rare and expensive indium and providing a different surface chemistry or energy level properties. One widely used system is extrinsically doped tin oxide, such as fluorine- or antimony-doped tin oxide (ATO). Very recently, two communications reporting mesoporous ATO electrodes were published [3, 4] and their potential for, e.g., electrochemiluminescence fabrication of efficient demonstrated [3]. However, the biosensors was manufacturing of 3D-transparent electrodes still remains a non-trivial task, hindering the full exploitation of their application potential. All the reported methods are practically solely based on self-assembly of sol-gel derived metal oxide precursors assisted by amphiphilic structuredirected agents (the so called Evaporation-Induced Self-Assembly process). As the formed inorganic frameworks are amorphous, they have to be treated at higher temperatures to induce the crystallization indispensible for electron conductivity. Such phase transformation without the collapse of mesostructure was achieved for ATO films only using special amphiphilic copolymers of the KLE type [4] with outstanding templating properties and the increased thermal robustness, which however are not commercially available. Easily available and rather cheap copolymers of the Pluronic family, successfully used for preparation of mesoporous crystalline metal oxides, have failed due to the different sol-gel chemistry of tin. The formation of a crystalline mesoporous structure of tin oxide requires a special post-synthetic treatment at carefully controlled humidity and temperature for several days, which is rather time-consuming.

Consequently, the development of a simple and generally applicable procedure for the preparation of

transparent conducting 3D-frameworks using easily available components is highly desirable. One passable solution might be the replacement of amorphous metal oxide precursor by crystalline building blocks, which could form the mesoporous crystalline network at much milder conditions. The pre-formed nanocrystals could also bring the additional advantage of a fine adjustment of the doping level and thus the electric conductivity, which is often better controlled in the particle synthesis. Nevertheless, the use of nanocrystalline building blocks for the preparation of mesoporous materials has been reported only for a few oxides, probably due to the fact that it is rather difficult to prepare stable and agglomeration-free nanoparticle dispersions.

Recently we have reported the preparation of crystalline monodisperse ATO nanoparticles 3-4 nm in size by a nonaqueous approach, which utilizes cheap and easily available metal precursors, being completed after heating the precursor mixture for several hours at 100-150°C in a closed glass vessel, without the need of an autoclave [5]. The obtained nanocrystals exhibit a high electric conductivity and are dispersible at high concentration in both water and a number of organic solvents. Consequently, these nanocrystals are suitable building blocks for assembly into a mesostructure. In this communication we present a procedure enabling the assembly of such crystals to mesoporous conducting films, this process being directed by commercially available Pluronic copolymers. The parameters influencing the self-assembly properties have been analyzed in detail, as well as the texture properties, crystallinity and conductivity of the obtained films.

2 RESULTS AND DISCUSSION

In spite of the apparent simplicity of the approach based on the directed assembly of nanoparticles to mesostructures (Scheme 1), their use as the building blocks is far from being straightforward because of a number of strictly required particle properties. In addition to a suitable morphology and a good dispersibility of the particles themselves, their dispersions should be compatible with the added structure-directing agent. Moreover, a suitable type of interaction should exist between particles and polymer molecules acting as a driving force for their self-assembly to the desired supramolecular structures. We have found that these interactions depend to a large extend on the bulk as well as surface chemical composition of the particles and on the solvent. Even if the ATO particles are well dispersible in polar solvents such as water or ethanol, the addition of Pluronic copolymers causes the precipitation of the particles. Tetrahydrofurane was found to be so far the only solvent, in which ATO nanoparticles form stable colloidal dispersions in the presence of Pluronic copolymers. The antimony percentage in the ATO nanoparticles is another important parameter governing the dispersibility and the self-assembly of particles. To form stable colloidal dispersions in the presence of the Pluronic copolymer, the percentage of antimony should exceed 6 mol % (in the investigated range from 0 to 40 mol %).



Scheme 1. The formation of mesoporous crystalline electrode layers by the self-assembly of crystalline nanoparticles directed by amphiphilic molecules. The arrows (right) indicate the direct electron flow to redox species immobilized in the 3D-conducting framework.

The surface composition of the ATO nanoparticles was found to be of primary importance for their self-assembling properties and the thermal stability of the formed mesostructures. When the as-synthesized particles were used for the film preparation, only a thermally unstable lamellar structure was formed. According to the thermogravimetry data, such particles still contain ca. 50 % of adsorbed benzyl alcohol and the benzyl alcoholate moieties, whose removal requires washing in organic solvents. Finally, as shown below, only washed ATO nanoparticles with Sb content exceeding 6 % could be assembled in the presence of the Pluronic copolymer to thermally stable periodic mesostructured films. The observed influence of the composition of the particles and their surface chemistry on their self-assembly behavior suggests an important role of the coordination of the Pluronic block-copolymer molecules, presumably of their hydrophilic polyethyleneoxide blocks, on the particle surface. Although we can only speculate about the structure of the formed coordination complexes due to the lack of the currently available experimental data, it will be surely influenced by the presence of the surface-adsorbed organic moieties as well as the surface charge and composition of the particles. As was demonstrated by the zeta-potential measurements, the point of zero charge (pzc) of the ATO particles changes linearly with the Sb content. This altering surface charge and the replacement of the surface Sn atoms by Sb ones, as demonstrated by the Raman measurements [5], could be one of the reasons of the remarkably different self-assembly behavior of Sb-doped particles compared to the undoped ones.

In the final step of the mesoporous ATO films assembly, the Pluronic-containing colloidal dispersion in THF of washed ATO nanocrystals with doping levels from 6 to 30 mol % (assigned further as ATO_6 etc) was coated on various substrates and calcined in air at temperatures varying from 300 °C (Pluronic combustion temperature) to 500 °C in order to remove the template and to sinter the nanoparticles. The obtained data show that 300 °C is enough to remove all the organics from the material. Scanning electron microscopy (SEM) images of the films (Fig. 1b) prove the very good uniformity of the films and their crack-free character. Transmission electron

microscopy (TEM) images (Fig. 1a) show that the nanoparticles with different doping levels form similar films with highly porous uniform 3D-architectures. The wormhole mesostructure contains ca. 100 nm large domains with some indication of pore ordering. The Fouriertransform spectra of the films calcined at 300 - 400 °C show two rings corresponding to the mesostructure periodicity of 14+1 and 8+0.5 nm, respectively (Fig. 1a, inset). The electron microscopy data are in a good agreement with small-angle XRD patterns, showing two reflections due to the pore organization with a similar mesostructure periodicity (Fig. 2a). The first reflection corresponding to a mesostructure d-spacing of ca. 14 nm slightly shifts to the higher angles due to a shrinkage of mesostructure in a direction perpendicular to the substrate. In contrast to sol-gel derived films, the mesostructure shrinkage of the films assembled from nanoparticles is only marginal, indicating high temperature stability of the mesoporous framework. The second ring/reflection, corresponding to higher order of periodicity, becomes weaker with the increase in the calcination temperature due to the increasing distortion in the mesostructure ordering.



Figure 1. Mesostructure and crystallinity of the films assembled from ATO_20 nanoparticles and calcined at 400 °C.: (a) TEM image, inset: the Fourier transform spectra; (b) SEM image (top view).

High-resolution TEM images of the mesoporous ATO films show the complete crystallinity of the pore walls, being composed of similarly sized nanocrystals. The d-spacing of the crystalline fringes and WAXS patterns of the film (Fig. 2b) correspond solely to the cassiterite SnO_2 phase without any traces of antimony oxides, indicating that no phase separation occurred during the temperature treatment. The crystal size determined from the line broadening of the WAXS patterns (Fig. 2b) slightly grows from 3.0 nm (size of the particles used for the film assembly [5]) to 4.3 nm after calcination at 500 °C. The sintering of nanoparticles within the pore walls leads to a slight mesostructure shrinkage and thus some deterioration of the mesostructure periodicity. The typical film thickness was 210 ±10 nm.

The texture properties and the accessibility of the internal surface of the ATO thin films were studied by krypton adsorption at ca 77 K. The Kr adsorption isotherms

on the films calcined at 300 to 500 °C (Fig. 2c) show that all the materials exhibit well-developed mesoporosity without any pore-blocking. While the variation in the calcination temperature does not essentially change the character of the porosity, there are some quantitative changes in the texture characteristics. The specific surface area related to the total film volume slightly decreases with increasing calcination temperature, but remains remarkably high achieving 300, 270 and 200 m²/cm³ for calcination temperatures of 300, 400 and 500 °C, respectively. The porosity equals 45, 30 and 55 % for the calcination temperatures as above. The pore width slightly increases with increasing calcination temperature from ca 6 nm (for 300 and 400 °C) to ca 8 nm (for 500 °C).

The Kr adsorption results in combination with the electron microscopy and X-ray diffraction data indicate a high thermal stability of the mesostructure assembled from the pre-formed nanocrystals.



Figure 2. Characterization of the mesoporosity and crystallinity of the films assembled from ATO_20 nanoparticles and treated at different temperatures: (a) small angle X-ray diffraction, (b) wide angle X-ray diffraction and (c) Kr adsorption isotherms. The inset in the Fig. 2b shows dependence on the calcination temperature of the crystal size estimated from the peak broadening.

The variation of the electric conductivity of the mesoporous ATO films with the Sb doping level in the precursor nanoparticles and the calcination temperature was determined. The film conductivity is the highest when the film is assembled from particles containing 8-10 % of Sb (Fig. 3a). These results are in good agreement with the conductivity of the nanoparticles themselves, which achieves a maximum at 4-10 % of Sb [5]. Conductivity of the films reasonably increases with increasing calcination temperature, which is due to the particle sintering, a slight increase in the crystal size and the related increase in the electron mobility. The highest conductivity of 0.8 S cm⁻¹ was obtained for the film assembled from the ATO 8 nanoparticles and calcined at 500 °C. This is practically the same conductivity which was obtained for the parent ATO_8 nanoparticles in pressed pellets treated at the same temperature (1 S cm⁻¹) [5], being quite high for a film with ca. 50 % of porosity.

To test of the applicability of mesoporous ATO films as electrode layers, they were deposited on flat conducting ITO substrates in order to minimize ohmic losses. Ferrocene moieties were covalently anchored via peptide bonds to their surface as standard redox probes. Fig. 3b shows an example of electrode performance of the film assembled from the ATO_10 nanoparticles calcined at different temperatures.



Figure 3. (a) Variation of the electric conductivity of the mesoporous films assembled from ATO nanocrystals with Sb content in the precursor nanoparticles and the calcination temperature of the prepared films. (b) The cyclic voltammograms of the ferrocenecarboxylic acid covalently anchored on the mesoporous ATO_10 layers calcined at 300 $^{\circ}$ C, 400 $^{\circ}$ C and 500 $^{\circ}$ C and on flat ITO electrode (black and inset). Scan rate is 50 mV s⁻¹.

The voltammograms of all samples exhibit Gaussianshaped peaks of reversible ferrocene oxidation and reduction, characteristic for modified electrodes with immobilized redox species. Both double layer charging and Faradaic currents of the ferrocene oxidation and reduction on the mesoporous electrodes drastically increase compared to those on the flat ITO electrode modified in the same way. The surface coverage of the electrochemically accessible ferrocene molecules obtained by the integration of peak-area corresponds to $1.9 \cdot 10^{-11}$ mol cm⁻² for the flat ITO electrode and $9.4 \cdot 10^{-10}$ mol cm⁻² (50-times), $6.5 \cdot 10^{-10}$ mol cm⁻² (35-times) and $5.5 \cdot 10^{-10}$ mol cm⁻² (29-times) for the mesoporous ATO electrodes calcined at 300 °C, 400 °C and 500 °C, respectively. The numbers in brackets indicate corresponding increase in surface coverage compared to the flat ITO electrode. This increase in the Faradaic charge is in excellent agreement with the specific surface areas of the films obtained by Kr adsorption measurements. Consequently, the mesoporous ATO films calcined at lower temperatures are suitable for the application as transparent electrode layers with the very high surface area, enabling direct electrochemical addressing of each redox molecule immobilized on its surface. The surface area of the mesoporous ATO layers seems to play a more important role in enhancing the charge collection efficiency compared to their specific conductivity. This can be due to the fact the total serial resistance of the "sandwich" electrodes composed of porous conducting layer on a dense conducting substrate is sufficiently low to provide an efficient electron transport. The transparency of the films assembled from the particles with different Sb content is above 93 % of transmission, which makes them promising candidates for electrode layers for the optoelectronic applications.

3 CONCLUSIONS

Transparent conducting layers of antimony-doped tin oxide with a uniform mesoporosity and crystalline framework can be easily manufactured by a directed assembly of pre-formed ATO nanocrystals using commercially available and cheap polymers of the Pluronic family [6]. The crystallinity of the nanoparticles serving as building blocks enables to obtain the fully crystalline inorganic frameworks with sufficient electric conductivity already at temperatures as low as 300 °C without any need for the elaborate post-synthetic treatment. Another attractive feature of this approach is the high thermal stability of the obtained mesostructure exhibiting practically no shrinkage due to the temperature treatment, which is a typical disadvantage of amorphous sol-gel derived precursors. The use of preformed nanocrystals, whose preparation can be controlled with a high precision, ensures a high reproducibility. Owing to the open and accessible character of porosity, the high surface area and the uniform pore size, the obtained mesoporous frameworks are promising host materials for the accommodation of functional redox moieties. The high potential of the obtained mesoporous layers as nanostructured transparent electrodes with the high surface area was demonstrated on an example of ferrocene molecules which were covalently immobilized in the conducting matrix, showing the significantly enhanced electrochemical response proportional to the electrode surface area.

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