Preparation and Optical Properties of Colloidal, Monodisperse, and Highly Crystalline ITO Nanoparticles

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The properties of tin-doped indium oxide (ITO), an n-type transparent conducting oxide (TCO), have been extensively explored due to many ITO applications such as flat panel display technology,[1] biomolecular microarrays,[2] solar cells,[3] and gas sensing devices,[4] that utilize the unique properties of the high optical transparency of ITO in the visible region and its controllable low resistivity. The synthesis of ITO nanoparticles with high crystallinity, homogeneous composition, and well-defined particle morphologies with narrow size distributions is of particular technological interest. The reasons lie in the factors of low manufacturing cost and easy processibility of nanoparticles into films, ceramics, and composites, especially, with high flexibility in terms of substrate structure and geometry. Several methods for the preparation of ITO nanoparticles have been previously reported such as coprecipitation of metal precursors followed by thermal treatment,[5] laser-induced fragmentation,[6] solvothermal synthesis,[7] microwave-assisted synthesis,[8] and emulsion techniques,[9] but these still suffer from broad size distribution and low crystallinity.

We report herein a simple one-pot synthesis of colloidal, monodisperse, and highly crystalline ITO nanoparticles of various sizes (3–9 nm in diameter) with variable tin oxide content (1–10 atom %), as well as their optical properties depending on the particle size and Sn content.

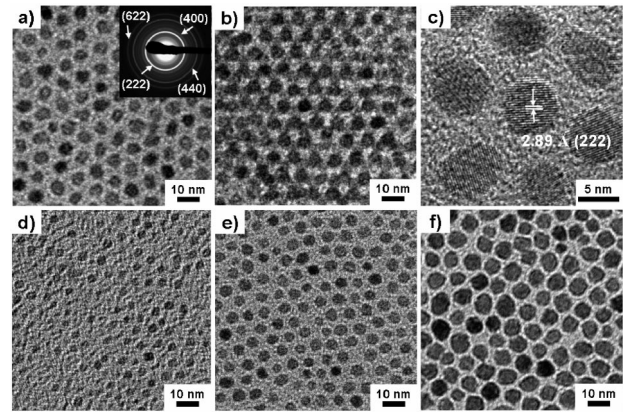

Figure 1. Low resolution TEM images of (a) 7 nm, (b) superlattice structure of 7 nm, (d) 3 nm, (e) 5 nm, and (f) 9 nm ITO nanoparticles of 5 atom % of Sn; (c) HRTEM images of 7 nm ITO nanoparticles. The SAED pattern is shown as an inset in (a).

A typical synthetic procedure is as follows.[10] A white slurry of both metal precursors, $In(acac)_3$ (acac = acetylacetonate) and $Sn(acac)_2Cl_2$ in variable ratios, in oleylamine was heated at 250 °C for 5 h under an argon atmosphere to produce a pale blue suspension, to which excess ethanol was added to induce precipitation. Centrifugation and repeated washing with ethanol gave from pale blue to blue powders of ITO nanoparticles, which could be easily redispersed in various organic solvents such as toluene and dichloromethane.

The low- and high-resolution TEM images of various ITO nanoparticles are illustrated in Figure 1. When a 1:12 molar ratio of metal precursors (5/95 Sn:In ratio) to oleylamine was used,[10] spherical ITO nanoparticles of 7 (6.8 ± 0.4) nm in diameter with 5 atom % of Sn (vide infra) were produced as shown in Figure 1a. The selected area electron diffraction (SAED) pattern of the nanoparticles is consistent with the cubic bixbyite structure of In_2O_3 featuring strong ring patterns assigned to the (222), (400), (440), and (622) planes (inset of Figure 1a). ITO nanoparticles can be readily assembled into a three-dimensional close-packed superlattice structure as shown in Figure 1b, when a TEM sample was prepared with a concentrated dichloromethane solution of nanoparticles, which also supports monodispersity of the nanoparticles. The HRTEM image in Figure 1c indicates that the nanoparticles have a single crystalline nature with an atomic lattice fringe image of 2.89 Å (222). Smaller nanoparticles of 3 (3.2 ± 0.4) nm (Figure 1d) and 5 (5.0 ± 0.4) nm (Figure 1e) were obtained, when 1:192 and 1:48 molar ratios, respectively, of both metal precursors-to-oleylamine were employed.[10] Lower concentrations of precursors in oleylamine tend to give smaller nanoparticles. Bigger nanoparticles of 9 (8.9 ± 0.5) nm (Figure 1f) were prepared[10] by use of the seed-mediated growth method employing 7 nm nanoparticles.[11]

Figure 2 shows XRD patterns reveal a highly crystalline nature for the various sizes of 5 atom % of Sn doped ITO

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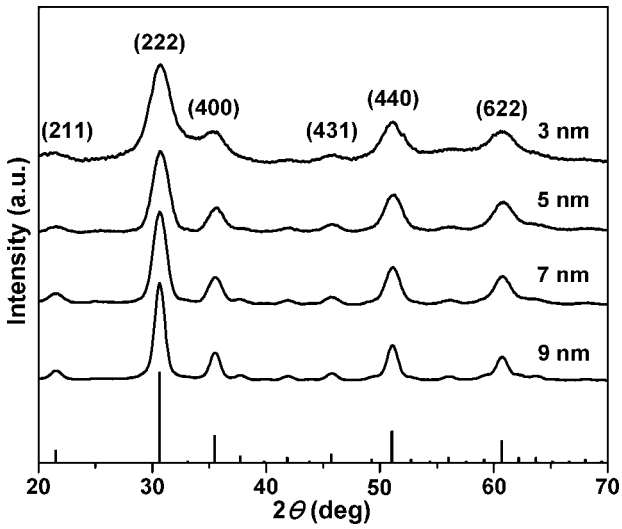

Figure 2. XRD patterns of 3, 5, 7, and 9 nm ITO nanoparticles with 5 atom % of Sn. The standard reflection pattern of cubic bixbyite In_2O_3 is shown as a bar diagram.

nanoparticles. The patterns match well with those of the standard cubic bixbyite In_2O_3 (JCPDS no. 06-0416) but are slightly shifted to higher 2θ values compared to those of pure *c*-In_2O_3 (Figure S1, Supporting Information),[10] which is attributed to decreased lattice spacings due to the presence of smaller tin (4+) ions (0.71 Å) in place of the indium (3+) ions (0.81 Å).[12] The lattice parameters extracted from the XRD measurements of 7 nm nanoparticles are 10.111, 10.096, 10.094, and 10.098 Å for 1, 3, 5, and 10 Sn atom %, respectively, which are consistent with the previously reported results.[12] These observations together with the absence of an additional phase in XRD assignable to crystalline SnO_2 clearly supports the formation of solid solutions of indium and tin oxides in our Sn doped ITO nanoparticles. The XRD reflection peaks become broader as the crystal size decreases, which is a general size-dependent phenomenon in nanoparticles. The crystallite sizes were additionally determined by using the Debye–Scherrer equation[13] and are 3.1, 5.0, 7.1, and 8.9 nm.

The Sn:In ratios in as-synthesized ITO nanoparticles were analyzed by ICP-AES, and the results are listed in Table S1, Supporting Information.[10] The final composition of the nanoparticles coincided well with the initial molar ratios of the two starting metal precursors used in the syntheses. ITO nanoparticles of 7 nm size with 1, 3, and 10 atom % of Sn doping were prepared using 1/99, 3/97, and 10/90 molar ratios of the Sn:In precursors. The TEM images and the XRD patterns of these ITO nanoparticles are shown in Figures S2 and S3, respectively, Supporting Information.[10]

The optical properties of the ITO nanoparticles were analyzed with photoluminescence (PL) spectroscopy. The PL spectra (excitation at 280 nm) of the 5 atom % of Sn doped ITO nanoparticles of four different sizes are provided in Figure 3a. The emission maxima appear at 3.84 (323), 3.80 (326), 3.77 (329), and 3.76 eV (330 nm) for 3, 5, 7, and 9 nm ITO nanoparticles, respectively. The blue-shift is observed as the particle size decreases, indicating that the prepared nanoparticles are in the quantum confinement regime.[14] The PL emission maxima of 7 and 9 nm ITO nanoparticles appear very close, implying that the exciton Bohr diameter for 5 atom % of Sn doped ITO nanoparticle is an estimated 7–9 nm. That of In_2O_3 is reported to be in the range of 5.2–10 nm.[15] The PL emission spectra of 7 nm ITO particles with various Sn content are shown in Figure 3b. As the Sn content increases, the PL emission maxima become blue-shifted (332, 330, 329, and 326 nm for 1, 3, 5, and 10 atom %, respectively). The UV–vis absorption spectra reveal a similar trend in absorption maxima according to Sn content (Figure S4, Supporting Information).[10] This is correlated with the Burstein–Moss effect that Sn doping leads to a partial filling of the conduction band and hence widening of the optically observed band gap of ITO.[16,17] The deep blue color of the highly Sn doped (10 atom %) ITO nanoparticles clearly indicates the presence of a high concentration of charge carriers in the conduction band.[5,7a] This result is, to the best of our knowledge, the first demonstration of the Burstein–Moss effect in ITO nanoparticles, although it is well established in ITO films.[16,17]

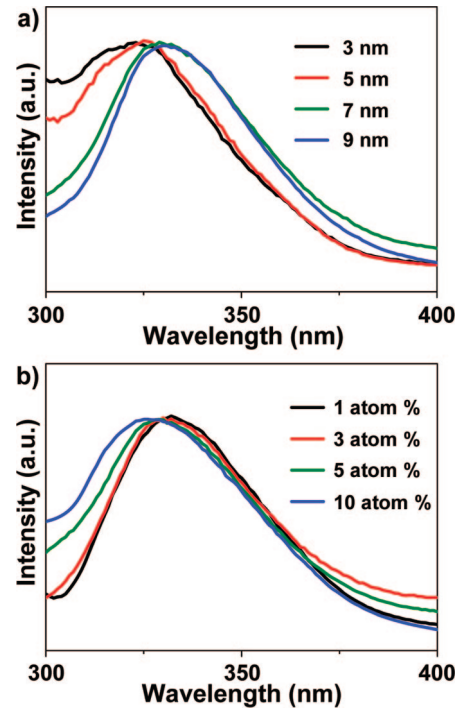

Figure 3. PL spectra of (a) ITO nanoparticles with various particle sizes and (b) 7 nm ITO nanoparticles with various Sn contents.

In conclusion, colloidal, monodisperse, highly crystalline ITO nanoparticles were prepared by a simple one-pot thermal decomposition of tin and indium precursors in oleylamine. Particle size (3–9 nm) and Sn content (1–10 atom %) can be readily controlled by changing the amount of oleylamine and the molar ratio of Sn:In metal precursors employed, respectively. The optical properties of the ITO nanoparticles

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reveal that the exciton Bohr diameter is around 7–9 nm and the PL emission maxima are blue-shifted as the particle size decreases and the Sn content increases. We are currently investigating application of the ITO nanoparticles on the fabrication of high quality ITO films utilizing their high solubility in various organic solvents and ready formation of superlattices on surfaces.

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Supporting Information Available: Synthetic procedures and characterization data for ITO nanoparticles are given (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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