Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 38:731–733, 2008

ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533170802525761

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Synthesis of Indium Tin Oxide (ITO) Nanoparticles from the Hydrolyzate of a Composite Complex Salt

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A composite complex salt—$(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5{\cdot}?\ H_2O$—was synthesized from the starting materials $InCl_3$, HCl, $SnCl_4$ and NH_4HCO_3. The hydrolyzate of $(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5{\cdot}?H_2O$ were prepared under the condition of room temperature and fiercely stirring, using NH_4HCO_3 as precipitator and polyethylene glycol as disperser. Indium-tin oxide (ITO) nanoparticles were prepared by calcined the hydrolyzate at 700°C for 1 h in air. The prepared ITO particles were characterized via X-ray diffractometry, scanning electron microscopy and laser particle size analyzer. The results indicated the average crystalline grain size, a primary particle size and an average aggregation size of prepared ITO powders is 34.6 nm, 50–100 nm and of 107 nm, respectively.

Keywords composite complex salt, deposition, indium-tin oxide (ITO), nanoparticles

INTRODUCTION

Due to indium tin oxide (ITO), it is a well-known material with high electrical conductivity and high transparency under visible light, and ITO film is widely used as a transparent electrode for optoelectrical devices. The preparation methods of ITO thin films include the chemical vapor deposition (CVD), the thermal evaporation, the ion plating, the ion beam assistant deposition (IBAD), and the magnetron sputtering. Among these methods, the most preferred method in production line is the magnetron sputtering using ITO ceramic target because it has some advantages in its controllability of sputtering condition and adaptability to large area deposition. The magnetron sputtering technique requires sufficiently dense targets without any additives to guarantee the highly conductivity of ITO film. Consequently, the preparation of ITO nanoparticles is more important. At present, there are many methods to prepare ITO nanoparticles, such as the chemical precipitation method, the decompression-volatile oxidation method, the spray-combustion method and the spray thermal decomposition method. Among these methods, chemical precipitation method is comparatively suitable for the large-scale production and is widely used because of its short production cycle and simple production equipment.[1–8]

In this paper, ITO nanoparticles were prepared from the hydrolyzate of a composite complex salt, which were synthesized from the starting materials $InCl_3$, hydrochloric acid, $SnCl_4$ and NH_4HCO_3.

EXPERIMENTAL PROCEDURES

Preparation of Complex Salt Crystals

Indium metal, HCl, $SnCl_4 \cdot 5H_2O$ and NH_4HCO_3 were used as the starting materials. The $InCl_3$ solution was prepared by dissolving indium metal in HCl. The reaction solution was prepared by mixing $InCl_3$, $SnCl_4$ solution according to the given weight ratio of In_2O_3 and SnO_2 (90:10), and then by adding hydrochloric acid according to the given ratio of T_{Cl} and T_{In} (5:1, T_{Cl} was the total molar concentration of chlorine ion, T_{In} was the total molar concentration of indium ion). pH value of the solution was controlled by NH_4HCO_3 solution (20%). A colorless transparent composite complex salt crystal—$(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5{\cdot}?H_2O$—was synthesized by drying the solution with pH = 2.5–3 at 80°C.

Received 18 July 2008; accepted 17 August 2008.
The work is sponsored by the Department of Education of Jiangxi Province, China (Grant No. GJJ09626).
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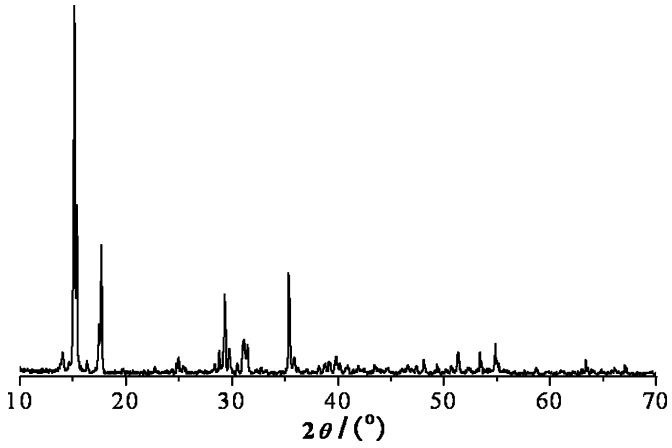

FIG. 1. XRD pattern of $(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5 \cdot ?H_2O$.

Preparation of ITO powders

The reaction solution was prepared by mixing $InCl_3$, $SnCl_4$ solution according to the given weight ratio of In_2O_3 and SnO_2 (90:10), and then by adding hydrochloric acid according to the given ratio of $T_{Cl}/T_{In} = 5{:}1$. Then the dispersant (polyethylene glycol) was added, and the deionized water was added to adjust the final $T_{In} = 1$ mol/L.Then NH_4HCO_3 solution (20%) was dropped into the reaction solution to adjust the pH value = 6–7 under room temperature and fiercely stirring conditions. The hydrolyzate of the composite complex salt, namely precursor or deposition was obtained by filtering the reaction solution. Excess NH_4^+ and Cl^- ions were removed by repeated washing. The powders were calcined at 700°C for 1 h in air to obtain the final product.

The produced composite complex salt crystal was examined by X-ray diffraction (XRD, RigaKu D/MAX 2500 V) using CuKa radiation, and the produced ITO powders was examined by powder X-ray diffraction (XRD, PANalytical X'Pert PRO). Particle morphology was characterized by transmission electron microscope (TEM, JEOL JEM-2010(HT). Particle size was characterized by TEM and laser particle size analyzer (Malvern Zetasizer Nano S90).

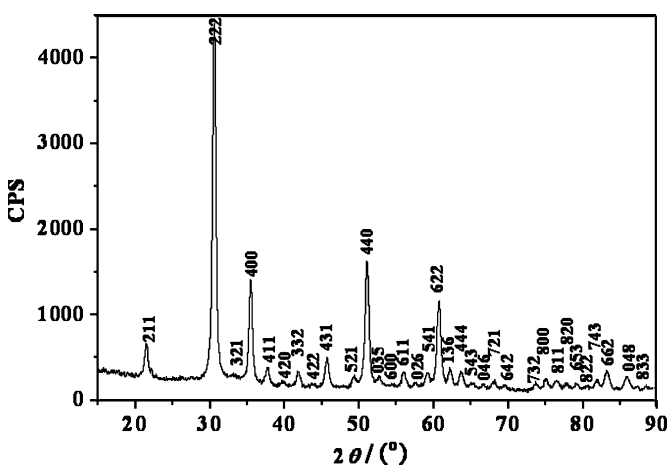

FIG. 2. XRD pattern of ITO.

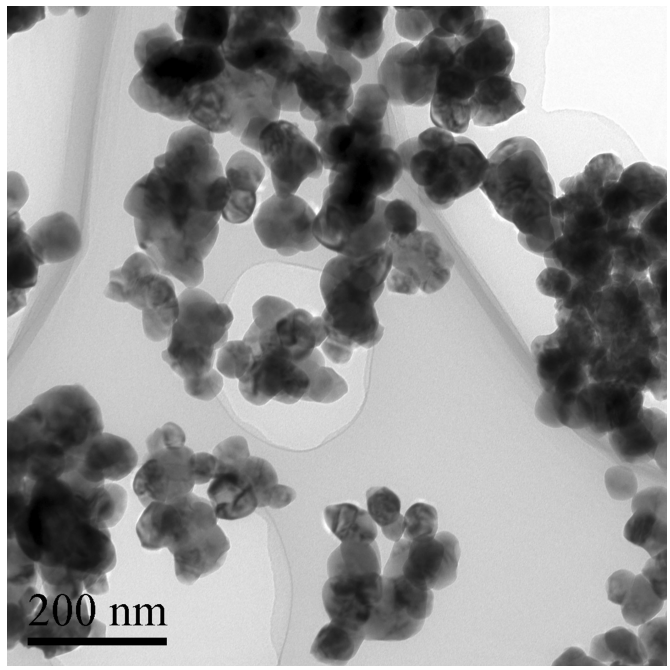

FIG. 3. TEM micrograph of ITO powders.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray powder diffraction pattern of the synthesized crystal. The pattern was obtained by use of an RigaKu D/max 2500 V diffractometer equipped with a Cu tube (Cu/K-alpha1, $\lambda = 1.54056$ Å). All peak positions in Figure 1 are extremely similar to PDF card (37–832) of $(NH_4)_2InCl_5 \cdot ? H_2O$. $(NH_4)_2SnCl_6$ peak is not observed in Figure 1. But every peak position in Figure 1 has slightly shifted

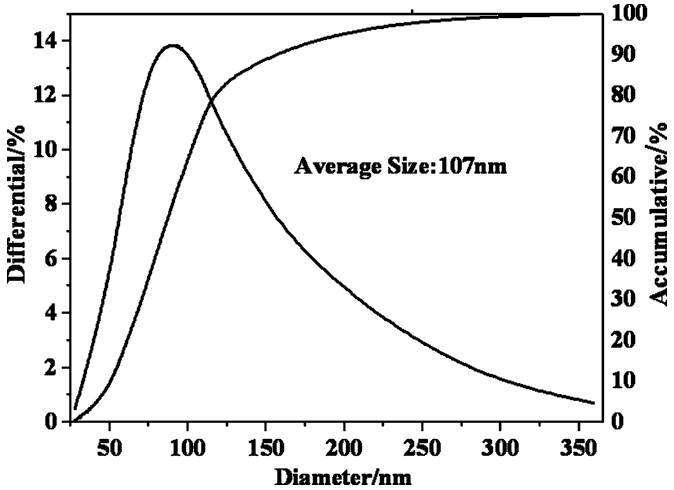

FIG. 4. Particle size analysis of ITO powders.

from low-angle to high-angle, namely every d-value is smaller than the corresponding d-value of the PDF card (37–832). Because the radius of Sn^{4+} is smaller than that of In^{3+}, doping tin caused the crystal cell of $(NH_4)_2InCl_5 \cdot ? H_2O$ to swell and crystal lattice of $(NH_4)_2InCl_5 \cdot ? H_2O$ to distort, transform and loosen. It was affirmed that the crystal with molecular formula—$(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5 \cdot ? H_2O$ is a new composite complex salt. The diffraction data of the new compounded salt have passed the strict qualification of the international centre for diffraction data (ICDD), the card number is 56–382.

The synthesis of the composite complex salt indicated that the composite complex ions system—$[In^{3+}\ Sn^{4+}]$-Cl^- existed in the reaction solution. Formed composite complex ions decreased the concentration of the dissociative $[In^{3+}\ Sn^{4+}]$. The decreased concentration of dissociative $[In^{3+}\ Sn^{4+}]$ caused the decreased supersaturation degree of reaction solution and the decreased growth speed of crystal nucleus, and in the end the particle size of ITO was decreased.

The ITO nanoparticles were prepared by calcining the prepared hydrolyzate of $(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5 \cdot ? H_2O$ under room temperature and fiercely stirring conditions, using NH_4HCO_3 solution as precipitator and polyethylene glycol as disperser. The XRD investigation (Figure 2) indicated that the prepared ITO is single-phase of In_2O_3 cubic bixbyite structure[9–11] and no new phase was formed by Sn-doping because SnO_2 peaks or $In_4Sn_3O_{12}$[3,10] peaks were not observed. The average crystalline grain size ($D = 34.6$ nm) was calculated from X-ray diffraction data, using the Scherrer equation: $D = k\lambda/(\beta \mathrm{Cos}\theta)$.[12] The TEM observation (Figure 3) indicated that the powder had a primary particle size from 50 to100 nm, and the laser particle sizer analysis (Figure 4) showed that the average aggregation size of powder was about 107 nm, which indicated the dispersion of the prepared ITO powders was better.

CONCLUSIONS

Indium-tin oxide (ITO) nanoparticles were prepared from the hydrolyzate of $(NH_4)_{1.91}(In_{0.91}Sn_{0.09})Cl_5 \cdot ? H_2O$. The hydrolyzate was prepared under room temperature and fiercely stirring conditions, using NH_4HCO_3 solution as precipitator and polyethylene glycol as disperser. The results indicated the an average crystalline grain size, a primary particle size and an average aggregation size of prepared ITO powders is 34.6 nm, 50–100 nm and of 107 nm, respectively. It indicates the dispersion of the prepared ITO powders was better.

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