Research Article

Preparation of ITO Nanoparticles by Liquid Phase Coprecipitation Method

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The nanoscale indium tin oxide (ITO) particles are synthesized by liquid phase coprecipitation method under given conditions with solution of indium chloride, tin chloride, and ammonia. The absolute ethyl alcohol or deionized water was used as solvent and the dodecylamine or hexadecylamine surfactant was used as a dispersant in the reaction system. The sample powder was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and high-resolution electron microscopy (HRTEM). Based on the transmission electron micrograph, the influences of the two different solvents and the two different dispersants on the nanoparticle size and dispersion were studied, respectively. The results showed that the ITO particles are finely crystallized body-centered cubic structure. The particle size has distributed in 30 nm to 90 nm.

1. Introduction

Tin-doped indium oxide (Indium tin oxide, ITO), a kind of n-type semiconductor material, has a wide forbidden band (3.3 eV to 4.3 eV). Indium tin oxide thin film has high transparency in the visible light region and lower electric resistivity [1, 2]. It has been used as electrodes in manufacturing of solar cells, flat panel displays, and gas sensors. The tradition deposition techniques of ITO film are DC sputtering, RF sputtering, or electron beam evaporation. It is the first step to fabricate indium and tin alloy target or ITO ceramic target. Afterwards the target is sputtered to glass substrate by the controlled electron beam. These techniques need costly equipments, and the utilization rate of the target materials is as low as 20% [3]. Because indium is a rare metal, it is necessary to explore a new route to deposit ITO thin film with high-Indium utilization rate. The synthesis nanoparticles of metal oxide from aqueous solutions and deposition thin films at low temperatures is an important way for preparation of transparent conductive film [4]. Dip-coating or spray deposition of light transparent, good conductive, and low-membrane resistant ITO film has been studied by the researchers [5–7]. The fabrication

of ITO nanoparticle is important in emulsion (so-called “ink”) preparation for spray deposition or dip-coating ITO film. The ITO thin film’s quality is related to the size and morphology of the nanoparticles. With the development of nanometer material research, several kinds of preparation methods for nanosized ITO emerged. The current methods for nanometer indium tin oxide preparation mainly include solid-phase method, liquid-phase method, and gas-phase method [8–10].

The liquid-phase method, with the advantages of simple operation and controllable granularity, can realize the atomic scale level of mixing. The doping of components achieves easily, and the nanoscale powder material has high-surface activity. The liquid-phase methods include liquid phase precipitation, hydrothermal (high temperature hydrolysis), Sol-gel (colloidal chemistry), radiation chemical synthesis, and so forth [11, 12]. In this research, the ITO nanoparticles, which will be used in spray coating of ITO thin film, are prepared by liquid-phase coprecipitation with indium chloride and tin chloride as main raw material. The ITO nanoparticles were characterized by means of transmission electron microscopy (TEM), and X-ray diffraction (XRD).

2. Experiment Method

2.1. Experiment Process. The synthesis process of ITO nanoparticle by liquid phase co-precipitation is as follows. A certain quality of indium chloride ($\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ 99%, Aldrich) and tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ 99%, Aldrich) was dissolved in pure deionized water or ethanol, keeping the ratio of $\text{In}_2\text{O}_3:\text{SnO}_2 = 9:1$. The concentrations of InCl_3 in solution are 0.1, 0.2, and 0.3 mol/L, respectively. Certain concentrations (1.25%, 2.50%, and 5.00%, resp.) of ammonia solutions were made by mixing certain amount of ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 25%) with pure water. The prepared InCl_3 solution was transferred into fixed three-neck flask, keeping in 303 K to 363 K temperature under electromagnetic agitation. The ammonia solution was added to the flask, controlling the stirring speed and testing the pH value till the required pH value. And a certain amount of dodecylamine or hexadecylamine (DDA or HDA, Fluka) was added as dispersant. The precipitate precursor of ITO was aged a certain time and washed with deionized water and absolute alcohol for three times, respectively. After washing, the precipitates were dried for one hour at 353 K. The dried samples were calcinated for 1, 1.5, and 2 hours at 773 K, 873 K, and 973 K, respectively to get the indium tin oxide nanopowder by thermal decomposing.

2.2. Characterizing Methods. The morphology and structure of the prepared nanoparticles were characterized by means of a transmission electron microscopy (TEM) and X-ray diffraction (XRD). The microstructure of the ITO samples were analysed on a Tecnai G2 20 S-TWIN model TEM with 200 kV acceleration voltage. For TEM analysis, the sample was dispersed in a few milliliters of tetrahydrofuran in an ultrasonic bath, and a drop of this dispersion was placed on a copper grid coated with a carbon film. The XRD measurements of nanopowder were performed on a D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

3. Results and Discussion

3.1. X-Ray Diffraction of the Nanoparticles. The precursor precipitate and the calcinated samples were examined by an X-ray diffractometer (D8 ADVANCE type), respectively to analyze phase and structure. The XRD patterns are shown in Figure 1. The XRD pattern of precursor precipitate prepared in ethyl alcohol solvent is shown in Figure 1(a). A strong and sharp peak can be seen in Figure 1(a), while the other diffraction peaks are more weaker. According to JCPDS calibration (PDF#76-1463), the precursor precipitate is $\text{In}(\text{OH})_3$ with body-centred cubic crystalline structure. The diffraction peaks are more complicated than the PDF76-1463 standard. The reason is that maybe there is a certain amount of $\text{Sn}(\text{OH})_4$ in the precursor. The XRD pattern in Figure 1(b) is the result of calcinating (973 K for 1 h) sample, which its precursor precipitate was prepared in pure water solvent. The XRD patterns of samples at different calcinating temperature (773 K, 873 K, and 973 K) are shown

in Figure 1(c), which their precursors were precipitated in ethyl alcohol solvent. According to the JCPDS (PDF#06-0416), the samples in Figures 1(b) and 1(c) are In_2O_3 powder with body-centred cubic crystalline structure. Kim, and so forth, synthesized ITO particle that had hexagonal structure and cubic structure. As the pH value of coprecipitated solution was increased, the amount of hexagonal crystal was decreased. ITO particle with mostly cubic structure was produced at higher than pH 10 [12]. The ITO particles that we prepared by co-precipitate method only have cubic structure. After 793 K, calcinating the diffraction peaks of the samples are more stronger and sharper, indicating that the In_2O_3 crystalline structure is more perfect. The crystallized characteristic is gradually becoming obvious with the calcinating temperature increasing from 773 K to 973 K by Figure 1(c). By comparison, it can be seen that the calcinating temperature plays a more important role than the calcinating time in improving crystal structure. As long as there is enough calcinating temperature, the perfect In_2O_3 nanocrystal structure can be obtained in a relatively short period of time. There are no peaks that represent the tin oxide, and the In_2O_3 lattice parameter does not change obviously, indicating that the tin atoms arrange into the In_2O_3 crystal lattice.

3.2. The TEM Analysis of ITO Nanoparticles. The particle size and morphology of the ITO samples were analyzed by a transmission electron microscopy (TEM, model Tecnai G² 20 S-TWIN). The TEM photographs of the samples are illustrated in Figure 2. The TEM photographs of the samples prepared in ethanol solvent and calcinated at 773 K and 973 K, respectively are shown in Figures 2(a) and 2(b). The TEM photograph morphology in Figure 2(c) stands for the sample precipitated in deionized water solvent and calcinated at 873 K. Comparing Figure 2(a) with Figure 2(b), it can be seen that at lower calcinating temperature (773 K), the particles of samples are finer, but they are more seriously agglomerated. When the thermal decomposition temperature is higher (973 K), the crystal size increases obviously and the agglomeration degree is reduced. The particles appear hexagon or short rod shapes.

The particle size of indium oxide samples after 773 K°C calcination is 30 to 50 nm, and the average particle size is 36.2 nm, basing on the statistics from a group of images. It is 50 to 90 nm after 973 K calcinations, and the average particle size is 78.3 nm. Comparing Figure 2(b) with Figure 2(c), it can be seen that although its thermo-decomposing temperature in Figure 2(b) is higher than Figure 2(c), its particle size has not grown up significantly, and that the nanoparticles dispersion has no obvious difference. Preparing in ethanol solvent does not improve the In_2O_3 nanoparticle dispersion degree. The high resolution electron microscopy (HRTEM) image of sample (b) is presented in Figure 2(d). The selected area electron diffraction (SAED) pattern is also in the same figure. The ITO nanoparticle is body-center-cubic structure and it crystallized well.

FIGURE 1: The X-ray diffraction patterns of samples. (a) The precursor precipitate, (b) the ITO nanoparticles prepared in deionized water solvent, (c) the ITO nanoparticles prepared in ethyl alcohol solvent and then decomposed at different temperatures.

3.3. The Particle Size Calculated by Scherrer Equation. The prepared ITO particles can be calculated by Scherrer equation, based on the XRD pattern. The Scherrer equation is as follow:

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl} \cos \theta_{hkl}}, \quad (1)$$

where D_{hkl} represents particle size (unit nm) being perpendicular to (hkl) crystal plane. β_{hkl} is broadening (unit Rad) of the diffract peak by the grain refinement. θ_{hkl} is diffraction angle of (hkl) crystal plane. λ is the wave length of the X-ray, where it is 1.5406 Å. K is a constant; its numerical value is related to defines of the β_{hkl} . K equals to 0.89 when β_{hkl} takes the half of the broadening of the diffract peak.

The particle size was calculated corresponding to the (222), (440), and (400) diffract peaks for every diffract pattern of calcinating samples. The average value of each sample is listed in Table 1.

Based on the calculated results, the particle size grows up gradually with the increase of the calcination temperature. The average particle size becomes 63 nm of 973 K calcinating from 22 nm of the 773 K calcinating. The calculated results are compared with the statistics of transmission electron

TABLE 1: The calculated results of ITO particle size by Scherrer equation.

Samples at different calcinating temperature (k)	773	873	973
Average particle size value (nm)	22	44	63

microscope. The particle size of indium tin oxide had been statistically analyzed by TEM images as in Figures 2(a) and 2(b), which the calcinating temperatures were 773 K and 973 K, respectively. The particle size of indium oxide samples after 773 K calcination is 30 to 50 nm, and the average particle size is 36.2 nm. It is 50 to 100 nm after 973 K calcinations, and the average particle size is 78.3 nm. The particle size from the TEM photograph results is larger than the calculated results by the Scherrer equation. This is mainly due to the various factors influence on the accuracy of particle size D_{hkl} computed by Scherrer formula, making the calculated value is less than the TEM measurements. First of all, if there is lattice imperfection in the crystal, the broadening of diffraction peak is caused not only by the grain size refinement but also by the lattice imperfection. Second, the X-ray diffraction peak is sharp. It is difficult to

FIGURE 2: The TEM and HRTEM images of ITO nanoparticles synthesized in different solvents. (a) The absolute ethyl alcohol used as solvent and the precipitate decomposed at 737 K, (b) the absolute ethyl alcohol used as solvent and the precipitate decomposed at 937 K, (c) the deionized water used as solvent and the precipitate decomposed at 837 K, (d) the HRTEM photograph and the selective electron diffraction pattern of sample (b).

FIGURE 3: The TEM images of ITO nanoparticles with different dispersants. (a) The dodecylamine surfactant as dispersant, (b) the hexadecylamine surfactant as dispersant.

measure the width value accurately, enlarging the calculation deviation.

3.4. Dispersant Effect on the Morphology and Dispersion of the ITO Nanoparticles. Two dispersants were used in the experiments, namely, dodecylamine and hexadecylamine. The dispersion performance of ITO nanoparticle was compared through the contrast experiment. The ITO nanoparticle TEM images, which prepared under the same conditions except using two kinds of dispersant, respectively, are shown in Figure 3. The ITO nanoparticle TEM photo with dodecylamine surfactant as dispersant is in Figure 3(a). While the ITO nanoparticle TEM photo with hexadecylamine surfactant as dispersant is in Figure 3(b). It can be observed from Figure 3 that ITO nanoparticles synthesized with dodecylamine are not dispersed well, and some particles are arranged into the long axis orderly. At the same time, the ITO nanoparticles synthesized with hexadecylamine are dispersed better than with dodecylamine. The morphology of ITO nanoparticles either with dodecylamine or with hexadecylamine as dispersant appears irregular shape. Some of the particles appear hexagon or short rod shapes.

4. Conclusion

The nanoscale indium tin oxide (ITO) particles are successfully synthesized by liquid phase co-precipitation method under given conditions with reactants of indium chloride, tin chloride, and ammonia. The absolute ethyl alcohol or deionized water was used as solvent, and the dodecylamine or hexadecylamine surfactant was used as a dispersant in the reaction system. The ITO particles are finely crystallized body centered cubic structure. The particle size has preferably dispersivity and distributes in 30 nm to 90 nm.

The dispersivity of ITO nanoparticle does not have significant difference prepared in absolute ethyl alcohol or deionized water solvent with hexadecylamine surfactant as dispersant in the reaction system. At certain conditions, the dodecylamine surfactant can organise the indium oxide nanoparticles in lines, but that self-assembly phenomena needs further study.

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