Journal of Alloys and Compounds 509 (2011) 4538–4542

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

# A novel aqueous co-precipitation process to prepare indium tin oxide nanopowders

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ARTICLE INFO

*Article history:*
Received 21 June 2010
Received in revised form 12 January 2011
Accepted 15 January 2011
Available online 22 January 2011

*Keywords:*
ITO powders
Aqueous co-precipitation process
Nanoparticles
XRD

ABSTRACT

In this paper, a novel aqueous co-precipitation process for preparing ITO (indium tin oxide) nanopowders was investigated. In this process, the solutions of $In^{3+}$–$Sn^{4+}$ ions and 25% $NH_3 \cdot H_2O$ were simultaneously added into the solution of $(NH_4)_2SO_4$–$NH_3 \cdot H_2O$, $NH_4Cl$–$NH_3 \cdot H_2O$ and $NH_3 \cdot H_2O$ to make different reaction solutions. When $(NH_4)_2SO_4$–$NH_3 \cdot H_2O$ solution was used as the primary reaction liquid with pH value in the range of 6.5–7.0, spherical ITO particles with uniform particle size (10–20 nm), low agglomeration and large specific surface were obtained. The ITO particles were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and energy-dispersive spectrometer (EDS). The EDS analysis indicated that the distribution of In and Sn elements in the ITO powders was uniform and their mass ratio was close to 9:1, which would result from the co-precipitation process that provided a stable chemical circumstance for $In^{3+}$ and $Sn^{4+}$ to be co-precipitated.

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## 1. Introduction

Indium tin oxide (ITO), as a kind of TCO (transparent conductive oxide) materials, is indium oxide doped with $Sn^{4+}$. It has been widely used in many fields such as solar cells [1–3], flat panel displays [4,5], radiation reflective coatings [6], magnetoresistance devices [7], and gas sensors [8,9] due to its excellent transparent conductivity, outstanding absorption for ultraviolet radiation, strong reflectivity for infrared ray and so on. ITO nanopowders with a narrow size distribution, definite shape and uniform composition are an important raw material for ITO target and film [10,11]. Therefore, many studies of ITO have been focused on preparation and properties of its powders, especially on its shape and size. In recent years, ITO nanoparticles with uniform and lower dimensional structure, such as aciculae, nanotubes, nanospheres, nanorods, and nanowires, have been prepared by different wet chemical methods including co-precipitation process [12–15], sol–gel process [16,17], hydrothermal process [18,19], concentration–precipitation method [20] and template method [21]. Among them, a sol–gol method has a long flow sheet and needs some organic solutions in the process, such as acetylacetone [16], citric acid, ethylene glycol and so on [17]. Compared with other synthesis method, a hydrothermal process usually needs higher synthesis temperature and pressure provided [18]. In addition, the template method is still difficult to be applied on a large scale but can help prepare ITO nanotubes.

However, aqueous co-precipitation process has been attractive because only simple equipments are needed in this process (economically favorable), it can attain molecular level mixing and it is easy to be industrialized. In a conventional chemical precipitation process, the salt solution with $In^{3+}$ and $Sn^{4+}$ ions is used as raw material and inorganic alkali as precipitator. The precipitator is injected into the premixed salt solution and ITO precursors are prepared through precipitation reactions. Then ITO particles are obtained after the ITO precursors are washed, dried, calcinated and milled. One problem in the above precipitation process is that the injection method will lead to extreme fluctuation of pH (from 1.0 to 10.0), which will lead to an unstable formation and growth circumstances for ITO precursors in solution. So it would be difficult to prepare the ITO powders with uniform morphology and particle size. For example, Kim et al. synthesized ITO particles of 20–60 nm in diameter by co-precipitation of indium chloride and tin chloride, and investigated the ITO particle size and shape at different pH values of the reaction solution. In their work, ITO particle size and shape became distinct when pH value was changed [12]. Furthermore, different pH values led to different phase structure in the synthesized ITO powders. Kim et al. reported that the preparation of corundum and bixbyite structure of ITO nanoparti-

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doi:10.1016/j.jallcom.2011.01.083

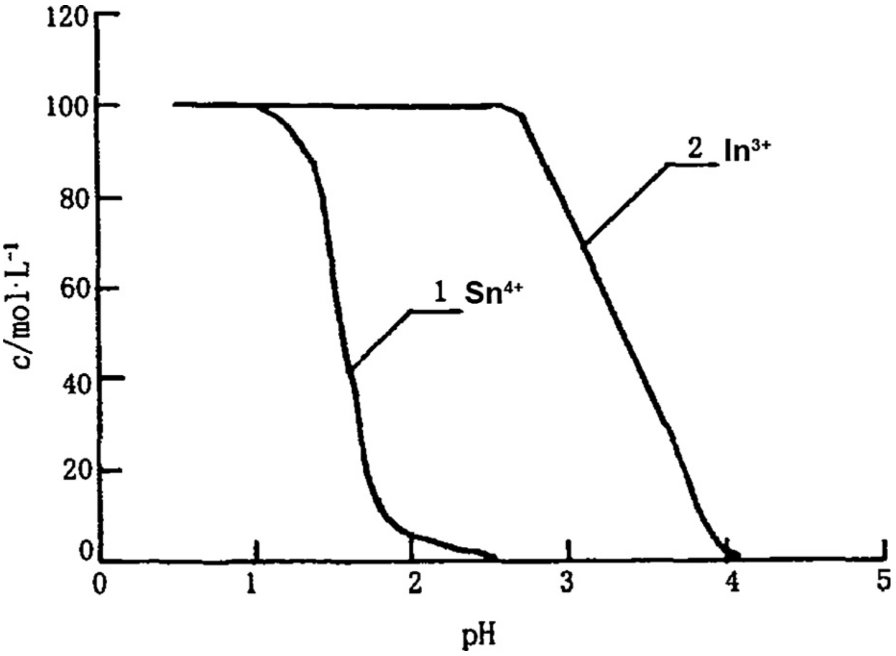

**Fig. 1.** The relation curves between molar concentrations and the pH in solution [22]: 1 – $Sn^{4+}$; 2 – $In^{3+}$ (c in *Y*-axis is molarity of $Sn^{4+}$ or $In^{3+}$ in solutions).

cles by the simple temperature and pH controlled coprecipitation in aqueous solution [14]. However, the $In^{3+}$ and $Sn^{4+}$ ions would not hydrolysize simultaneously during the chemical precipitation process, which would affect the doping uniformity of $Sn^{4+}$ ions in ITO precursors. For instance, Li and his group used ammonia water to make $In^{3+}$ and $Sn^{4+}$ co-precipitate to produce ITO precursors, then the precursors with mixture phases including $In(OH)_3$, InOOH and $Sn_3O_2(OH)_2$ were prepared instead of the $In(OH)_3$ phase doped $Sn^{4+}$ ions [15]. From Fig. 1, it can be seen that $Sn^{4+}$ ions (100 mol $l^{-1}$) will be $Sn(OH)_4$ precipitate when pH > 1.1 and $Sn^{4+}$ ions almost disappear from the solution while pH value is above 2.6. But the precipitation behavior of $In^{3+}$ ions is observably different from that of $Sn^{4+}$ ions. The hydrolysis process of $In^{3+}$ ions will happen when pH value is in the range of 2.8–4.1. Therefore, in order to obtain simultaneous precipitation of these two ions, the pH of the reaction solution need to be >4.1 as soon as possible.

In order to avoid the effect of pH value change during precipitation process, some solution systems were employed recently. Pan and his group used the mixture solution of triethanolamine and polyvinylpyrolidone as the co-precipitation system and adjusted the pH of the solution to 8.00 using diluted HCl solution at 80 °C. Then the $InCl_3$ solution containing about 10 wt% of $SnCl_4$ was added dropwise into the system during which ammonia water was injected into the solution system as well to stabilize the pH value. By this way, they obtained spherical and cubic ITO nanoparticles respectively by controlling the ratio of polyvinylpyrolidone [23]. Yu et al. synthesized ITO uniform nanowires and nanorods with corundum structure by a co-precipitation-anneal method. In which, ether played crucial roles to help prepare one-dimensional ITO nanoparticles and effectively reduce the hydrolysis rate of $Sn^{4+}$ resulting in the formation of the co-precipitates [24].

In this work, in order to reduce the pH value fluctuation in the conventional chemical precipitation process and make $In^{3+}$ and $Sn^{4+}$ co-precipitate completely, a novel aqueous co-precipitation process for preparing ITO nanoparticles was studied. The inorganic solutions, such as $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$, $NH_4Cl$–$NH_3{\cdot}H_2O$ and $NH_3{\cdot}H_2O$, were employed as primary reaction liquids. The mixed solution of $In^{3+}$–$Sn^{4+}$ ions and the precipitator solution of 25% $NH_3{\cdot}H_2O$ were simultaneously injected into the primary reaction liquid. The injection rates were controlled to maintain the pH of the reaction system stable. The influences of different primary reaction liquids and different pH values of the reaction system on ITO nanoparticles were investigated.

## 2. Experimental procedures

### 2.1. Materials

All the chemicals used in this work are analytical reagent grade (AR) and are used without further purification. Metal indium with low impurities (99.995 wt%, the composition listed in Table 1) was used as $In^{3+}$ ion source by dissolving in dilute sulfuric acid. $SnCl_4{\cdot}5H_2O$ was used as the $Sn^{4+}$ ion source. 25 wt% of $NH_3{\cdot}H_2O$ was used to adjust the pH in precipitation process, and to prepare the primary reaction liquids by mixing it with $(NH_4)_2SO_4$ and $NH_4Cl$, respectively. Absolute ethanol was used as the dispersion medium in washing process.

### 2.2. Experimental

Metal indium was dissolved in dilute sulfuric acid to make 50 g/l $In^{3+}$ solution and $SnCl_4{\cdot}5H_2O$ was dissolved in de-ionized water to make 30 g/l $Sn^{4+}$ solution. The $In^{3+}$–$Sn^{4+}$ mixture solution was prepared according to the mass ratio of $In_2O_3$:$SnO_2$ = 9:1. 250 ml primary reaction solutions of $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$, $NH_4Cl$–$NH_3{\cdot}H_2O$ and $NH_3{\cdot}H_2O$ were prepared separately in a three-necked bottle in 70 °C water bath with mechanical stirring at 1000 r/min. By using two separate peristaltic pumps, the solutions of $In^{3+}$–$Sn^{4+}$ and 25% $NH_3{\cdot}H_2O$ were simultaneously added into the primary reaction liquid. The injection rate for the mixed $In^{3+}$–$Sn^{4+}$ solution was maintained 3.0 ml/min, and the injection rate for ammonia

**Table 1**
The composition of metal indium (mass %).

| In | Pb | Zn | Cd | As | Al | Cu | Fe | Sn | Tl | Others |
|---|---|---|---|---|---|---|---|---|---|---|
| 99.995 | 0.0005 | 0.0005 | 0.0004 | 0.0005 | 0.0003 | 0.0004 | 0.0005 | 0.0004 | 0.0003 | 0.0012 |

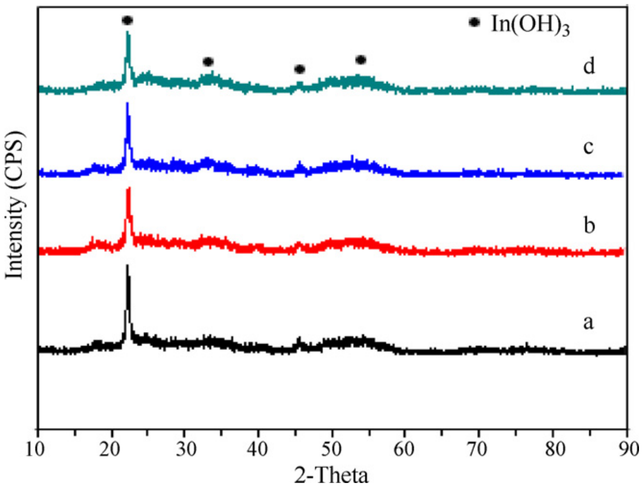

**Fig. 2.** XRD patterns of ITO precursors prepared in $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ with different Sn contents: (a) 0 wt% $SnO_2$; (b) 5 wt% $SnO_2$; (c) 10 wt% $SnO_2$; (d) 15 wt% $SnO_2$.

was adjusted to maintain a constant pH value. After the precipitation process, the reaction solution was heated to 80 °C and continually stirred for 30 min, then aged at room temperature for 12 h. The resultant suspension was filtered and washed with deionized water and absolute ethanol by ultrasonic dispersion to remove the residual impurities, such as $SO_4{}^{2-}$ and $Cl^-$ after test procedures employing chemical reagents of $BaCl_2$ (AR) and $AgNO_3$ (AR). The final filter cake was dried at 85 °C in a vacuum drying oven for 16 h and then calcined at 700 °C for 4 h to obtain the ITO nanopowders.

### 2.3. *Characterization of ITO powders*

The phase and the crystallographic structure of the product were characterized by X-ray diffraction (XRD) using a Rigaku (Japan) D/max-3B X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation operated at 40 kV and 30 mA. Transmission electron microscopes (TEM, H-800 and JEM-2010) were used to observe the morphology and particle size distribution of the ITO nanopowders. Energy dispersive spectrometer (EDS) affiliated in 30ESEM-TMP was employed to investigate the composition uniformity of the doped Tin.

## 3. Results and discussion

### 3.1. *Analysis for ITO precursors and samples prepared in $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$*

Fig. 2 shows the X-ray diffraction patterns of the ITO precursors from ITO powders containing 0, 5, 10 and 15 wt.% $SnO_2$. The XRD peaks are consistent with the data of card 16-0161 in the JCPDS file of $In(OH)_3$ with a cubic phase and there are no any other crystal peaks, which indicates the $Sn^{4+}$ has been doped into the precursors. But the amorphous scattering peaks in every pattern indicate that the crystal precursors are not perfect, and depend on the aging time and temperature during the preparation process. When Sn was added, the intensity of the peaks decreased and the peaks broadened.

Fig. 3 shows the XRD pattern of the sample prepared in the primary reaction liquid of $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ at pH 6.5–7.0. It can be seen that the XRD peaks are consistent with the data of the card 6-0416 in the JCPDS file showing a cubic structure of $In_2O_3$. The peaks with the $2\theta$ values of 30.499°, 35.377°, 50.936° and 60.561° are associated with the crystal planes of $In_2O_3$ of (2 2 2), (4 0 0), (4 4 0) and (6 2 2), respectively. There are no diffraction peaks of $SnO_2$ phase or any other phase in XRD pattern, which can be attributed to the fact that over-saturation of $Sn^{4+}$ and $In^{3+}$ could conduce to co-precipitation process when pH is 6.5–7.0. So all the $Sn^{4+}$ ions were doped into the $In_2O_3$ crystal lattice and formed a single cubic structure. XRD peaks of sample are shifted to the left which may result from doping $SnO_2$ in $In_2O_3$ crystal lattice [25,26]. Sharp diffraction peaks imply that the ITO powders are highly crystalline. The XRD patterns for the samples prepared in other primary reaction liquid were similar to that prepared in $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ solution.

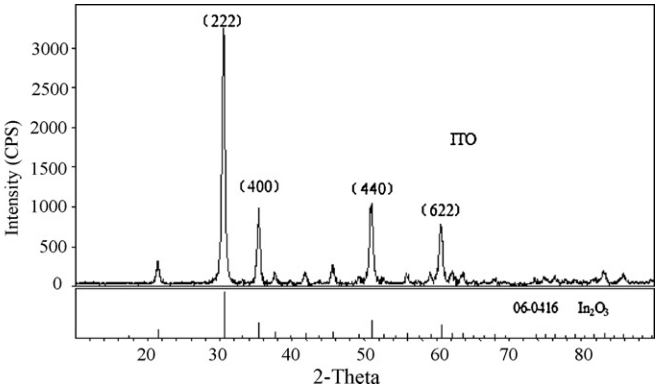

**Fig. 3.** XRD pattern of the ITO nanopowders prepared in $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ at pH 6.5–7.0.

ITO particles were also prepared by controlling reaction system at different pH values when $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ solution was used as primary reaction liquid. Their average crystal sizes were calculated according to Debye Scherrer formula from their XRD patterns and the specific surface were measured as well. The results are listed in Table 2. Obviously, ITO nanoparticles obtained with pH value in the range of 6.5–7.0 have smallest crystal size and largest specific surface. The results imply that excessive $H^+$ or $OH^-$ ions in the reaction solution may lead to the growth of ITO nanoparticles. On the other hand, when $H^+$ ions are slightly less than or equivalent to $OH^-$ ions in precipitation reaction solution, it will provide strong electrostatic force among colloidal particles of ITO precursor and result into small crystal size. The $d_{BET}$ values (17.36 nm, 15.75 nm, 13.85 nm, 17.03 nm and 15.39 nm) corresponding to ITO powders at different pH values in Table 2 were deduced by the test results of the specific surface $S_{BET}$ based on the formula $d_{BET} = 6/\rho \cdot S_{BET}$ (in which $\rho = 7.02\ g/cm^3$ is the density of prepared ITO powders and suppose the ITO particles prepared have a perfect spherical shape). It can be seen that there are small differences between the average crystal size $D$ and $d_{BET}$ at different pH values, such as when pH value was in the range of 6.5–7.0, $d_{BET}$ is merely more 0.64 nm than $D$, which would imply the single crystal ITO particle was perhaps prepared.

### 3.2. *The influence of different primary reaction liquids on ITO nanoparticles*

Fig. 4(a–c) shows TEM images of ITO nanopowders prepared in different prime reaction liquids: (a) $NH_4Cl$–$NH_3{\cdot}H_2O$ with pH 6.5–7.0; (b) $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ with pH 6.5–7.0; and (c) $NH_3{\cdot}H_2O$. For comparison, ITO powders were also prepared by traditional chemical precipitation process ($NH_3{\cdot}H_2O$ was injected into

**Table 2**
The crystal size and BET surface area of ITO particles prepared at different pH in $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ solution.

| pH | Average crystal size $D$ (nm) | Specific surface $S_{BET}$ ($m^2/g$) | $d_{BET}$ (nm) |
|---|---|---|---|
| 4.5–5.0 | 14.59 | 49.23 | 17.36 |
| 5.5–6.0 | 13.42 | 54.26 | 15.75 |
| 6.5–7.0 | 13.21 | 61.71 | 13.85 |
| 7.5–8.0 | 15.72 | 50.19 | 17.03 |
| 8.5–9.0 | 13.27 | 55.55 | 15.39 |

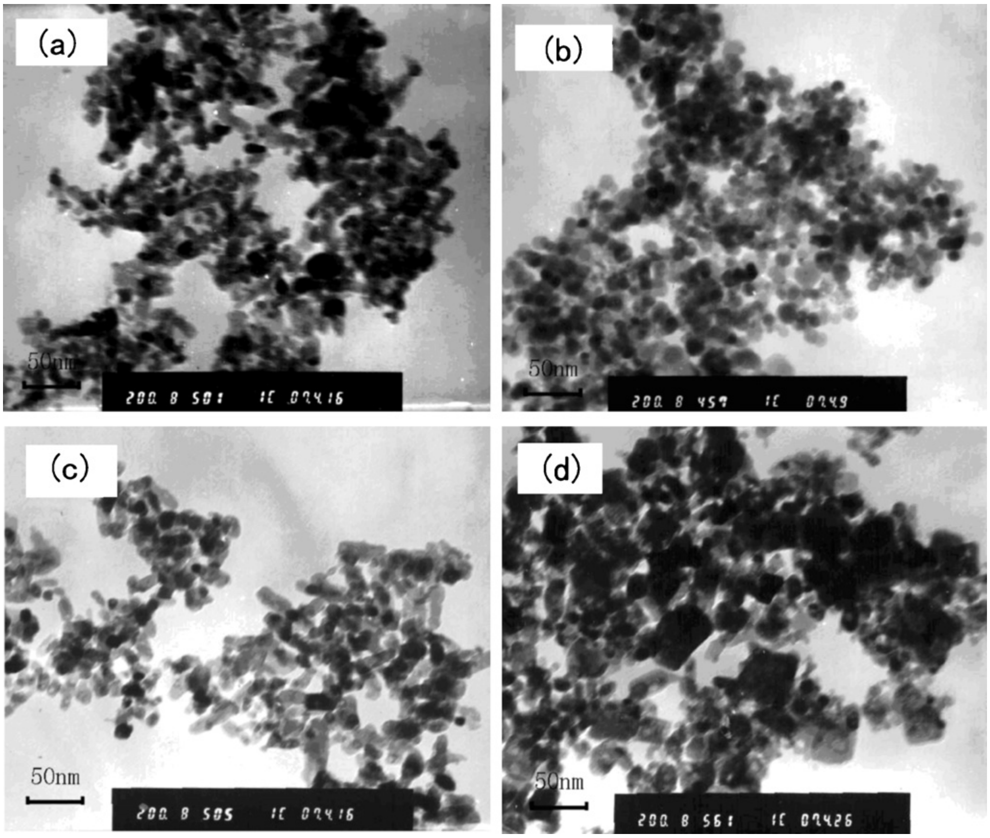

**Fig. 4.** TEM images of ITO nanopowders prepared in different prime reaction liquids: (a) $NH_4Cl–NH_3·H_2O$ with pH 6.5–7.0; (b) $(NH_4)_2SO_4–NH_3·H_2O$ with pH 6.5–7.0; (c) $NH_3·H_2O$; (d) traditional chemical precipitation process.

mixed solution of $In^{3+}–Sn^{4+}$ ions at 3.0 ml/min until pH is 6.5–7.0). It can be seen that the ITO powders in Fig. 4(a–c) have uniform particle size, narrow particle distribution (10–30 nm) and less agglomeration. But the ITO powders in Fig. 4(d) have a wider particle size distribution in the range of 20–70 nm and more agglomeration. The results indicate that the injection precipitation process by two separate pumps in primary reaction liquids is helpful for producing uniform ITO nanoparticles. This could be attributed to the stable co-precipitation circumstance provided by primary reaction liquids, namely, $NH_4Cl–NH_3·H_2O$ solutions and $(NH_4)_2SO_4–NH_3·H_2O$ solutions.

With respect to the morphology of ITO nanoparticles, spherical particle morphology was evident from Fig. 4(b). Fig. 4(a, c, and d), on the other hand, shows that the particles have irregular shape. The ITO sample in Fig. 4(b) was also investigated at higher magnification by high resolution TEM as shown in Fig. 5, which clearly shows the spherical morphology and uniform particle size of 10–20 nm. The irregular shape of the particles in Fig. 4(a, c, and d) is due to different growing circumstances for ITO precursors in different primary reaction liquids. When $NH_4Cl–NH_3·H_2O$ or $(NH_4)_2SO_4–NH_3·H_2O$ is used as primary reaction liquid, $NH_4^+$ was adsorbed on the particle surface of ITO precursors and electronic double layer is formed. Then the repulsion among ITO precursor particles is strengthened and to prevent nanoparticles from agglomerating. However, when $NH_4Cl–NH_3·H_2O$ was used as the primary reaction liquid, $Cl^-$ ions in the reaction solution were difficult to wash completely. Fortunately, this drawback can be avoided when $(NH_4)_2SO_4–NH_3·H_2O$ is used as primary reaction liquid, where the $NH_4^+$ ions can form electronic double layer on particle surface of ITO precursors and $SO_4^{2-}$ ions with heavier molecular weight and bigger ionic radius than $Cl^-$ ions can cause steric restriction among precursor particles agglomerating. Additionally, $SO_4^{2-}$ ions existing in reaction solution may be helpful for preparing spherical ITO particles.

### 3.3. EDS analysis

Energy-dispersive spectrometer analysis was employed to detect 5 different regions on the ITO powder surface to investigate the composition of ITO powders which were prepared at pH 6.5–7.0 in $(NH_4)_2SO_4–NH_3·H_2O$ solution. The contents of element In and Sn in different regions are listed in Table 3. It can be seen that the contents of element In and Sn are in the range of 73.85–74.39 wt% and 7.75–8.06 wt%, respectively, which are close to the theoretical content of 74.44 wt% and 7.88 wt% according to the initially designed composition of ITO powders, i.e. $In_2O_3:SnO_2 = 9:1$ (mass ratio). In addition, the mass ratios of $In_2O_3$ and $SnO_2$ in Table 3 are 8.77:1, 8.96:1, 8.87:1, 9.16:1 and 8.72:1, which are close to the designed value of 9:1. The results indicate that the element distribution of In and Sn in ITO powders is uniform and the mass ratios of $In_2O_3$ and $SnO_2$ is close to the designed value, which should be attributed to the smooth co-precipitation process in a stable chemical circumstance.

**Table 3**
The contents of element In and Sn in different regions of ITO powders.

| Number of region | In (wt%) | Sn (wt%) | $In_2O_3:SnO_2$ (mass ratio) |
|---|---|---|---|
| 1 | 73.85 | 8.02 | 8.77:1 |
| 2 | 74.39 | 7.89 | 8.96:1 |
| 3 | 73.99 | 7.93 | 8.87:1 |
| 4 | 74.67 | 7.75 | 9.16:1 |
| 5 | 73.96 | 8.06 | 8.72:1 |

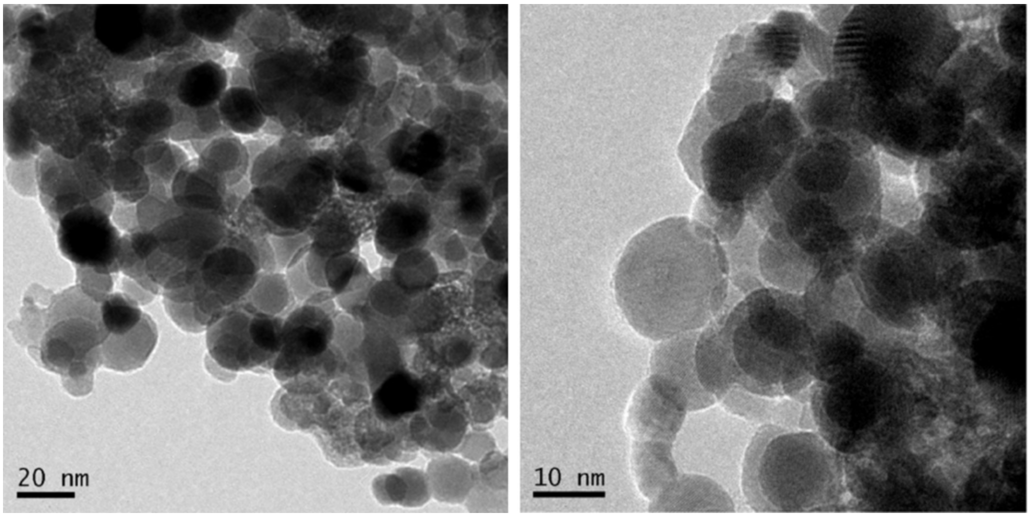

**Fig. 5.** HTEM images of ITO nanopowders prepared in $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ with pH 6.5–7.0.

## 4. Conclusions

1. By using a novel aqueous co-precipitation process, ITO nanopowders with cubic ferrimanganic structure, uniform particle size, narrow particle distribution (10–30 nm), and less agglomeration were prepared. Compared with traditional chemical precipitation process, the current injection precipitation process by two different pumps in primary reaction liquid is helpful for producing uniform ITO nanoparticles, which should be attributed to the stable co-precipitation circumstance provided by the primary reaction liquids, $NH_4Cl$–$NH_3{\cdot}H_2O$ solutions and $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ solutions.
2. When $(NH_4)_2SO_4$–$NH_3{\cdot}H_2O$ solution was used as the primary reaction liquid with pH value in the range of 6.5–7.0, spherical ITO particles with 10–20 nm particle size, small crystal size and large specific surface were obtained. The EDS analysis indicated that the element distribution of In and Sn in ITO powders was uniform and the mass ratio of $In_2O_3$ and $SnO_2$ was close to the designed value, which should also be due to the smooth co-precipitation process of $In^{3+}$ and $Sn^{4+}$ ions in the stable chemical circumstance.

## Acknowledgments

This work was financially supported by NSFC-Yunnan Project (u0837604), NSFC (51004058), research fund of Yunnan Education Department for Young researcher (No. 07C40291), and research fund of Kunming University of Science and Technology for Young researcher (No. 2007003). The authors are grateful to Prof. Kan Jiade, Prof. Liu from Yunnan University, Prof. Wang from Kunming University of Science and Technology and Prof. Song from Kunming Medicine college for their help with the XRD analysis, TEM pictures, and EDS analysis.

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