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ITO nano-powders prepared by microwave-assisted co-precipitation in aqueous phase

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Abstract: By using microwave-assisted co-precipitation in aqueous phase, adding surface activation agent PEG-6000 into the mixture of $InCl_3$ solution and $SnCl_4$ solution, and dropping the ammonia solution with the density (volume ratio) of 1:0 to 1:4, ITO precursor was prepared at different reaction system temperatures of 35 ℃−85 ℃, then ITO nano-powder was obtained after it was calcinated at 800 ℃for 1 h. The morphology of ITO nano-powder was characterized by SEM and its electrical conductivity was determined by conductivity meter. The effects of different temperatures and ammonia concentration in microwave-assisted reaction system on its morphology and electric conductivity were discussed. The experimental results indicate that with the dilution of the ammonia solution or the rise of reacting system temperature, the morphology of ITO particles is transformed from spherical to rod-like one with the decline of its electric conductivity. And the electric conductivity of ITO nano-powders with spherical morphology is higher than that of ITO nano-powders with rod-like morphology.

Key words: ITO nano-powder; surface activation agent PEG-6000; microwave assistance; co-precipitation; aqueous phase

1 Introduction

The performance of nano-materials is not only depending on its chemical compositions, but also closely related with their granule's structure and appearance. The overwhelming majority nano-materials structure and the morphology depend on application performance directly. Therefore, study on the control of nano-material structure and morphology has become one of the fronts and hot spots of the current material science research[1−7]. At present, lower dimensional and quasi-one-dimensional structural ITO nano-particles, such as nanometer sphere[8], nanometer acicular[9], nanolines[10], nanorods[10−12] and nanotubes[13], all have caused attention enormously. Usually, the processes for preparing ITO particles are: co-precipitation process[8, 10, 12, 14−15], as well as vapor-liquid-solid (VLS) process[16], and sol-gel process[11], hydrothermal method[17], spray combustion method[18−19] and microemulsion method[20]. The product is produced with specially high purity and good homogeneity by using the co-precipitation process, and its granularity is fine, its ingredients, nature and particle morphology are controllable. By adding surface activation agents such as polyethylene glycol, the particle morphology can also be affected. CHEN et al[21] used polyethylene glycol as the surface activation agent and had successfully synthesized the Fe_3O_4 nanorods by adopting oxidization co-precipitation process. Because the microwave has a strong penetrability and excellent selectivity, the system is heated by body heating with the heating media absorbing microwave energy at the same time, and the points in the medium are of the same heating rate, there is not temperature gradient. Therefore, the reaction solution is of uniform heating in the reaction process, the particles are produced with a rather narrow size distribution[22−23] and thus the powders are prepared by the use of microwave-assisted heating process with homogeneous particle, small size in diameter and good dispersion[24−25]. The microwave-assisted co-precipitation in aqueous phase is a process of taking metal or metal salt as raw material, microwave-assisted heating while mixing, and preparing composite powders by co-precipitation in aqueous[26−27]. ITO nano-powders prepared by microwave-assisted co-precipitation were reported rarely, especially the effects of the reaction system factors on their morphology, and the effects of the morphology on their performance.

In this work, surface activation agent PEG−6000 was used to prepare the ITO precursor by adopting

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microwave-assisted co-precipitation process, and ITO nano-powders was gained, and the morphology was characterized and the electric conductivity was also studied.

2 Experimental

2.1 Preparation of ITO nano-powder

1 mol/L of $InCl_3$ solution was prepared and mixed with corresponding proportion of $SnCl_4$ solution according to $m(In_2O_3)/m(SnO_2)$=9. Take 50 mL of the above mixed solution, heat it up to a certain temperature, such as 35, 45, 55, 75 and 85 ℃ and maintain the temperature; then add 0.5 g of surface activation agent PEG-6000, fully stir till it became clear emulsion; then make it hydrolyze by dropping ammonia water with density of 1:0, 1:1, 1:2, 1:3 and 1:4(volume ratio) till white precipitation was produced when its pH value was 7−8, continue to stir for 1 h and age for 2 h. The sediment was obtained by centrifugal filter and washing with distilled water till there was no Cl^- to be traced by using $AgNO_3$ solution for examination, and then filter and wash with ethyl alcohol. The obtained precipitated sediment was dried at 100 ℃ for 12 h, and the precursor powder was obtained by grinding the dried sediment; the obtained precursor powder was calcined at 800 ℃ for 1 h; and after air cooling, ITO nano-powder was produced. The sample was analyzed by SEM, and the electric conductivity was determined by conductivity meter.

2.2 Sample performance and characterization

The ITO nano-powder morphology analysis was implemented by using the S−4800 high resolution field launches scanning electron microscope made in Japanese Hitachi Corporation. The electric conductivity of the sample was determined by adopting the digital display DOS−12A conductivity meter made in Shanghai Jinmai Instrument Co. Ltd.

3 Results and discussion

3.1 Morphology of ITO nano-powders

When the concentration of ammonia dropped was 1:4(volume ratio), solution pH value was 7, ITO nano-powders were prepared at different reaction system temperatures. The SEM images of samples are shown in Fig.1.

It can be seen from Fig.1 that ITO particles change

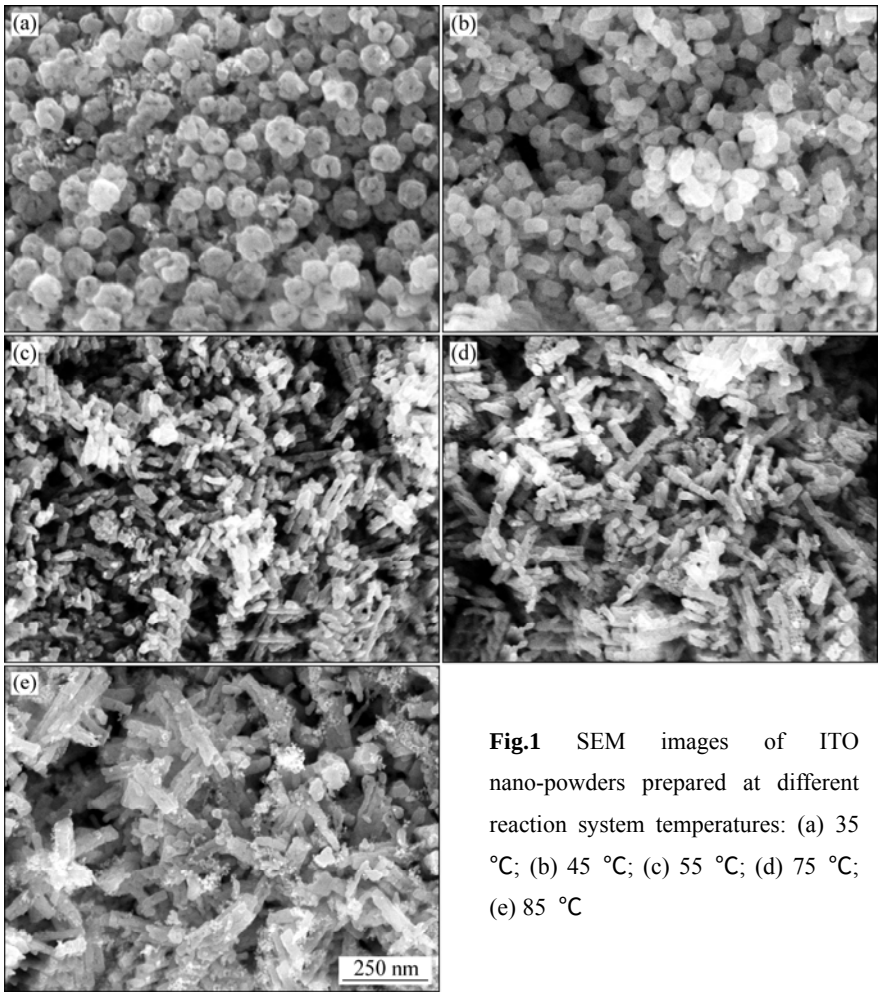

Fig.1 SEM images of ITO nano-powders prepared at different reaction system temperatures: (a) 35 ℃; (b) 45 ℃; (c) 55 ℃; (d) 75 ℃; (e) 85 ℃

gradually from spherical morphology to rod-like one with 3:1−8:1 of aspect ratio with the rise of reaction system temperature when the concentration of ammonia dropped and the solution of pH value kept unchanged. According to the mechanism analysis of surface morphology of ITO nanorods[28], it is helpful for the precursor of ITO particles to grow with the shape of rod with the rise of reaction system temperature.

When the reaction temperature was 55 ℃, the solution pH value was 7, ITO nano- powders were obtained prepared by dropping the different concentrations of ammonia (volume ratio). The SEM images of samples are shown in Fig.2.

It can bee seen from Fig.2 that ITO particles change gradually from near-spherical morphology to rod-like one with 3:1−5:1 of aspect ratio as the concentration of ammonia dropped is diluted when the reaction system temperature and the pH value of solution kept unchanged. According to the mechanism analysis of surface morphology of ITO nanorods[28], it is helpful for the precursor of ITO particles to grow with the shape of rod as the concentration of ammonia added dropped is diluted.

3.2 Electric conductivity of ITO nano-powders

When ammonia concentration dropped is 1:4 (volume ratio), the reaction solution pH is 7, the effects of the reaction system temperatures (35, 45, 55, 75, 85 ℃) on the electric conductivity (σ) of ITO nano-powders are shown in Fig.3.

It can be see from Fig.3 that the electric conductivity of ITO nano-powders is a downward trend with the rise of the solution of the reaction system temperature. This is because the carrier rates of the movement speed up with the rise of reaction system temperature, absorption of conduction current by dielectric materials will be a corresponding increase, resulting in decreased electric conductivity.

When the temperature of the reaction system is 55 ℃, reaction solution pH is 7, the effects of the different ammonia concentrations (volume ratio of ammonia to distilled water of 1:0, 1:1, 1:2, 1:3, 1:4) dropped in

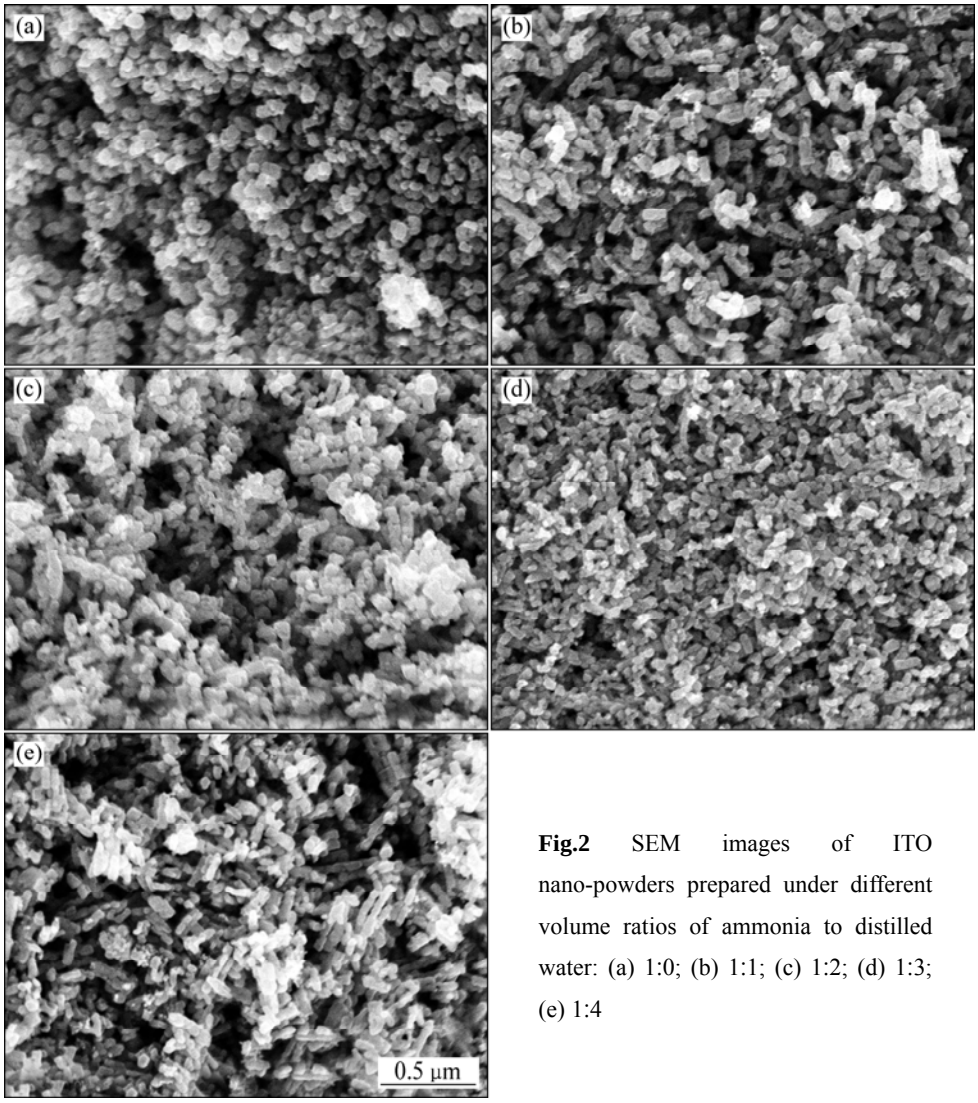

Fig.2 SEM images of ITO nano-powders prepared under different volume ratios of ammonia to distilled water: (a) 1:0; (b) 1:1; (c) 1:2; (d) 1:3; (e) 1:4

reaction system on the electric conductivity of ITO nano-powders are shown in Fig.4.

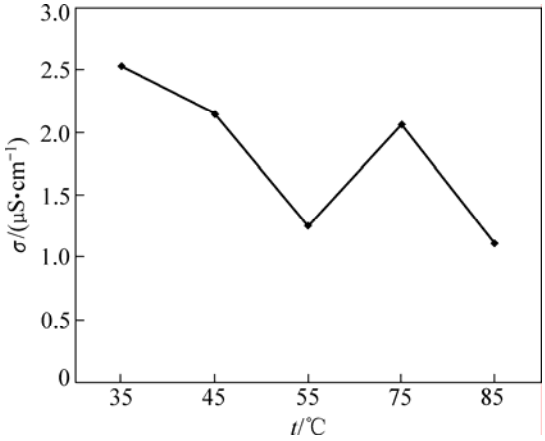

Fig.3 Electric conductivity curve of ITO nano-powders prepared at different reaction system temperatures

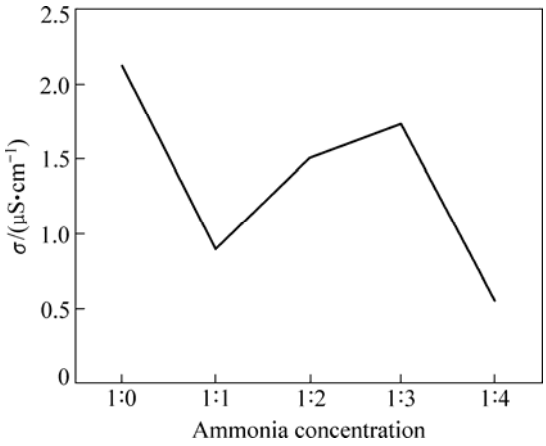

Fig.4 Electric conductivity curve of ITO nano-powders prepared by dropping ammonia with different concentrations in reaction system

It can be seen from Fig.4 that the electric conductivity of ITO nano-powders is a downward trend within 0.5−2.5 μS/cm as the ammonia dropped in the solution of the reaction system is diluted. This is because the carriers of ITO particles will be a corresponding decrease with the reducing of ITO precursors, as the ammonia dropped in the solution of the reaction system is diluted, resulting in decreased electric conductivity.

4 Conclusions

1) When the concentration of ammonia dropped is 1:4(volume ratio) and solution pH value is 7 in the microwave-assisted reaction system, the morphology of ITO particles is transformed from spherical to rod-like one with the rise of reaction system temperature and the decline of its electric conductivity.

2) When the temperature of the reaction system is 55 ℃ and reaction solution pH is 7 in the microwave-assisted reaction system, the morphology of ITO particles is transformed from spherical to rod-like one with the decline of electric conductivity as the ammonia solution is diluted.

3) The electric conductivity of ITO nano-powders with spherical morphology is higher than that of ITO nano-powders with rod-like morphology.

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