

## Influences of dehydrating process on properties of ATO nano-powders<sup>①</sup>

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**Abstract:** Sb-doped SnO<sub>2</sub>(ATO) nanometer powders were synthesized by hydrolysis of alkoxides, using SnCl<sub>4</sub>•5H<sub>2</sub>O and SbCl<sub>3</sub> as raw materials. Some dehydrating processes, such as n-butanol/xylene mixed solvent heterogeneous azeotropic distillation, organic dehydrating agent and other dehydrating processes, were used to treat the wet colloids for preparing nonagglomerated ATO nanoparticles. The influences of dehydrating processes on the particle size, agglomeration and resistance were investigated using X-ray diffraction (XRD), transmission electron microscopy (TEM) and Brunauer-Emmet-Teller (BET). It is indicated that the dehydrating methods have great influences on the products properties, and that n-butanol/xylene mixed solvent heterogeneous azeotropic distillation processing and organic dehydrating agent can effectively remove the residual H<sub>2</sub>O molecules in wet colloids, and be used to prepare powders with high surface areas, about 85.32 m<sup>2</sup>/g, low agglomeration and good conductivity.

**Key words:** ATO; conductive nanometer-sized powder; agglomeration; dehydration

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### 1 INTRODUCTION

Crystalline Sb doped tin oxide (ATO), cassiterite structure, is a wide band gap n-type semiconductor. Because of its optical property (transparent for visible light and reflective for IR) and electroconductibility, good chemical and mechanical stability, it has many applications, such as transparent conductive electrodes, photovoltaic devices, photosensors, catalyst, antistatic coatings and electrochromic materials<sup>[1-4]</sup>. A variety of techniques have been used to prepare ATO superfine powders, some involve dry processes, others are based on wet chemical processes, including chemical coprecipitation<sup>[5]</sup>, sol-gel-related process<sup>[6]</sup>, emulsion method<sup>[7]</sup>. Compared with dry process, wet chemical process is a low-cost method to fabricate superfine powders. However, the process suffers the disadvantage of producing hard agglomerate during drying and calcining procedures due to the high surface tension stress, physically adsorbed and / or chemically coordinated H<sub>2</sub>O molecule, and hydroxyl group on hydrate particles surface. The key issue to decrease the agglomeration has been considered to decrease the tension stress and to remove the residual H<sub>2</sub>O molecule with maximum limit by proper dehydrating process<sup>[7, 8]</sup>. The dehydrating methods adopted currently include refrigeration drying<sup>[9]</sup>,

supercritical drying<sup>[10]</sup>, organic solvent washing and heterogeneous azeotropic distilling<sup>[11]</sup>. The former two kinds of methods which needs specialized equipments, are not used as widespread as the latter two, which are simple and easy to operate. The method of organic solvent washing mainly uses ethanol, isopropanol and acetone to substitute for H<sub>2</sub>O molecules remained in the gels, but this substitution is limited and the agglomeration can not be completely eliminated. Compared with organic solvent washing method, heterogeneous azeotropic distillation is a more effective anti-agglomeration method. But, up to now, the solvent used in heterogeneous azeotropic distillation mainly is n-butanol. No any other solvents are found to be utilized in the process, and also the report on the preparation of free agglomerate nanometer-sized powder with organic dehydrating agent are not found.

In the present study, nanometer-sized ATO powders are prepared through hydrolysis of metal alkoxides. In order to eliminate the agglomerate, an improved heterogeneous azeotropic distillation process, n-butanol/xylene mixed solvent heterogeneous azeotropic distillation, and a kind of organic dehydrating agent are used in dehydrating procedure. This paper discusses the effect of the two dehydrating process, compared with other processes, on the properties of ATO superfine powders. It is found that the

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n-butanol/xylene mixed solvent heterogeneous azeotropic distillation process and organic dehydrating agent can effectively dehydrate, and obtain high performance nanoscaled ATO powders.

## 2 EXPERIMENTAL

### 2.1 Preparation of samples

A requisite amount of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{SbCl}_3$  (AR, in the mass ratio of 7:1), were dissolved in absolute ethanol. After refluxing in a flat-bottom flask equipped with a condenser for 8 h, a white suspension was produced. When cooled to room temperature, the suspension was isolated by centrifugation, and a clear metal alkoxides solution was obtained. Under magnetic stirring, the surfactant was added into the as-prepared alkoxides solution. Then the solution was heated to  $50 \sim 70^\circ\text{C}$ , and the hydrolysis was performed as an aqueous ammonia solution was added in dropwise. When the pH value of the solution reached 1–3, light yellow ATO colloid was obtained. After aging at room temperature for 2 h, the colloid was washed with distilled water several times until no white deposit of AgCl was observed in waste water, as tested by  $\text{AgNO}_3$ . The as-washed gel was divided into 5 parts, each part was performed different dehydration processing. The dehydrating methods are given in Table 1. The dehydrated gels were dried at  $100^\circ\text{C}$  for 2 h, calcined at  $550^\circ\text{C}$  for 2 h, and finally transformed into shallow blue ATO powders.

**Table 1** Samples dehydrating methods

| Sample No. | Dehydrating methods                                       |
|------------|-----------------------------------------------------------|
| I          | Washing with distilled water                              |
| II         | Azeotropic distilling with n-butanol                      |
| III        | Washing with absolute ethanol for two times               |
| IV         | Azeotropic distilling with xylene/n-butanol mixed solvent |
| V          | Dehydrating with organic dehydrating agent                |

### 2.2 Characterization of samples

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/Max2550VB<sup>+</sup> diffractometer using  $\text{Cu K}\alpha$  radiation at 40 kV and 30 mA. The scan rate was  $8^\circ/\text{min}$  and covered the range between  $15^\circ$  and  $80^\circ$  ( $2\theta$ ). The average crystallite size ( $d_{\text{XRD}}$ ) was deduced from the half-height line broadening by applying Scherrer formula and assuming Gaussian profiles for experimental and instrumental broadenings.

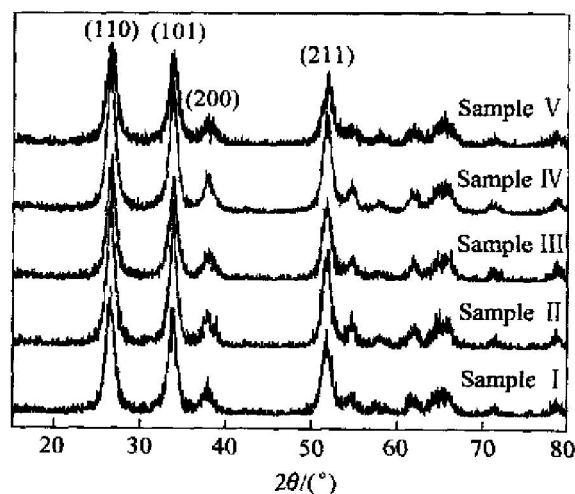
Transmission electron microscopy (TEM, Hitachi H-

800 microscope) was performed to observe the particle size and morphology. Specific surface area was measured by the BET method (Quantachrome Monosorb, USA) using  $\text{N}_2$  adsorption. The particle size was also obtained by the formula  $D_{\text{BET}} = 6 / (6 \cdot S_{\text{BET}})$ . The resistivity  $\rho$  of powders was obtained using a self made equipment and a microhmmeter (HZ2520, Beijing).

## 3 RESULTS AND DISCUSSION

### 3.1 Characteristics of samples and analysis

Fig. 1 presents the XRD spectra of nanosized ATO powders sintered at  $550^\circ\text{C}$  for 2 h. All of the diffraction patterns were identical to that for tetragonal  $\text{SnO}_2$  (JCPDS file number 21–1250), showing characteristic of cassiterite structure. It can be easily seen from Fig. 1 that the X-ray diffraction peaks of these samples broadened. It is owing to both the microstrain and the particle size diminution of the nanocrystallines.



**Fig. 1** XRD patterns of powders prepared via different dehydrating methods (calcined at  $550^\circ\text{C}$  for 2 h, respectively)

The values of the powders BET specific surface area ( $S_{\text{BET}}$ ), particle size ( $d_{\text{XRD}}$  and  $D_{\text{BET}}$ ), resistivity ( $\rho$ ) and green density are listed in Table 2. From Table 2, we can see that the particle sizes determined with XRD-LB and BET techniques show obvious difference. According to GAO et al.<sup>[12]</sup>, the value of  $d_{\text{XRD}}$  can be thought as the original crystallite size, and that of  $D_{\text{BET}}$  may be the average size of the particles with hard agglomerates, the results of  $D^3/d^3$  are the mean agglomeration of the particles. When the powders are heated at lower temperature ( $< 600^\circ\text{C}$ ), the crystallites grow slowly, and the crystallite sizes are mainly determined by the hydrolysis parameters. With the same hydrolysis parameters, the difference of the original crystallite size,  $d_{\text{XRD}}$ , is not big.

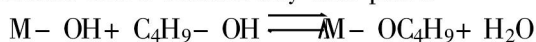
But the agglomerate degree of the particles prepared through different dehydrating routes is not equal, so the values of  $D_{\text{BET}}$  have very great difference.

**Table 2** Characteristics of ATO powders prepared via different dehydrating methods

| Sample No. | $S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$ | $\rho/(\Omega \cdot \text{cm})$ | Density/ $(\text{g} \cdot \text{cm}^{-3})$ | $d_{\text{XRD}}/\text{nm}$ | $D_{\text{BET}}/\text{nm}$ | $D^3/d^3$ |
|------------|---------------------------------------------------|---------------------------------|--------------------------------------------|----------------------------|----------------------------|-----------|
| I          | 53.71                                             | 0.88 ~ 0.6                      | 3.77                                       | 5.8                        | 16.9                       | 25        |
| II         | 64.14                                             | 1.8 ~ 1.34                      | 2.66                                       | 7.1                        | 14.1                       | 8         |
| III        | 49.93                                             | 0.88 ~ 0.6                      | 3.77                                       | 6.7                        | 18.2                       | 20        |
| IV         | 72.19                                             | 1.82                            | 2.62                                       | 6.4                        | 12.5                       | 7         |
| V          | 85.32                                             | 2.3 ~ 1.93                      | 2.76                                       | 5.5                        | 10.6                       | 7         |

Since ethanol washing for hydrous particles can partly substitute for the  $\text{H}_2\text{O}$  molecules in the gel, the agglomeration degree of particles is lower than that washed only with distilled water. But the former particle size is bigger than the latter, and the value of  $S_{\text{BET}}$  is lower. This phenomenon was also observed in preparing  $\text{TiO}_2$  superfine powders by hydrolysis of metal alkoxide<sup>[12, 13]</sup>.

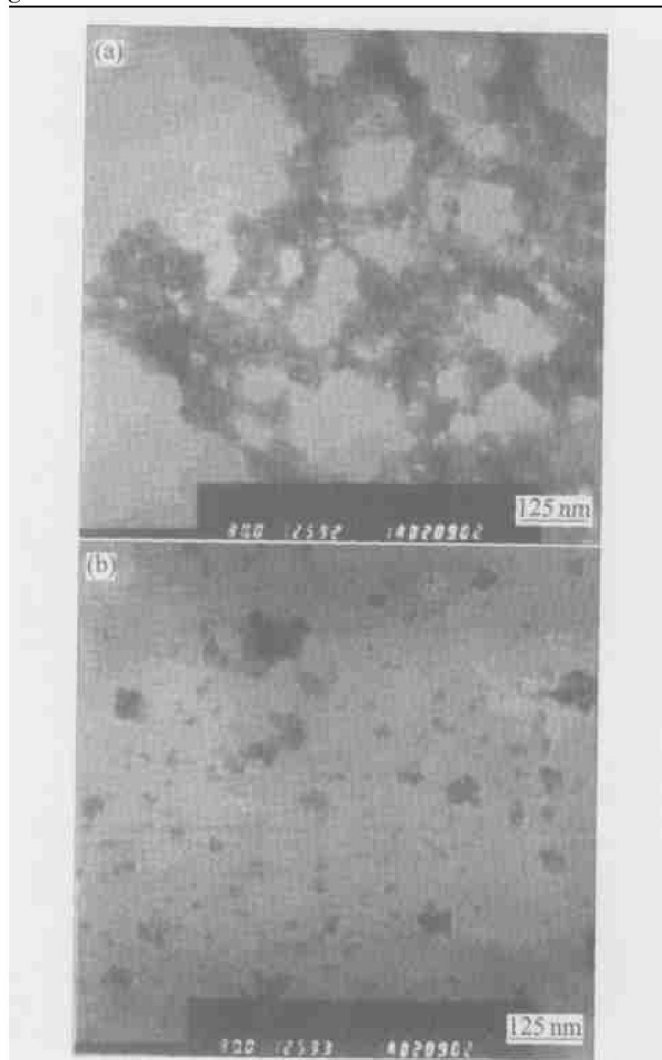
In the case of typical azeotropic distillation process, the hydrous oxides are mixed thoroughly with appropriate amount of *n*-butanol, then carefully heated to the azeotropic point (93 °C) of water-*n*-butanol system, at which water content reaches 44.5% in the vapor of azeotropic composite. As the distillation process goes on, water in the suspension is gradually removed up to the boiling point of *n*-butanol (117 °C). During distillation, the following reaction between the hydroxyl on the surface of particles and *n*-butanol may take place:



i. e. the surface OH groups of particles are substituted by  $-\text{OC}_4\text{H}_9$  groups. Consequently, the possibility for the particles to get close as well as the formation of chemical bonds is greatly eliminated. For all that, at the end of the process, a little amount of  $\text{H}_2\text{O}$  molecules will still remain in the system, which will lead to the crystallite growing and forming hard agglomeration to some extent. However, by using a high boiling point hydrophobic organic solvent, xylene, to mix with *n*-butanol for azeotropic distillation process, the  $\text{H}_2\text{O}$  molecules remained in the wet colloid are removed more thoroughly to get lower degree of agglomerate.

Fig. 2 shows the morphologies of wet colloids treated with distilled water washing and xylene/*n*-butanol mixed solvent azeotropic distillation process. From Fig. 2, it is seen that the colloid particles, only washed by distilled water, connect to each other to form a net-chain structure. The similar structure cannot be found in the micro-

graph of the sample treated by mixed solvent azeotropic distillation process; instead, the small dispersal aggregates can be seen.



**Fig. 2** TEM micrographs of ATO wet colloids (a) —Sample I; (b) —Sample IV

Although overwhelming majority  $\text{H}_2\text{O}$  molecules on the surface of colloid particles can be removed by azeotropic distillation process, the crystallization water inside the colloid particles cannot be replaced, for the volume of the organic solvent molecules is much bigger than that of  $\text{H}_2\text{O}$  molecules<sup>[12]</sup>. On the other hand, the dehydration process of azeotropic distillation is carried on gradually. Thus the particles may aggregate and grow up during the process, which will lead to bigger grain size. When the wet colloid is treated with organic dehydrating agent, which can more easily react with adsorbed water and OH group and graft on the surface of colloid particles, well dispersed and very loose powder is obtained. Among all of samples, the one treated with organic dehydrating agent has the biggest specific surface areas ( $S_{\text{BET}} = 85.32 \text{ m}^2/\text{g}$ ), the smallest crystallite size ( $d_{\text{XLB}} = 5.5 \text{ nm}$ ) and mean agglomerate ( $D^3/d^3 = 7$ ).

Fig. 3 shows the TEM micrographs of pow-



**Fig. 3** TEM micrographs of ATO powders (calcined at 550 °C for 2 h, respectively)  
(a) —Sample I ; (b) —Sample IV;  
(c) —Sample V

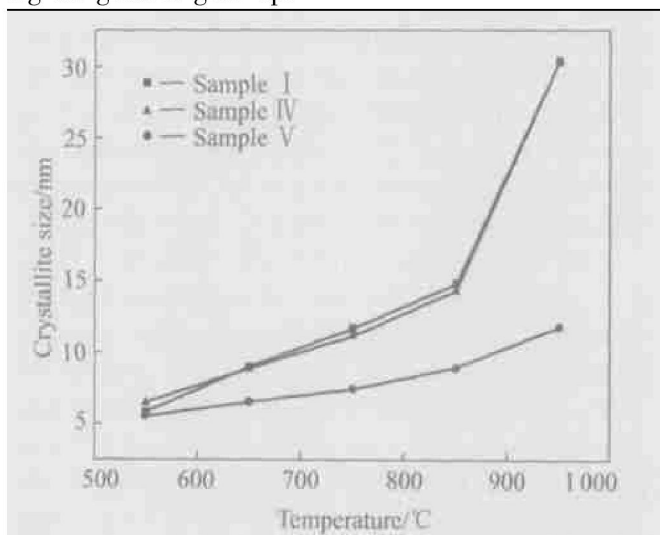
ders sintered at 550 °C for 2 h. It can be seen that the ATO particles are dispersive and uniform for xylene/ *n*-butanol mixed solvent azeotropic distillation, but heavily agglomerated when simply washing with distilled water was performed. The morphology of particles treated with organic dehydrating agent is discernable and uniform but ag-

gregated together. Combining the specific surface areas based on BET measurement, the aggregation may be a porous cluster, which has something to do with the function of organic dehydrating agent.

### 3.2 Crystallite growing

Ordinarily, the average crystallite size of nanoparticles increases with the calcining temperature rising. When the temperature is below 600 °C, the crystallizing process carries on and the average crystallite size increases slowly. However, the grain size accelerates rapidly as the calcining temperature is above 600 °C<sup>[14, 15]</sup>.

In present work, the crystallizing behavior of ATO particles was investigated at 550–950 °C. The results are shown in Fig. 4. It is indicated that the crystallizing process can be obviously divided into two periods. In the first period, from 550 °C to 850 °C, the crystallite size increased slowly. When the temperature was above 850 °C, the crystallite size grew up quickly. But the increasing rate of the sample V was apparently slower than others, even calcined at 950 °C for 2 h, the crystallite size was only 11.1 nm, and that of others reached 30 nm. It may have relation with the porous cluster structure of the sample. This kind of structure may have the function of limiting the grain to grow up.

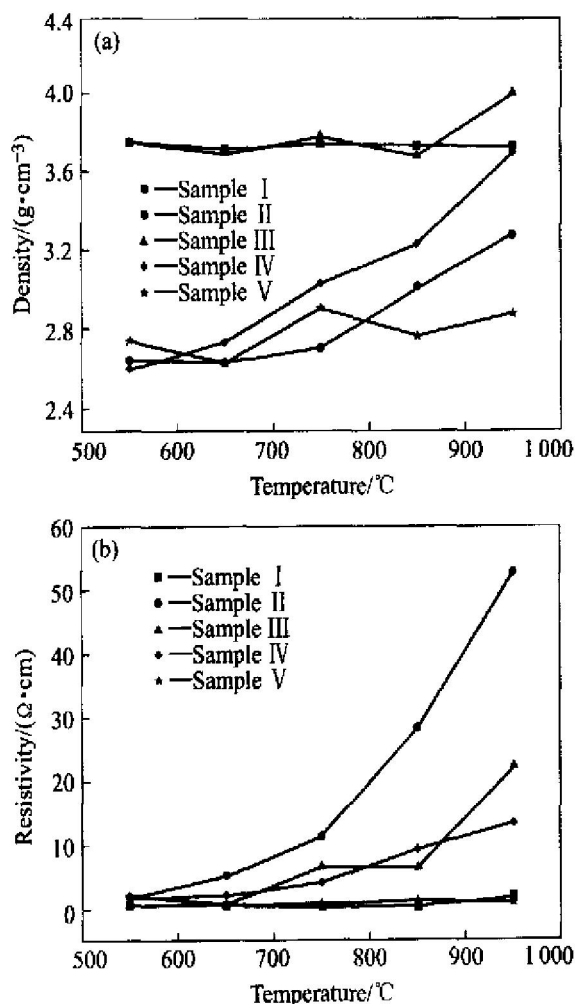


**Fig. 4** Relationship between crystallite size of ATO powders and calcining temperature

### 3.3 Green density

Fig. 5(a) shows the green density of powders at certain pressure as a function of calcining temperature. The green density of samples I and III are close and big, and nearly kept constant as the calcining temperature increases. The reason is that the particles of the two samples have formed hard agglomeration, as temperature increases, the particles inside the aggregate stuck to each other and grew up, but the whole physical volume of the aggre-

gate did not change obviously.



**Fig. 5** Effects of heating temperature on green density (a), and resistivity (b) for powders prepared via different dehydrating methods

The green density of the sample V is lower than those of the former two. As temperature rises, it tends to increase, but the variation is not big, which also verifies that the porous cluster structure of the sample can prevent the grain from growing up. The green densities of samples II and IV are very small when calcined at 550 °C for 2 h. However, as the temperature stepped up, it increased quickly.

### 3.4 Electrical conductivity

Three parts decide the resistance of powders, namely

$$R = \sum R_g + \sum R_c + \sum R_b$$

where  $\sum R_g$  is the intrinsic resistance of powders,  $\sum R_c$  is the direct contact resistance, and  $\sum R_b$  is the band contact resistance. The last two items are very important for powders. The bigger the  $S_{BET}$  is, the more obvious the influence of the last two items on total resistance ( $R$ ) is. The resistivity arrangement of samples (calcined

at 550 °C for 2 h) in ascending sequence is  $\rho_I \approx \rho_{III} < \rho_{II} < \rho_{IV} < \rho_V$ , which is consistent with specific surface areas arrangement.

The variation of electrical conductivity with heat treatment temperature is shown in Fig. 5(b). It can be seen that the resistivity of most samples decreases little at first, but starts rising at higher temperature. However, the resistivity of the samples II and IV increases all through. The possible reason is that the particles performed with azeotropic distillation tend to volatilize the antimony oxide (the melting point of  $Sb_2O_3$  is 655 °C) and reduce the concentration of  $Sb^{5+}$  more easily due to dispersive and nonagglomerate nanoparticles, and thus the carrier concentration decrease,  $\sum R_g$  increases. The volatilization of antimony oxide is supported by electron energy spectrum analysis.

## 4 CONCLUSION

ATO nanoparticles were obtained through the hydrolysis of metal alkoxides, followed by different dehydrating processes with wet colloid. Crystallite size determination based on the Scherrer method shows that all samples are in the nanometer range. The dehydrating process has marked influence on the properties of the powders. Xylene/*n*-butanol mixed solvent azeotropic distillation and organic dehydrating agent have strong dehydrating ability, and can be used to prepare nonagglomerate nanoparticles. The dehydrating ability of different dehydrating method in descending order is: organic dehydrating agent, xylene/*n*-butanol mixed solvent azeotropic distillation, *n*-butanol azeotropic distillation, ethanol washing, distilled water washing. The lower the agglomerate is, the bigger the specific surface areas and the resistivity are. As calcining temperature increases (from 550 to 950 °C), the crystallite growing and the resistivity variation of the powders prepared via different dehydrating routes have different behaviors. As for powders prepared through organic dehydrating agent treating, the specific surface areas reach 85.32 m<sup>2</sup>/g, crystallite size is 5.5 nm (at 550 °C for 2 h), and at higher calcining temperature, the crystallite grows slowly, the resistivity is small and varies little.

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