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Study on preparation of In_2O_3 superfine powder via polymer-network process

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Abstract: Nanocrystalline, single-phase undoped In_2O_3 was prepared by a polymer-network synthesis technique with indium nitrate as the starting material; several methods such as X-ray diffractometry (XRD) and transmission electron microscopy (TEM) were employed to obtain detailed information on the crystallography and microstructual appearance of In_2O_3 superfine powders. The influence of the concentration of starting solution, calcination temperature and time on the particle size was also that investigated by means of the XRD patterns. Results indicate that the obtained powders are mostly crystalline single phase with uniform size and also that the size of the products can be controlled under proper condition.

Key words: indium trioxide; nanoscale particle; polymer-network method

The properties of any particular material such as strength, surface area and sensitivity can greatly change when the crystallite size of its is decreased from a millimeter to a nanometer[1,2]. Indium trioxide is one such material, preparation and characterization of which have attracted more and more attention from material scientists due to its many particular properties when the size of a particle is decreased to a nanometer. For instance, superfine In_2O_3 powder has excellent sensitivity and selectivity of responses to gas and light which make it become a new type of material with great potential applications in gas sensors[3] and optical limiting services[4] in addition to its working as the battery's inhibitor in substitution for mercury.

In the conventional preparation methods, such as decomposition of nitrate, hydrolysis method and homogeneous deposition method, the products are pure but the size of the powder is large. Recently in materials chemistry there has been a growing trend to use, so called, soft chemistry routes to synthesize superfine powders such as the sol-gel[5,6] method which has been used to prepare nanocrystalline In_2O_3 powders in addition to its use in atomizing combustion method[7]. In this work, we employed a process for preparing the superfine indium trioxide powders using a polymer-network method[8-12]. The different factors that influence the particle size, i.e., the effect of starting concentration of indium ions, the temperature and time of calcination were also discussed.

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1 Experimental

1.1 Preparation of nanocrystalline In_2O_3 powder

Acrylamid, N, N'-methylene-bisacrylamide and ammonium persulfate were added in turn to the aqueous solutions of indium nitrate with various concentration. The mixture was stirred and then put into a water bath boiler at a certain temperature. With the slow increase of water temperature the mixing solution turned into gel at 78 ℃ which was then followed by drying at 120 ℃ for 48 h and calcinations in a tube furnace at different temperatures for different time periods to obtain the In_2O_3 light yellow superfine powders. The specific process is shown in Fig.1.

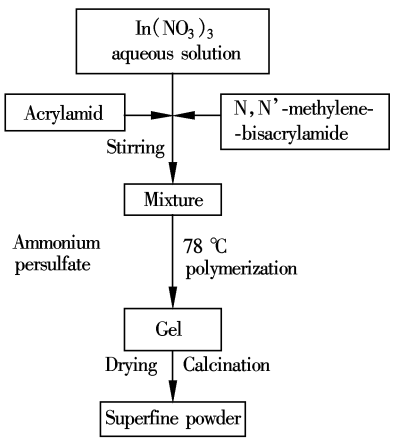

Fig.1 Flowchart to prepare In_2O_3 by ploymer-network method

1.2 Characterization of samples

The X-ray diffraction (XRD) profiles were obtained using a Rigaku (Japan) D/max-γB X-ray dif-

fractometer with Cu-K α radiation (λ = 0.154 178 nm) at a scanning speed of 4(°)/min in the 2θ range from 20° to 80°, through which the phase compositions and the particle sizes were analyzed and determined. Transmission electron microscopy (TEM) micrograph was taken using a Hitachi H-800 type transmission electron microscope to observe the microstructual appearance and the dispersion of nanoscale In_2O_3.

2 Result and Discussion

2.1 X-ray analysis of the superfine In_2O_3 powder

Figs.2 – 4 are the X-ray diffractograms of the selected samples. The analysis of XRD patterns is based on the Joint Committee on Powders Diffraction Standard (JCPDS), card No.6-0146. Tab.1 lists the mean particle sizes calculated by the Scherrer formula on the basis of data from the X-ray diffraction profiles and cell parameter a values of those selected samples. All of these are used for comparison to investigate the influence of preparation conditions on the synthesis of In_2O_3. The result shows that every peak in each of those X-ray diffraction patterns can be attributed to In_2O_3 and cell parameter a values tabulated in Tab.1 are compatible with those of the JCPDS card, from which we can infer that the superfine In_2O_3 powders have a cubic phase. The influence of different conditions is discussed in detail as follows.

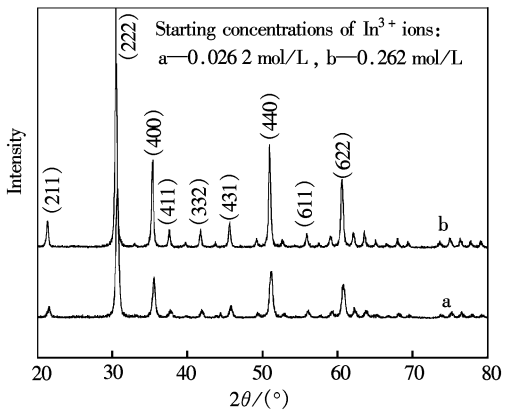

Fig.2 XRD patterns of the samples prepared with different starting concentrations of In^{3+} ions (calcination temperature 500 ℃, calcination time 2 h)

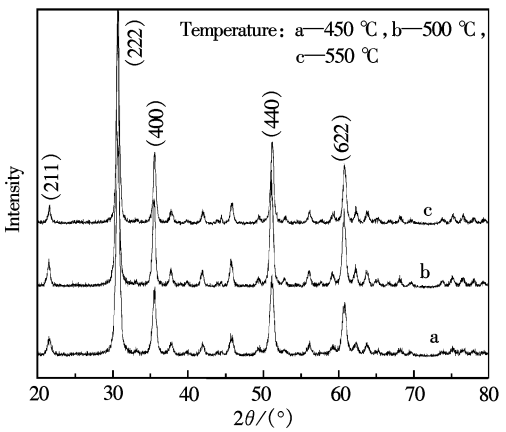

Fig.3 XRD patterns of the samples prepared after calcination at different temperatures (starting concentration of In^{3+} ions 0.026 2 mol/L, calcination time 2 h)

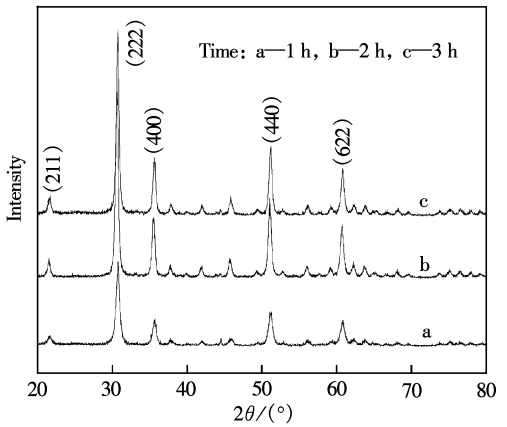

Fig.4 XRD patterns of samples prepared after calcination for various time (starting concentration of In^{3+} ions 0.026 2 mol/L, calcinations temperature 500 ℃)

Tab.1 The mean particular sizes and the mean cell parameter a values of samples

Item		The mean particular size/nm	The mean cell parameter a
Fig.2	a	19.10	10.078
	b	57.50	10.131
Fig.3	a	13.78	10.092
	b	18.53	10.109
	c	19.10	10.078
Fig.4	a	16.32	10.078
	b	18.53	10.078
	c	20.37	10.084
JCPDS			10.118

2.1.1 Effect of the starting concentration of $In(NO_3)_3$

Fig.2 shows the XRD patterns of superfine In_2O_3 powders which were prepared with various starting concentrations of In^{3+} ions under the same conditions such as calcination temperature and time. It is indicated that with the increase of the starting concentration the width of lattice plane decreases and the mean particle size increases, which is in accordance with the data tabulated in Tab.1. This may be due to the fact that the amount of solute fixed in each of the inelastic loop structures of the organic network is in proportion to the starting concentration of In^{3+} ions. When the starting concentration decreases, the amount of solute fixed will decrease also and the activities of In^{3+} ions will fall into a

smaller scope which can effectively reduce the probability of interaction between the In^{3+} ions. This makes the mean particle size of the product decrease correspondingly.

2.1.2 Effect of calcination temperature

Fig.3 shows the XRD patterns of the superfine In_2O_3 powders obtained from calcinations of the dried gels at various temperatures with the same starting concentration of In^{3+} ions (0.026 2 mol/L) and calcination time (2 h). Combined with the corresponding analysis of data tabulated in Tab. 1, the effect of calcinations temperature on the particle sizes is clear. When the calcination temperature varies with a range from 450℃ to 550℃, the width of lattice plane decreases and the mean particle size increases. It is indicated that with the increase of calcination temperature, the array of In^{3+} ions in the nanocrystalline In_2O_3 tends to be regular and the crystallitic structure has the tendency for integrity, as a result of which the mean particle size increases correspondingly.

2.1.3 Effect of calcination time

Fig.4 shows the XRD patterns of the superfine In_2O_3 powders which were obtained from the calcination of the dried gels for 1, 2, and 3 h, respectively with the same starting concentration of In^{3+} (0.026 2 mol/L) and calcination temperature (500 ℃). From Fig.4, the corresponding diffraction peaks sharpen slowly with the increase of calcination time which indicates the mean particle sizes increase with calcination time proportionally. This is also verified by the data in Tab. 1. And for 500 ℃, 1 h, the diffraction peaks are not so obvious which may be due to the incompleteness of the crystallization. This reveals that although the reduction of calcination time can help to inhibit the growth of nanocrystalline, the phase of crystalline may lack integrity. Consequently the suitable time for calcination should be determined on the basis of repeated experiments.

2.2 TEM analysis of the superfine In_2O_3 powder

In Fig.5 and Fig.6, we give the TEM image and the electron diffraction (ED) image of the superfine In_2O_3 powder, which was obtained from the calcination of the dried gels prepared with C_{sc} = 0.026 2 mol/L (the starting concentration of In^{3+}) at 450 ℃ for 2 h. It is indicated in Fig. 5 that the superfine In_2O_3 powder has a relatively well-distributed structure, without obvious agglomeration, whose particles are in the form of sphere shapes and the size values of the particles fall into the scope 10 to 20 nm. This is in accordance with the XRD result (13.78 nm). It is also well seen from Fig.6 that the ED pattern consists of homocentric circles with a series of light spots, which shows that this superfine powder has complete crystallization and impurities.

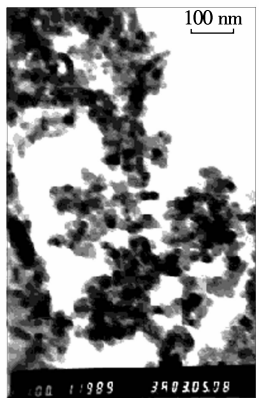

Fig.5 TEM image of nanoscale In_2O_3 powder

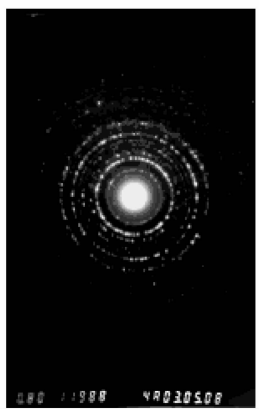

Fig.6 ED image of nanoscale In_2O_3 powder

3 Conclusion

Nanocrystalline In_2O_3 powders with mean particle sizes varying from about 10 nm to 20 nm can be prepared by polymer-network method. The formation of organic network can effectively inhibit the aggregation of In_2O_3, which makes the particles of In_2O_3 evenly distributed without obvious agglomeration. Some preparation factors such as the starting concentration of In^{3+}, calcination temperature and calcination time have influences on the particle sizes of the product powders, which give a clue that the particle sizes of the product powders can be controlled in a desirable range by choosing the optimal preparation conditions. In polymer-network method the low-cost inorganic nitrates can be used as starting materials and the technological process is relatively simple and easy to be controlled. The product powders can also have good dispersion and

high purity. These attractive virtues of polymer-network make it especially suitable for the preparation of oxides and mixed oxides.

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高分子网络法制备 In_2O_3 超细粉的工艺研究

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摘要: 以硝酸铟为起始原料, 利用高分子网络法合成纯的单相 In_2O_3 纳米晶. 采用 X 射线粉末衍射(XRD)和透射电镜(TEM)等检测手段对所得粉体的组成、大小和微观形貌进行了表征和分析. 同时, 根据 XRD 衍射图谱结果进一步讨论了不同原料质量浓度、煅烧温度和煅烧时间对产物粒径的影响. 实验结果表明所得晶粒晶相单一, 粒度均匀并且可以选择适宜的条件制备所需粒径的纳米氧化物.

关键词: 三氧化二铟; 纳米颗粒; 高分子网络法

中图分类号: TF123