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Preparation and properties of nano-sized SnO_2 powder①

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[Abstract] SnO_2 powder was prepared by chemical precipitation method. Effects of starting materials concentration, pH value of final system and treating temperature on the particle size were investigated by means of X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The parameters of chemical precipitation were optimized. It is concluded that the concentration of starting material and pH value of final system has little effect on the SnO_2 particle size, but heat treatment do greatly affect the particle size. If the treating temperature is lower than 500 ℃, the particle size has a good stability; otherwise, the particle size remarkably increases with increasing temperature. The dispersing agents have various influences on SnO_2 powder as the polarity of dispersing agents changed.

[Key words] SnO_2; nano-sized; chemical precipitation method; particle size
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1 INTRODUCTION

SnO_2 is one of the main materials used in gas sensor. Because of the humidity and gas sensing function, it attracts more and more attentions. But the present problem is how to improve the stability and sensibility of gas sensor. Researchers have taken many measures to resolve this problem. One of the measurements is decreasing particle size. Because SnO_2 is the surface-controlled gas sensor, it is significant to decrease the size of raw materials. Nanoscale materials refer to those whose particle size is 1~ 100 nm and the sudden changes of material properties accompanied with the size change[1]. Compared with the traditional crystalline and amorphous materials, nanoscale materials have more atoms on surface and grain boundary, it makes the nanoscale materials have many extraordinary properties. When the size of particle and the ratio of surface atoms are in certain range, the properties of materials prefer to controlled surface atoms than internal lattice's[2]. Taking nano-sized SnO_2 as the raw material of gas sensor should have great significance. There are many methods to prepare nano-sized powder, such as high energy ball milling, mechanically alloying, Sol-Gel method, sol-emulsion method, oxidizing of Tin with nitric acid, gas evaporation process, hydrothermal method, liquid-phase method[3~ 10], and so on. Many of them have too many parameters to be controlled and need expensive devices. So, it is difficult to realize industrialization. But chemical precipitation method used for this work can overcome these shortcomings.

2 EXPERIMENTAL

Tin oxide powder was prepared by chemical precipitation method. Aqueous solution of $SnCl_4$ was made by dissolving $SnCl_4 \cdot 5H_2O$ (Alfa Aesar, MA) in distilled water. Adding adequate NH_4OH to solution, white precipitates were obtained. After filtered, precipitates were washed by distilled water for several times to remove the chloride. Then, heating the precipitates at various temperatures for several hours, and milling the acquisition, SnO_2 powder could be got.

3 RESULTS AND DISCUSSION

Table 1 shows the diameter of particles which was

Table 1 Relationship between starting materials and particle size

No.	$c(SnCl_4)$ / ($mol \cdot L^{-1}$)	$c(NH_4OH)$ / ($mol \cdot L^{-1}$)	D / nm
1	0.25	0.25	4.01
2	0.25	0.50	3.96
3	0.25	1.00	4.05
4	0.25	1.50	3.98
5	0.50	0.25	4.03
6	0.50	0.50	3.99
7	0.50	1.00	4.02
8	0.50	1.50	3.97
9	1.00	0.25	4.03
10	1.00	0.50	3.94
11	1.00	1.00	3.93
12	1.00	1.50	4.05
13	1.50	0.25	4.01
14	1.50	0.50	4.00
15	1.50	1.00	3.95
16	1.50	1.50	4.02

All of those samples were treated at 300 ℃ for 2 h and ground in planet ball-mill for 10 min with 300 r/min, values of D were calculated by using Scherrer formula.

made from different concentrations of $SnCl_4$ and

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NH_4OH solutions and treated at the same temperature for various hours. The particle size was calculated by using Scherrer formula[11].

$$D = 0.89\lambda/(B \cdot \cos\theta) \qquad (1)$$

where λ—wave length of X-Ray (0.154 178 nm);
B—full-width-at-half-maximum;
θ—diffraction angle

The particle size of samples with various starting materials concentration treated for the same time fluctuated about the same size. It can be found from experiments that the concentration of $SnCl_4$ and NH_4OH solutions has little effect on the radius of SnO_2 particles.

When the dosage of NH_4OH was enough to react with $SnCl_4$, particle size was not influenced by the final pH value, as shown in Fig. 1. Fig. 2 indicates the X-ray diffraction patterns of samples treated at various temperatures for 2 h, such as 200 ℃, 300 ℃, 400 ℃, 500 ℃, 600 ℃, 700 ℃, and so on. All of those samples were ground for 10 min in the planet ball-milling with 300 r/min. The treating temperature had a great influence upon the SnO_2 powder size. For the sample calcinated at 300 ℃ for 2 h, there has a widen peak with the diffraction angle of 27.0°, 33.4°, 51.8°. With increasing temperature, the corresponding diffraction peak became more and more acute. If the treating temperature was higher than 600 ℃, the X-ray diffraction pattern of SnO_2 powder was similar to that of the large grains. We calculated the particle size of samples treated at various temperatures through Scherrer formula. As listed in Table 2, it indicates that if the treating temperature is lower than 500 ℃, the size is less than 10 nm, but the particle size increase significantly when temperature is beyond 600 ℃. The samples treated at 300~ 500 ℃ have a good stability in particle sizes. The data calculated by using Scherrer formula response to the result observed through TEM, i. e. when temperature is higher than 600 ℃, the size increases with temperature rapidly. But compared with the result reported by some researchers[12], the increasing rate in the experiment is smaller. Practically, SnO_2 gas sensors usually worked at 200~ 300 ℃. So, it is important to have a good stability in particle size in the range.

Table 2 Particle size of samples treated at various temperatures for 2 h

t/ ℃	D/nm
300	4.05
400	6.03
500	9.04
600	16.88
700	32.46
800	48.62

The nanoscale powder prepared by this method

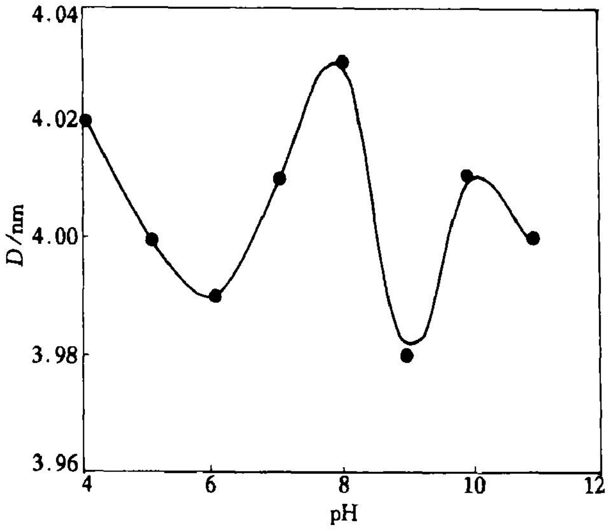

Fig. 1 Influence of pH value on particle size

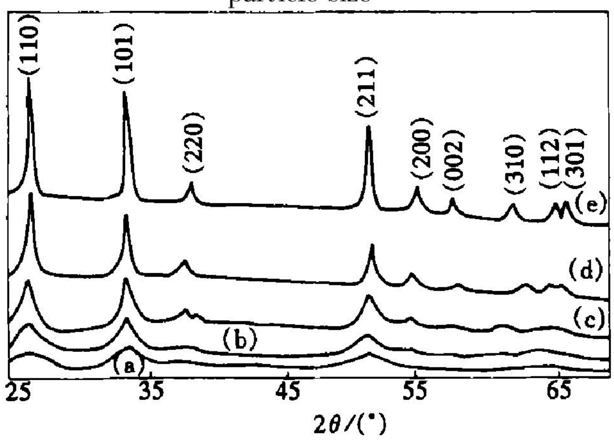

Fig. 2 X-ray diffraction patterns of SnO_2 powder treated at various temperatures for 2 h
1—300 ℃; 2—400 ℃; 3—500 ℃;
4—600 ℃; 5—700 ℃

can meet the require. In order to remain its gas sensibility, the working temperature must be controlled under 500 ℃ because hereafter the sample size is remarkably increased with increasing temperatures.

Fig. 3 are TEM images and electron diffraction patterns of sample treated at 300 ℃, 800 ℃ for 2 h, respectively. The particle size becomes large with increasing temperature. The shape of particle treated at 300 ℃ is spherical, but the latter has some ledges. It is because the crystalline structure becomes more and more perfect, the atoms, with an irregular distribution which located at the particle boundaries, crystallize gradually by the force of calcination. Electron diffraction patterns that is composed of rings with different radius and some diffraction spots indicate that SnO_2 powder has two kinds of structures: crystallite and non-crystallite. Also, such result is corresponding to the widen diffraction peaks in X-ray patterns.

The dispersing of SnO_2 powder is an important factor. We try to dispose three kinds of dispersing agents. A, the mixture with proportion of Ethanol / Acetic acid / Acetone as 1∶1. 53; B, Ethanol absolute and cyclohexane mixture with the volume proportion of 1∶4 ; C, 0. 2 mol/ L Tartaric acid and 0. 7 mol/ L citric acid dissolved in 1L distilled water. Fig. 4 are SEM images of SnO_2 powder and large grains dispersed with various dispersing agents. Though Fig. 4 shows the fact that the aggregates observed are mainly constituted by clusters of several tiny spheres[13], the dispersing result of these samples is different. The polarity order of dispersing agents from small to large is: A < B < C. The sample dispersed with A was divided into many blocks and the B looked like cloud. But the C had an appearance of lotus-root. So the dispersing effect was

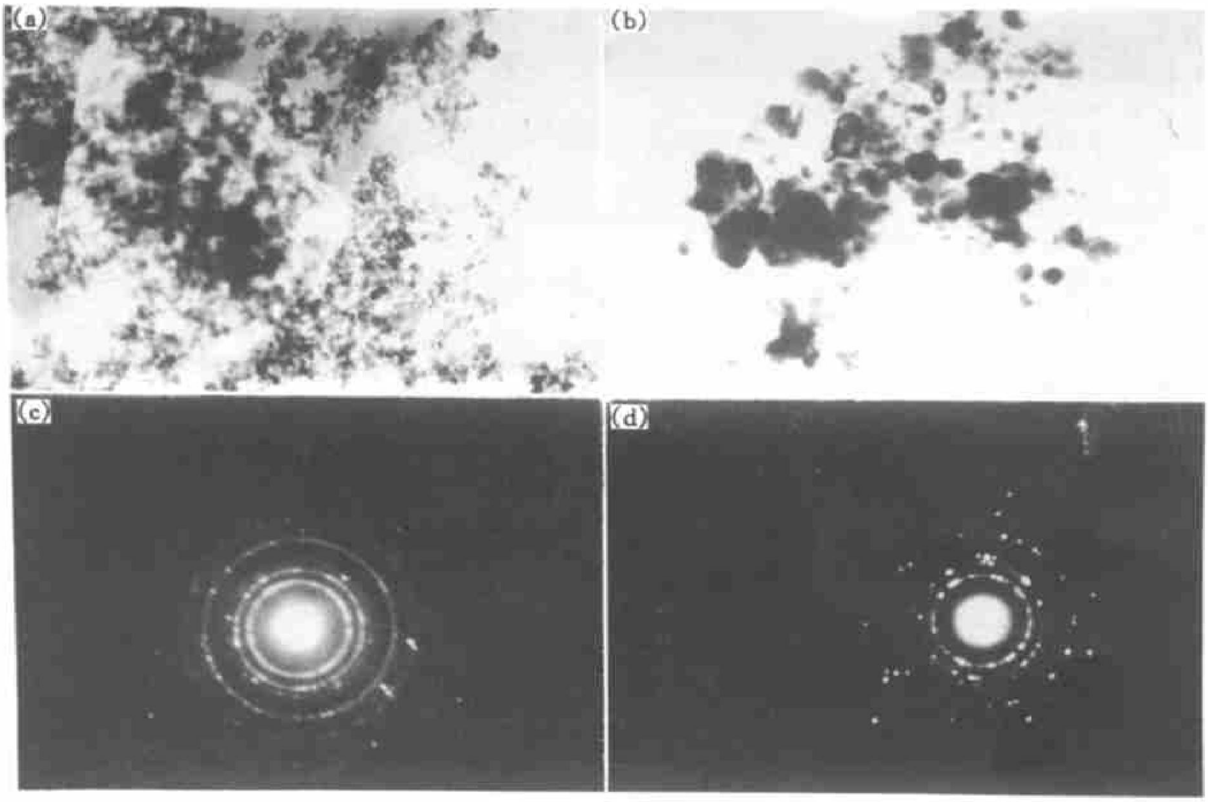

Fig. 3 TEM images and electron diffraction patterns of SnO_2 powder treated at various temperatures
(a) —TEM image (300 ℃) ; (b) —Electron diffraction pattern(300 ℃) ;
(c) —TEM image (800 ℃); (d) —Electron diffraction pattern(800 ℃)

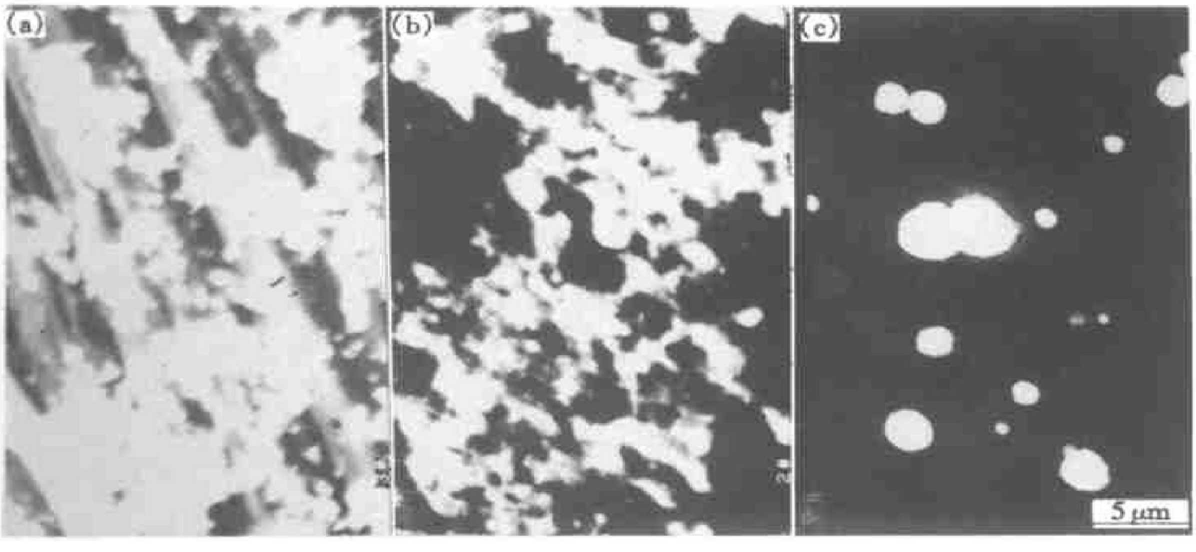

Fig. 4 SEM images of powder dispersed with different dispersing agents and large grains
(a) —Dispersed with A; (b) —Dispersed with B; (c) —Dispersed with C

in the sequence of A, B and C, its reason is the difference of Sn and O in electronegativity being appropriately equal to the polarity of dispersing agent A.

4 CONCLUSIONS

1) SnO_2 nano-sized powder whose size is less than 50 nm can be obtained by using chemical precipitation. The concentration of starting materials and the pH value of final system have little effect on the particle size with the same heat treatment.

2) The treating temperature has great effect on the particle size, and the particle size can become large with increasing treating temperature. When treating temperature is below 600 ℃, the size of samples is less than 10 nm. SnO_2 powder treated at 200~ 300 ℃ has good stability, it is significant to the SnO_2 gas sensor. The particle size can be controlled by changing treating temperature.

3) The dispersing result varies from one dispersing agent to another, it relates to the dispersing agent polarity. Dispersing agent A, which is the mixture with proportion of Ethanol/Acetic acid/Acetone 1:1.5 3, is the best.

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