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Ultrafine SnO_2 prepared by supercritical fluid drying technique (SCFDT) for gas sensors

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Abstract

A sol–gel process, followed by supercritical fluid drying (SCFD) was employed to prepare ultrafine tin oxide. Two different procedures were introduced and the powder properties of these two products were measured and compared, including the particle size, specific surface area and pore size distribution. Because the same reactive mechanism occurs in the gas sensing process and catalytic process, the sensor properties can be improved largely by the use of ultrafine tin oxide. In this paper, different gas sensing properties were observed when the two products were used as base materials of gas sensors. The effects of pH value on the pore structure and response (reversion) time of the sensors are also discussed.

Keywords: Tin oxide; Ultrafine particle; Gas sensor; Supercritical fluid drying technique; Response and reversion time

1. Introduction

The preparation of ultrafine tin oxide has attracted much attention recently, since it shows outstanding properties when used as a gas sensing material and catalyst support. A number of methods have been developed to synthesize the ultrafine particles (UFP) of tin oxide. Among these, physical methods [1–3] usually require more sophisticated equipment and higher cost, and the particle size cannot be easily reduced to < 40 nm. A chemical method, the sol–gel process [4], has been considered an effective one in recent years because of its low cost and uniformity in product composition. However, it often requires a tedious drying process and a strict method of preparation [5].In the present paper, a supercritical fluid drying technique (SCFDT) was used to treat the colloidal particles from sol–gel.

Under supercritical conditions, solvent can be removed without the appearance of a gas–liquid interface, therefore, the aggregation of fine particles can be avoided to a great extent, and nanometer size SnO_2 can be obtained. Many preparation parameters affect the powder properties. In this work, ultrafine SnO_2 was prepared by the SCFDT using two different procedures. The properties of the powders including particle size, specific surface area and pore size distribution were measured. Furthermore, pH value effects were studied.

Tin oxide is well known as a gas sensor. The sensing mechanism [6] is based on the reaction of adsorbed oxygen species on its surface with other toxic gases, such as CO, CH_4, etc., result-

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ing in a conductivity change when it contacts these gases. Therefore, in our eyes, the gas detection process is in effect a rapid surface gas–solid reactive process, in which tin oxide is the catalyst support and dopants such as ThO_2 and $PdCl_2$ are active components. Considering that the ultrafine particles may give a larger surface area and more active sites, we used ultrafine tin oxide as the base material (support) for the sensor (catalyst) system. After two typical samples of two different procedures were compared, series A of procedure 1 was shown to be better, especially with respect to the response and reversion time of the sensor.

2. Experimental

2.1. Preparation of SnO_2 UFP. Different procedures of sol–gel-SCFDT

$SnCl_4 \cdot 5H_2O$ (AR), NH_4OH (AR) and an organic solvent, ethyl alcohol (AR), were used as starting materials. SnO_2 powder was prepared by a sol–gel process followed by SCFD and calcination. Two procedures were used.

The first one has been reported previously [7], and included four steps. (1) Gel preparation: $SnCl_4$ in aqueous solution was hydrolyzed and precipitated by adding NH_4OH at different pH values, $SnCl_4$ concentration and temperature. (2) Solvent replacement: the water was replaced by ethanol several times after ageing, washing and filtration, and the so-called alcogel was prepared. (3) supercritical drying: alcogel was put into an autoclave, filled with ethanol and the temperature was raised until the pressure in the autoclave exceeded the critical values of the solvent, the supercritical state was kept for a given period, then the vapor was slowly vented. At this stage, N_2 was used to flush the autoclave to prevent ethanol from condensing onto the gel during cooling. When ambient pressure and temperature were reached, a porous dried aerogel filled with air was obtained. (4) Calcination: the dried aerogel SnO_2 was calcined at 773 K for 2–4 h to obtain the nanometer size SnO_2. The second procedure was very similar to the first one, except that the hydrolyzation was directly carried out in ethanol and step (2) was omitted.

Products of the first procedure were called series A, and a typical sample was named A1. Powders made by the second procedure were series B, and B1 was another typical sample. The preparation parameters for both samples A1 and B1, including concentration, acidity and ageing time, were maintained at the same levels. The SCFD conditions were 548 K and 8.0 MPa.

2.2. Sensor preparation

Ultrafine powders A1 and B1 were used as the two base materials. After UFP-SnO_2 was mixed with ThO_2, $PdCl_2$, Al_2O_3, SiO_2, asbestos and some water, the mixture was ground for 3–4 h in order to obtain a paste with a uniform composition. The paste was then coated onto a 4 mm long electrode and sintered at 1023 K for 3 h. Then the sample sensor was aged for 72 h to obtain stable properties. (Details of the preparation process are described elsewhere [8].)

Electrical conductivity measurements were taken with a constant-current method. Fig. 1 shows the detecting circuit diagram here, Vf is the heating voltage for the CO sensor, and Vk is a constant voltage of 10 V. RL is a fixed resistance. When the resistance of the sensor changes, the voltage, VRL, will also change.

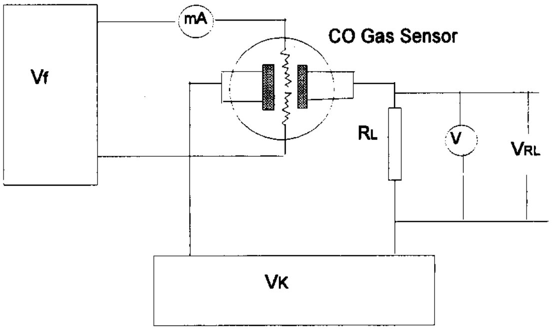

Fig. 1. Detection circuit diagram.

The sensitivity of the sensor is defined as $S = V_{RL}$ (in CO gas)/V'_{RL} (in clean air) or simply V/V_o.

2.3. Characterization

XRD (Dmax-A, Japan), TEM (Hitachi H-600, Japan), and N_2 adsorption (ASAP 2000, Micromeritics Co., USA) were applied to characterize the structure, particle size, specific surface area and pore distribution of the product SnO_2 powder.

3. Results and discussion

3.1. Comparison of powder properties

There are three main differences in properties of products synthesized by the two procedures. (1) Particle size: ultrafine powder prepared directly from the alcogel has smaller particle size, ranging from 2 to 5 nm; while ultrafine SnO_2 prepared by procedure 1 has a slightly larger particle size, ranging from 4 to 9 nm. (2) Specific surface area: the surface area of the powder prepared by procedure 1 is smaller than that by procedure 2. (3) Pore distribution: powder prepared by procedure 2 has a two-peak pattern with a wider distribution, whereas powder prepared by procedure 1 has a single-peak pattern with a larger pore diameter and volume.

Table 1
Properties of the typical samples of A1 and B1

	Surface area S_{BET} (m^2/g)	Pore volume V (cm^3/g)	Mean pore diameter r_p (nm)	Particle size d (nm)
A1	59	0.2206	15.4	7–9
B1	86	0.2813	13.1	3–5

TEM micrographs of typical sample A1 and B1 are given in Fig. 2, which show that both samples are equally sized. The size of SnO_2 particle is estimated to be 3–5 nm in Fig. 2b and 7–9 nm in Fig. 2a.

Table 1 gives the powder properties of the two products. The higher surface area and smaller particle size for series B are due to the colloidal property. Two different hydrolysis processes take place when $SnCl_4$ is dissolved in distilled water or ethanol. For procedure 1, a hydrolysis process takes place directly:

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl \qquad (1)$$

$$SnCl_4 + 4NH_3 \cdot H_2O = Sn(OH)_4 + 4NH_4Cl \qquad (2)$$

$$Sn(OH)_4 + Sn(OH)_4 = H_2SnO_3 + H_2O \qquad (3)$$

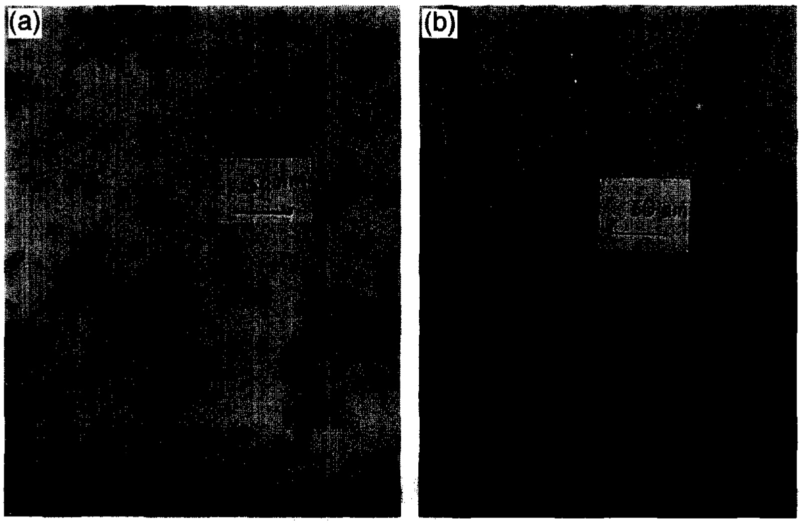

Fig. 2. TEM micrographs of tin oxide samples. (a) Sample A1 by procedure 1. (b) Sample B1 by procedure 2.

On the other hand, when $SnCl_4$ is dissolved in ethanol, a new substance $Sn(OC_2H_5)_4$ forms, then it hydrolyzes into $Sn(OH)_4$. This process can be expressed as follows:

$$SnCl_4 + 4C_2H_5OH = Sn(OC_2H_5)_4 + 4HCl \quad (4)$$

$$Sn(OC_2H_5)_4 + 4H_2O = Sn(OH)_4 + 4C_2H_5OH \quad (5)$$

$$Sn(OC_2H_5)_4 + 4NH_3 \cdot H_2O = Sn(OH)_4 + 4C_2H_5OH + 4NH_3 \quad (6)$$

$$Sn(OH)_4 + Sn(OH)_4 = H_2SnO_3 + H_20 \quad (7)$$

$Sn(OC_2H_5)_4$ hydrolyzes slowly, resulting in a smaller particle size and larger surface area.

The pore distribution determined by N_2 adsorption is given in Fig. 3. Although A1 and B1 both have larger pore volumes (see Table 1), different desorption curves are shown. For B1, a wider distribution from 1 to 100 nm is obtained, whereas A1 has a narrower distribution. This property can affect the sensing performance greatly, especially the response and reversion time of the sensors, which is described in the following section.

3.2. Gas sensing properties

One of the advantages of using UFP as base materials of sensors is that UFP can save energy efficiently [9]. Fig. 4 shows sensitivity as a function of heating current for MQ-Y1, A1 and B1. MQ-Y1 is a typical commercial sensor made in the Taiyuan Electronics Plant in China. Results are obtained from the detection circuit described above. For MQ-Y1, the most suitable current is 70 mA to CO, and the minimum sensitivity obtained is 4. The maximum sensitivity for B1 and A1 is 80 and 35, respectively, at a current of 20 mA. Ultrafine sensors can work at lower heating currents and give more higher sensitivities, the working temperature can be reduced greatly. The larger sensitivity for B1 is due to the smaller particle size and larger surface area. SnO_2 sensors by SCFD are characterised by their high sensitivity.

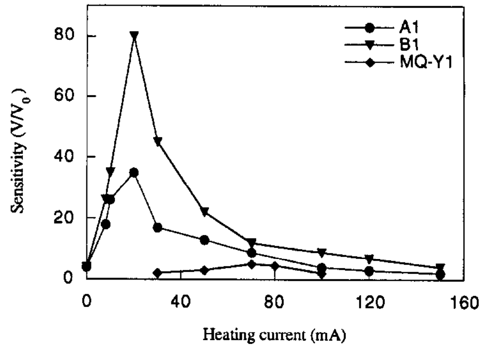

Fig. 4. Gas sensitivities as a function of the heating current for MQ-Y1, A1 and B1. The detected gas is 100 ppm CO. Two powders A1 and B1 are used as the base materials for two sensors.

In addition to sensitivity and selectivity, the response and reversion time is very important. One of the problems in applying commercial sensors at low temperatures is slow response and long relaxation (reversion) time, especially the latter. Fig. 5 shows sensitivity as a function of response (reversion) time for A1 and B1 in

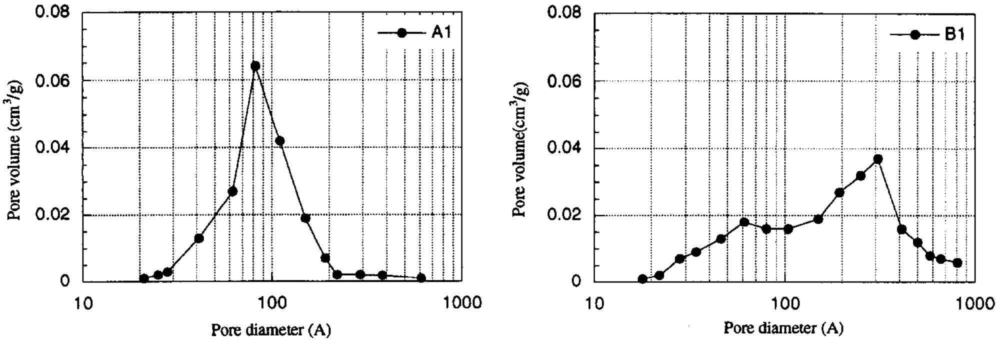

Fig. 3. Pore volume as a function of pore diameter (desorption loop) for ultrafine tin oxide. Left, sample A1. Right, sample B1.

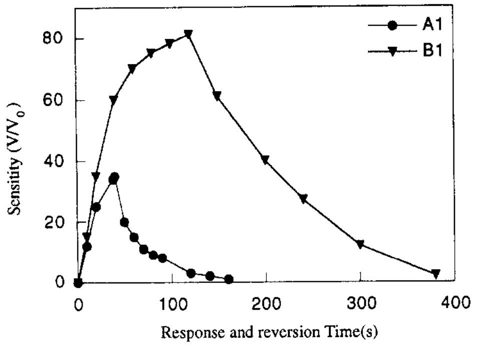

Fig. 5. The response and reversion time of sensors made from the two different powders. The detected gas is 100 ppm CO, the same heating current of 20 mA was maintained.

100 ppm CO. The heating current was 20 mA, The response time of A1 is 30 s and of B1, 60 s. In terms of reversion time, B1 relaxes in 240 s, making it unacceptable for practical use. Sample A1 can revert in about 60 s. The sensors made from UFP of series A have quick response and shorter reversion time, and thus are promising candidates for use in low temperature gas sensors. Difference between the two sensors is largely caused by the different pore structure of the two series. A wide pore size distribution is not preferred.

3.3. Effects of pH value on pore size and response (reversion) time for procedure 1

Even for the same operating procedures of SCFDT, the properties of SnO_2 powders change greatly with preparation conditions. Reported studies on the effect of preparation parameters show that the particle size and surface area of SnO_2 depend on many factors. In this study, the influence of the solution acidity for series A on the pore size and response (reversion) time is studied in detail. Fig. 6 shows the relationship between the mean pore diameter, response (reversion) time and the pH value. The correlation reveals that the mean pore diameter of the powder decreases and the response(reversion) time shortens with the decrease of pH value.

4. Conclusion

Two typical samples made by the sol–gel-SCFDT method are compared in this paper. Series B has a smaller particle size, larger surface area but wider pore distribution, while series A has a narrower distribution. Since UFP SnO_2 by series A has large surface area and a narrow pore distribution with a large pore volume, it shows excellent gas sensing properties, such as low working temperature, high sensitivity and quick response(reversion) time. Furthermore, the pH value affects response and reversion time significantly, and the higher the pH value results in larger pore diameters of the product with a short response and reversion time.

Fig. 6. Effects of pH value on pore structure and response (reversion) time.

References

[1] L.I.Popcva, M.G. Michailov and V.K.Gueorguiev, Thin Solid Films, 186 (1990) 107.

[2] T.M.Wen, K.F. Huang, M.S.Chen and Y.S.Gou, Thin Solid Films, 158 (1988) 69.

[3] S.Muranaka, Y. Bando and T.Takado, Thin Solid Films, 86 (1981) 11.

[4] L.L. Hench and J.K.West, Chem. Rev., 90 (1990) 33–72.

[5] K. Tanaka, A. Nozue and K. Kamiya, Jpn. J. Appl. Phys., 28 (1989) L934.

[6] N.Yamazoe and N.Miura, in S.Yamauchi (Ed.), Vol. 4, Elsevier, Amsterdam, 1992, Chapter 2, p. 20.

[7] F. Lu, S.Y. Chen and S.Y. Peng, in G. Poncelet, J. Martens, B. Delmon, P.A. Jacobs and P. Grange (Editors), Preparation of Catalysts VI, Elsevier, Amsterdam, 1994, p. 489.

[8] X.P.Wang, J. Electron. Technol., 8 (1991) 7–8.

[9] F. Lu, S.Y.Chen and S.Y.Peng, Funct. Mater., 26 (1995) 298–301.