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High surface area SnO_2 nanoparticles: Synthesis and gas sensing properties

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Abstract

SnO_2 nanoparticles with high surface area have been synthesized by a homogeneous precipitation ethanol-thermal method with $CO(NH_2)_2$ and $SnCl_4{\cdot}5H_2O$ as starting materials. FT-IR, XRD, BET and TEM have been employed to characterize the as-prepared samples. The results show that the homogeneous precipitation ethanol-thermal method can effectively restrain the agglomeration, by which the SnO_2 powders obtained are well dispersed and less aggregated with a size of 8–9 nm and high-specific surface area over 200 $m^2\,g^{-1}$. On the other hand, the SnO_2 powders prepared via the single homogeneous precipitation method showed lower specific surface area of 55 $m^2\,g^{-1}$. The results of gas sensing measurements show that the sensors fabricated by the SnO_2 nanoparticles obtained by the homogeneous precipitation ethanol-thermal method exhibit excellent sensitivity behavior to methanol and ethanol gases at room temperature. When the concentration of ethanol is 80 ppm, the sensitivity is ca. 25, and the recovery time is less than 25 s at room temperature.

Keywords: Nanostructures; Semiconductors; Chemical synthesis; Chemical techniques

1. Introduction

SnO_2 is an n-type semiconductor with a wide band gap of 3.65 eV, and has been widely used as gas sensors [1–4], electrode materials [5], catalyst supports [6], solar cells [7,8], etc. Especially, SnO_2 nanoparticles have been intensively studied for gas sensing applications not only because of their relatively low operating temperature, but also due to the fact that they can be used to detect both reducing and oxidizing gases by adding various doping elements [9–19]. Generally, SnO_2 powders with high surface area are in favor of the applications of gas sensors. Therefore, more and more efforts have been focused on the preparation of SnO_2 with high surface area. Song and Kim [20] synthesized SnO_2 powders with surface area of 86 $m^2\,g^{-1}$ through a water-in-oil microemulsion method. Song and Kang [21] employed a homogeneous precipitation method to prepare SnO_2 powders with specific surface area of 24–44 $m^2\,g^{-1}$, while SnO_2 powders with specific surface area of 15–18 $m^2\,g^{-1}$ were obtained through a precipitation method in comparison. Chen and Gao [22] obtained SnO_2 nanoparticles with high-specific area of 107–169 $m^2\,g^{-1}$ and particle size of 3 nm via a water-in-oil microemulsion-assisted hydrothermal process. Fujihara et al. [23] fabricate thermally stable SnO_2 particles with specific surface area over 110 $m^2\,g^{-1}$ by a hydrothermal route followed by annealing treatments at 400 or 500 °C.

In this paper, a homogeneous precipitation ethanol-thermal method has been developed to fabricate SnO_2 nanoparticles with specific surface area over 200 $m^2\,g^{-1}$, and the sensing properties of samples have been studied at room temperature.

2. Experimental

2.1. Synthesis

All the chemical reagents were analytically pure and used without further purification. SnO_2 particles were prepared by a homogeneous precipitation method modified in terms of the route in literature [21] and a homogeneous precipitation ethanol-thermal method, respectively. In a typical procedure of the first method, urea ($CO(NH_2)_2$) and $SnCl_4{\cdot}5H_2O$ were dissolved in distilled water at room temperature with concentrations of 0.15 and 0.05 mol L^{-1}, respectively. Then, the solutions were mixed, and heated to 90 °C for 5 h to promote the hydrolysis of $SnCl_4$ and the formation of SnO_2. The precipitates obtained were separated by centrifugation, washed with deionized water until the absence of

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Table 1
Synthesis conditions, Scherrer crystal sizes and BET surface areas of SnO_2 samples (a–f)

Samples	Synthesis conditions	Crystal sizes[a] (nm)	BET surface areas ($m^2\ g^{-1}$)
(a)	Prepared by homogeneous precipitation	10.5	55
(b)	Prepared by homogeneous precipitation ethanol-thermal method with the concentration of $SnCl_4$ of 0.05 mol L^{-1} and ethanol-thermal treatment at 140 °C for 15 h	7.8	218
(c)	Prepared by homogeneous precipitation ethanol-thermal method with the concentration of $SnCl_4$ of 0.05 mol L^{-1} and ethanol-thermal treatment at 140 °C for 24 h	8.1	214
(d)	Prepared by homogeneous precipitation ethanol-thermal method with the concentration of $SnCl_4$ of 0.05 mol L^{-1} and ethanol-thermal treatment at 140 °C for 30 h	8.5	205
(e)	Prepared by homogeneous precipitation ethanol-thermal method with the concentration of $SnCl_4$ of 0.05 mol L^{-1} and ethanol-thermal treatment at 170 °C for 24 h	9.0	201
(f)	Prepared by homogeneous precipitation ethanol-thermal method with the concentration of $SnCl_4$ of 0.15 mol L^{-1} and ethanol-thermal treatment at 140 °C for 24 h	8.6	207

[a] Average crystal size for SnO_2 was estimated by XRD using the Scherrer formula based on the (1 1 0) reflection.

chloride ion, which was tested by an aqueous $AgNO_3$ solution, and then washed with ethanol for three times. The resulting products were dried at 110 °C for 3 h and then calcined at 500 °C for 2 h to obtain samples. By the second method, the modified point in comparison with the first method was that the precipitates obtained after washed with ethanol were dispersed in ethanol and placed into a Teflon-lined autoclave. Ethanol-thermal treatments were carried out at 140 °C for 15, 24 and 30 h and 170 °C for 24 h, respectively. The SnO_2 nanoparticles were obtained after centrifuging the resulting precipitates and then drying at 110 °C for 3 h.

2.2. Characterization of the as-prepared samples

Phase structures of the as-prepared samples were identified with X-ray powder diffraction (XRD) taken on a Rigaku-D-Max rA 12 kW diffractometer with Cu Kα radiation (λ = 1.54056 Å) at an operation voltage and current of 40 kV and 300 mA, respectively. Morphologies and particle sizes of the samples were observed with a Hitachi H-800 transmission electron microscope (TEM) operated at an acceleration voltage of 200 kV. Fourier transform infrared (FT-IR) spectra of the samples were recorded on an AVATAR 360 Fourier-IR spectrophotometer with KBr as compressed slices. The specific surface areas of the samples were analyzed on a BET surface analyzer (ASAP2010, Micro-meritics).

2.3. Gas sensing measurement

The samples were completely ground in an agate mortar, and the SnO_2 paste was formed through adding terpineol. Then, the resultant paste was coated on an alumina ceramic tube with already deposited gold electrodes with 1.5 mm spacing. After sintering at 420 °C for 2 h and 300 °C for 120 h, the sensor element was installed into a HW-C30A (Hanwei Group, Henan) gas sensing intelligent apparatus, which served as voltage sources. For consistency, a potential of 5 V was applied across the gold electrodes for all measurements, and all the gas sensing experiments were carried out in a closed glass container (10 L in volume) equipped with appropriate inlet and outlet for gas flow. The sensor sensitivity (Rair/Rgas) is defined as the ratio of the sensor resistance in air to that in the presence of ethanol or methanol gas.

3. Results and discussion

The synthesis conditions, Scherrer crystal sizes and BET surface areas of SnO_2 samples (a–f) are listed in Table 1, and their XRD patterns are shown in Fig. 1. All the diffraction peaks of the XRD can be readily indexed to tetragonal SnO_2 with rutile structure (JCPDS 21-1250). Fig. 1(a) and (b–f) exhibit the XRD patterns of samples prepared by the homogeneous precipitation and homogeneous precipitation ethanol-thermal method, respectively. It is apparent that the XRD peaks are by far sharper and narrower for the sample (a) prepared via the homogeneous precipitation method than that for the samples (b–f) prepared by the homogeneous precipitation ethanol-thermal method, which reveals that the average crystal size of SnO_2 particles prepared via the former method is larger than that prepared by the later one. The average crystal sizes of SnO_2 particles prepared by the above-mentioned two methods are ca. 10.5 nm and below 9.0 nm, respectively, estimated by the Scherrer formula based on the (1 1 0) reflection of XRD. With prolonging the ethanol-thermal treatment times, the diffraction peaks become narrower and stronger due to the fact that the average crystal sizes grow larger and the crystallinity is improved. The average crystal sizes for samples (b–d) are 7.8, 8.1 and 8.5 nm for the SnO_2 samples with the ethanol-thermal treatments at 140 °C for 15, 24 and 30 h, respectively. The average crystal sizes are 8.1 and 9.0 nm for the SnO_2 samples (c) and (e) with the ethanol-thermal treatment temperatures of 140 and 170 °C, respectively, which implies that the crystal size grows large with the ethanol-thermal treatment temperature increasing. The peak width of the sample (f) pre-

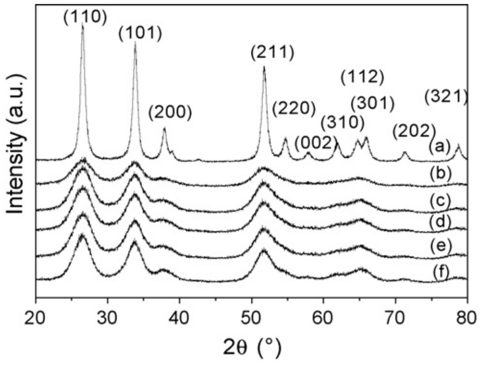

Fig. 1. XRD patterns of the as-prepared SnO_2 samples (a–f).