



Honeycombed SnO₂ with ultra sensitive properties to H₂

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ABSTRACT

Honeycombed SnO₂ is synthesized by a simple wet chemical method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and N₂ adsorption–desorption isotherms. The porous diameter of the honeycombed SnO₂ is about 2 μm. Sensing investigation reveals that the obtained SnO₂ with a very small BET surface area (19.7 m² g⁻¹) owns ultra sensitive properties to H₂ at 340 °C. The response is 8.4 when the sensors are exposed to 1 ppm H₂, and the response and recovery times are 4 and 10 s, respectively. The theoretical model for the infection of porous diameter on the sensing properties is provided.

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1. Introduction

Metal oxide sensors are increasingly demanded for their widely applications in air-quality detection, inflammable-gas inspection, environmental monitoring, security and process control [1]. Among the applied metal oxides, tin dioxide (SnO₂) plays a key role as one of the more representative sensing materials in solid-state gas sensors, presenting a significant surface reactivity with many important reducing (CO, H₂, C₂H₅OH, and CH₄) and oxidizing gases (O₂, Cl₂, and NO₂) [2]. SnO₂ sensors with various characteristics have been frequently reported [3], and most commercial sensors are also fabricated by this material. However, pure SnO₂ only shows very low responses to gases and its sensing reacting speeds are also very slow. Therefore, different techniques have been used to improve the performances [4].

Since the sensing mechanism of the semiconducting gas sensor is based on the surface reaction of semiconducting oxide, surface characteristic is one of the most influential factors for high sensitivity [3]. Doping extraneous elements into SnO₂ can infect the grain size, surface architecture, and concentration of free charge carriers, therefore induce a significant effect on its sensing properties correspondingly [5]. This method is simple and adjustable, but the low stability and poor consistency of the obtained

materials restrict their applications. And as the doping mechanism is far more complicated than the reported experiential explanation, no instructional empirical approach is available for this method currently [5]. On the other hand, reforming materials with one-dimensional nanostructures or porous nanostructures can greatly improve sensor properties as more gas molecules can be absorbed on the sensor surface [6]. Especially, porous SnO₂, based on its ordered pore distributions, high pore volumes and high surface areas, has attracted much research interest in developing its potential applications in chemical sensors [7]. However, most researchers in this field only focus on mesoporous materials with small pores (smaller than 50 nm) [8]. The porous materials with huge pores (larger than 1 μm) are rarely investigated.

Herein, we report a honeycombed SnO₂ nanostructure synthesized by a simple wet chemical method. The pore diameter is about 2 μm in the honeycombed SnO₂, which is quite huge when it is compared with the diameter of gas molecules. But the sensing investigation shows this material owns ultra high H₂ responses and very short reacting times. The results may provide an effective approach to understand and design SnO₂-related sensing materials.

2. Experimental

The chemicals peroxyacetyl nitrate (PAN, *M_w* = 150,000, 1.184 g/mL at 25 °C) and N,N-dimethylformamide (DMF) were purchased from Sigma–Aldrich, USA. All chemicals were of high purity grades. Firstly, 9.0 g PAN was slowly dissolved in 50 mL

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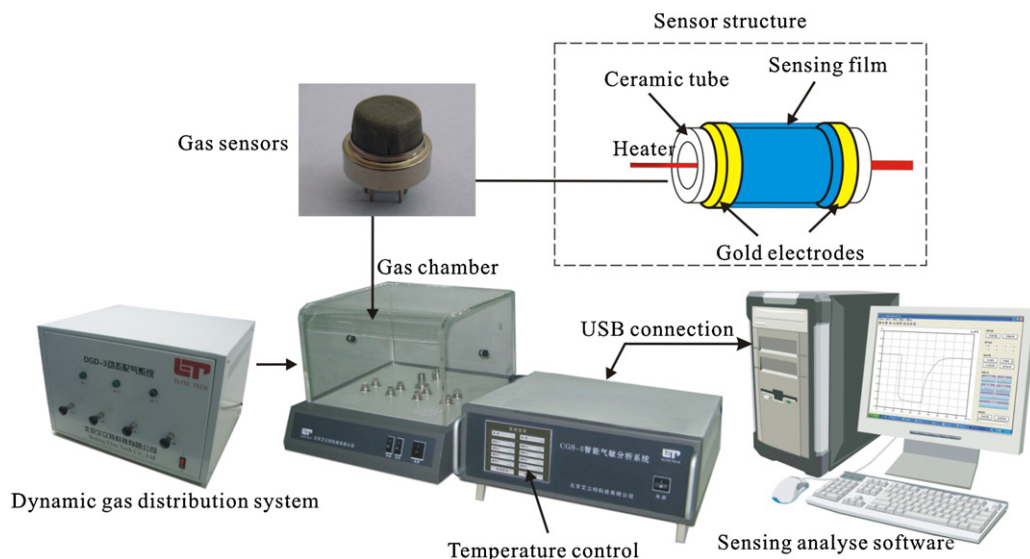


Fig. 1. Schematic diagram of the experimental process.

DMF at 50 °C with vigorous stirring for about 12 h and then 5 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added under stirring. Thus, a clear viscous solution of PAN/ SnCl_4 was obtained under stirring for 5 h in a water bath at 50 °C. The solution was dropped into the deionized water. The porous materials thus formed were dried initially 2 h at 80 °C under vacuum, and then calcined at 600 °C at a rate of 120 °C/h and remained 6 h at the required temperature.

Scanning electron microscopy (SEM) images were performed on a SHIMADZU SSX-550 (Japan) instrument equipped with energy dispersive X-ray (EDX) spectroscopy. X-ray diffraction (XRD) analysis was conducted on a Scintag XDS-2000 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The nitrogen isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2020M system. The specific surface area, S_{BET} , was determined from the linear part of the BET plot.

The as-calcined sample was mixed with deionized water (resistivity = $18.0 \text{ M}\Omega \text{ cm}^{-1}$) in a weight ratio of 100:20 to form a paste. The paste was coated on a ceramic tube on which a pair of gold electrodes was previously printed, and then a Ni–Cr heater was inserted in the tube to form a side-heated gas sensor (Fig. 1). The thickness of the sensing films was measured to be about 300 μm . Gas sensing properties were measured by a CGS-8 intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd., China) (Fig. 1). The testing ambience was controlled by a DGD-III dynamic gas distribution system. The background gas was artificial air. Gas sensors were inserted in the sensor sockets in the test chamber. When the resistances of all the sensors were stable, target gas was introduced into the chamber (1 L in volume) through a steel plug. After the sensor resistances reached a new constant value, the position of the sensor was turned so the sensor could be surrounded by air quickly. The sensing tests were performed in a super-clean room with a constant temperature of 25 °C. The response value (S) was designated as $S = R_a/R_g$, where R_a was the sensor resistance in air (base resistance) and R_g was a mixture of target gas and air. The time taken by the sensor resistance to change from R_a to $R_a - 90\% \times (R_a - R_g)$ was defined as response time when the target gas was introduced to the sensor, and the time taken from R_g to $R_g + 90\% \times (R_a - R_g)$ was defined as recovery time when the ambience was replaced by air.

3. Results and discussion

Fig. 2(a) and (b) shows low-resolution and high-resolution SEM images of the as-synthesized SnO_2 , respectively. Lots of

honeycombed pores are observed in the low-resolution image, and the average porous diameter is about 2 μm , which is more than three magnitudes larger than the diameter of gas molecule. The thickness of porous wall is about 100 nm, as shown in Fig. 2(b). The formation of pores by the co-working of DMF and PAN is very well-known and widely discussed in the literatures [8]. Basically, the pores are created by the evaporation of the precursory solution. When the precursory materials was dried and calcined at high temperatures, DMF and PAN can be evaporated and the evaporative cooling in the materials could lead to the condensation of moisture

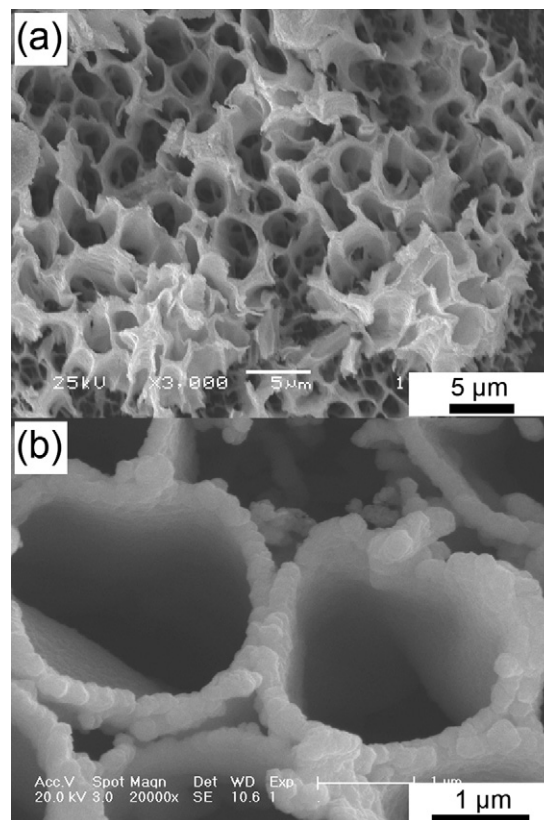


Fig. 2. (a) Low-resolution and (b) high-resolution SEM images of honeycombed SnO_2 .

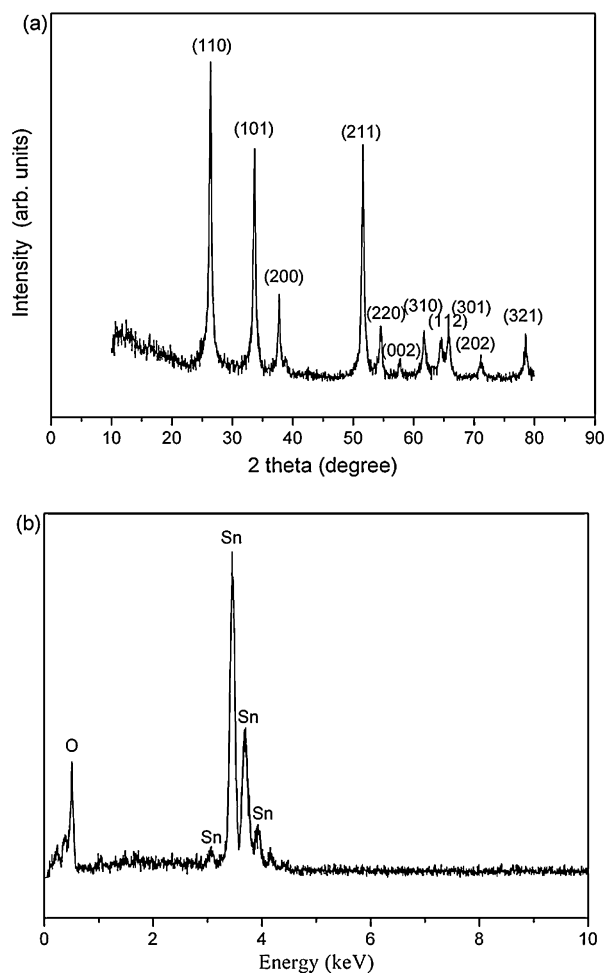


Fig. 3. (a) XRD and (b) EDX patterns of honeycombed SnO₂.

and the formation of pores. The BET surface area of the honeycombed SnO₂ is only about 19.7 m² g⁻¹, which is much lower than most reported sensing materials [9]. This is because the pores of the honeycombed SnO₂ are too big, therefore cannot be described by nitrogen isotherms and the corresponding BET surface area results.

Fig. 3(a) shows the XRD pattern of the as-prepared honeycombed SnO₂. The sample is polycrystalline in nature. The prominent peaks corresponding to (1 1 0), (1 0 1) and (2 1 1) crystal lattice planes and all other smaller peaks coincide with the corresponding peaks of the rutile structure of SnO₂ given in the standard data file (JCPDS File no. 41-1445) [10]. The EDX pattern in Fig. 3(b) indicates the sample is composed of Sn and O. No patterns corresponding to any impurity is observed, indicating a high purity of the obtained product.

Response and recovery characteristics of honeycombed SnO₂ to 1 ppm H₂ at 340 °C is shown in Fig. 4. The response and recovery times are about 4 and 10 s, respectively. The recovery time is more than twice longer than the response time. This is because the gas desorption is a heat-absorbing process, and the honeycombed structure is concave, these factors lead to a much slower recovery speeds of the sensors [11,12]. The sensors are also tested at different temperatures, as shown in the insert of Fig. 4. The response increases and reaches its maximum, and then decreased rapidly with further increasing the temperature. The maximal response appears at 340 °C, showing the optimized testing condition of the current sensors. At elevated temperatures the response is increased because of the formation of O⁻ ions, but is decreased because of the decrease in the adsorptive reaction. Thus, the optimal temperature

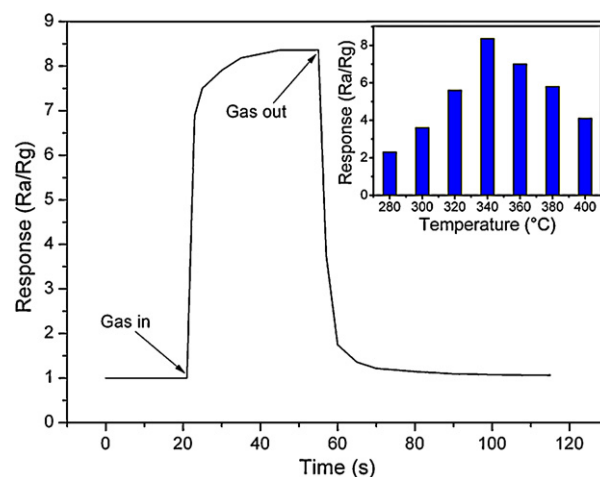


Fig. 4. Response and recovery characteristics of honeycombed SnO₂ to 1 ppm H₂ at 340 °C, the insert show the responses of the honeycombed SnO₂ to 1 ppm H₂ at different temperatures.

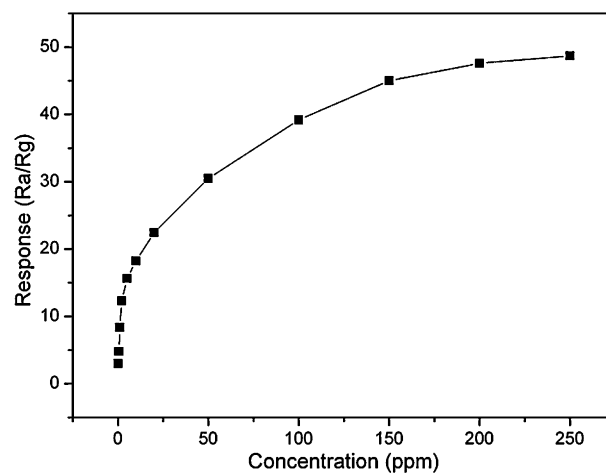


Fig. 5. Responses of honeycombed SnO₂ to different concentrations of H₂ at 340 °C.

for a gas sensor is that at which the two factors are balanced. This behavior is in agreement with previous results [12].

Fig. 5 shows the sensor response versus H₂ concentration at 340 °C. The sensors based on honeycombed SnO₂ exhibit extremely

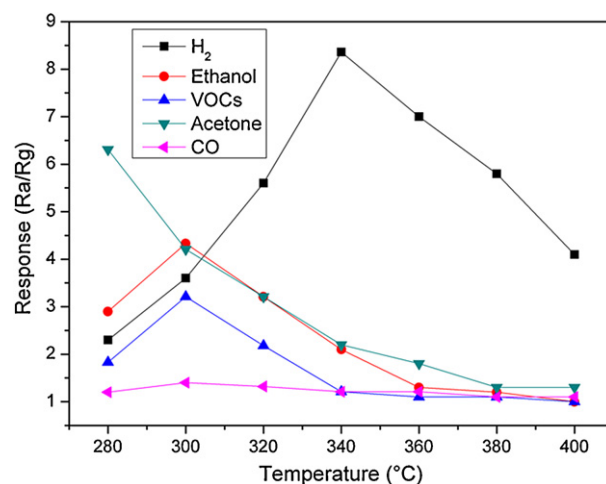


Fig. 6. Responses of honeycombed SnO₂ to 1 ppm different gases at 340 °C.

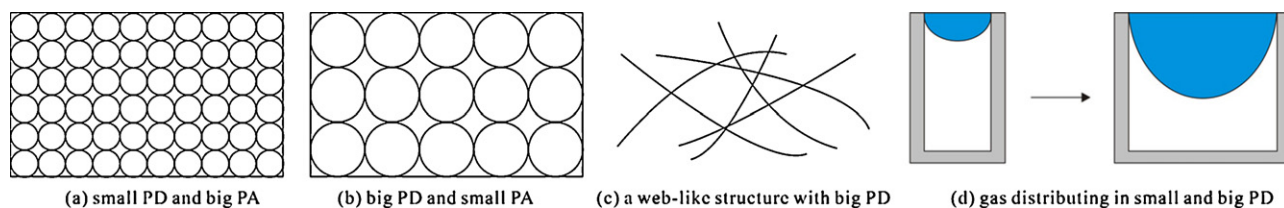
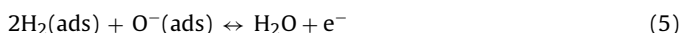


Fig. 7. (a–c) Three different porous structures, and (d) gas distributing in small and big pores.

high responses in the tests. For instance, the responses are about 3.1, 8.4, 18.3, and 39.4 to 0.05, 1, 10, and 100 ppm H₂. The low detecting limit (0.05 ppm) combining with the high responses indicating the obtained sensors are very suitable for H₂ detection at low concentrations.

The sensors were exposed to 1 ppm different gases to test the selectivity. The results in Fig. 6 indicate that honeycombed SnO₂ owns various selectivities when the operating temperatures are changed. Much higher response is found for honeycombed SnO₂ to H₂ at 340 °C. But the sensors show better sensing response to ethanol and acetone at 300 °C. These results are due to the as-synthesized honeycombed SnO₂ is undoped, thus have responses to many gases [5].

As an N-type semiconducting oxide, the sensing mechanism of honeycombed SnO₂ can be explained as follow. Oxygen can be chemisorbed in various forms including O₂⁻, O⁻ and O²⁻, which are determined by the operating temperature of the sensor [3]. The operating temperature of the current sensor is 340 °C, and the reacting oxygen is O⁻ in case of SnO₂. Therefore, the H₂ sensing mechanism of the obtained honeycombed SnO₂ can be described as follows:



Compared with many reported H₂ sensors [13], the current sensor exhibits much higher response and quicker response and recovery speeds. This is mainly because of the huge porous structure of the honeycombed SnO₂. Porous structures can make the materials absorb more gas molecules, thus benefits for the sensor performances [13]. Two parameters, which are porous amount (PA) and porous diameter (PD), should be considered for the sensing application of porous materials. The total available area (TA) for gas transfers on the sensor surface can be calculated by:

$$\text{TA} = \text{PA} \times \pi \left(\frac{\text{PD}}{2} \right)^2 \quad (6)$$

Lower PD means larger PA in the same sensor. And geometrical comparison reveals that PD with nm level is enough for gas transfers. Therefore, many papers only investigated the mesoporous materials with PD at tens of nm to avoid the waste of material surface (Fig. 7(a)). However, recent researches prove that big PD (more than 100 nm) materials also show high responses (Fig. 7(b)) [14]. Even a web-like structure can greatly improve the response of materials (Fig. 7(c)) [15]. Most of these big PD materials with very small BET surface areas can show ultra-sensitive characteristics. These results imply that big pores are more effective in the sensing application than small pores. And this phenomenon can be explained by the pervasive volume of the gas molecules. Both the pervasive surface area and pervasive depth are depended on PD, thus bigger PD can lead to larger

volume of the vaulted gas distributing, as shown in Fig. 7(d). Therefore, the high response and short reacting times of the obtained materials can be known by the huge pores in this material.

4. Conclusions

In conclusion, the sensing properties of honeycombed SnO₂ are investigated. The material with very a small BET surface area (19.7 m² g⁻¹) shows ultra sensitive to H₂ at 340 °C. The response is up to 8.4–1 ppm H₂, and the response and recovery times are 4 and 10 s, respectively. The conflict between low BET surface area and high response is theoretically explained by referring the pervasive volume of the gas molecules in pores. The results not only show honeycombed SnO₂ is a good candidate for fabricating high performance H₂ sensors, but also provide a possible route to re-understand high sensitive materials with porous structures.

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