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Improvement of Gas Sensing Properties for SnO_2/Zeolite Composites Prepared by Electrospinning

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Abstract

In order to improve the selectivity of the SnO_2 gas sensor, different proportions of stannous chloride and nano-ZSM-5 zeolite mixed solution were synthesized, and SnO2/ZSM-5 composites were synthesis by electrospinning. The structure and morphology of the compounds and gas sensing properties were tested. Comparing with the gas sensing properties of the electrospinning SnO_2 fibers. The response values of these SnO_2/ZSM-5 composites gas sensors to formaldehyde vapor were increased, but the responses to other volatile organic vapors (VOCs) such as acetone, methanol, ethanol were suppressed, indicating an improved gas sensing properties property to formaldehyde. With the increase of the mass ratio of stannous chloride in the mixing process, the response of the composites to formaldehyde was gradually improved. When the mass ratio of stannous chloride to zeolite was 3:1, the composite material has the highest response to formaldehyde. The possible reasons for this contrary observation were proposed to be related to the "synthetic effect" of the catalytic property, molecular sieve property and adsorption property by the zeolite. The sensing mechanism of these composites sensing material was briefly analyzed.

Key words: Gas sensor; Zeolite; Tin dioxide; Selectivity; Electrospinning.

1 Introduction

They are the general name of a class of organic compounds. Most of them are irritating, toxic and carcinogenic. Long-term exposure to VOCs can damage human health. Formaldehyde is a kind of VOCs. As an important organic solvent. A standard of 0.08 ppm averaged over 30 min for long-term exposure in formaldehyde vapor has been established by the World Health Organization (WHO)[1].

Gas sensors made of metal oxides possesses good sensing properties such as high sensitivity, short response and recovery times and low cost. Tin dioxide is a kind of common metal oxide gas sensing material. The SnO_2 sensor has good response for many VOCs gases, such as methanol[2],ethanol[3],formaldehyde[4],acetone[5], etc. However, this type of sensor has some disadvantages, such as poor selectivity and low sensitivity. Therefore, the improvement of the gas sensing properties of SnO_2 sensor has become a focus of research. Many studies have also been carried out around this method. Although the SnO_2 nanofibers prepared by electrospinning can improve the sensitivity and reduce the operating temperature, but the selectivity of the sensing material has not been improved significantly. Various methods including temperature control, doping noble metal and adding of zeolite may be used to improve sensor selectivity[6, 7]. Among them, the adding zeolite is a lowest cost and most convenient method.

In this work, we are focus on synthesizing SnO_2/ZSM-5 fibers to improve the gas sensing properties of this type of materials. Nano-sized ZSM-5 zeolites were prepared by template method. The fibers can avoid the agglomeration of tin dioxide and ZSM-5 zeolite comparing with the common material, and easy to perform the advantage of the two materials. Using the adsorption property, molecular sieve property and catalytic property of zeolite, the composites could improve the gas sensing properties.

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2 Experimental

The nano ZSM-5 used in this work was prepared by hydrothermal synthesis following template method[8]. The SnO_2/ZSM-5 fibers were prepared by electrospinning method. The spinning solution of SnO_2/ZSM-5 fibers were made by dissolving the mixture according to the mass in Table 1.

Tab.1 The mass of the chemicals for the four kinds of SnO_2/ZSM-5 composites spinning solution

Fiber	$SnCl_2 \cdot 2H_2O$ (mg)	ZSM-5 (mg)
SZ2	400	200
SZ3	375	125
SZ4	480	120
SZ5	500	100

3 Results and discussions

3.1 Materials characterization

The XRD patterns of the ZSM-5 zeolite treated before and compound with SnO_2 using electrospinning method are shown in Fig.1. We can see from curves of Fig.1 that broadened peaks appear at 26.578,33.772,37.768 and 51.755 degree (2θ)in the XRD patterns of SZ2,SZ3,SZ4 and SZ5 compared with ZSM-5 zeolite, which can be indexed to the crystal planes of (110),(101),(200) and (211) of the SnO_2. With the increase of SnO_2 content in the composites, the diffraction peak intensity of SnO_2 increases, while the diffraction peak intensity of ZSM-5 decreases gradually.

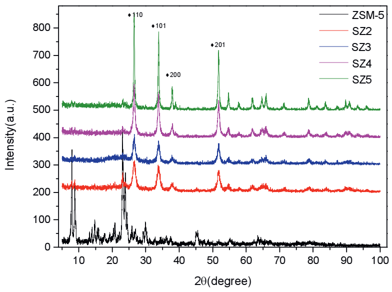

Fig.1 XRD patterns of ZSM-5 and SnO2/ZSM-5 composites

Fig.2(a) give the SEM images of ZSM-5 zeolite. It can be seen from the Fig.2(b)) that the SnO_2/ZSM-5 fibers inhibits the agglomeration of zeolites obviously.

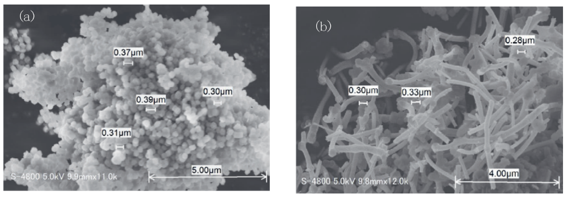

Fig. 2. SEM images of (a) ZSM-5 (b) SZ3

3.2 Gas sensing properties

Operating temperature is an important parameter for semiconductor gas sensor. Fig.3 (a) illustrates the responses of the SnO_2 gas sensor and four kinds of SnO_2/ZSM-5 gas sensors to 10 ppm formaldehyde vs. operating temperature ranged from 200°C to 450°C.We can see from Fig.5 (a), the optimum operating temperature of each SnO_2/ZSM-5 composites and SnO_2 nanofiber for formaldehyde are both 250°C. The responses of SnO_2/ZSM-5 composites sensors to 10 ppm different VOCs gases are plotted together and compared to the SnO_2 sensors' in the bar diagram presented in Fig.3(b).The target gases include formaldehyde, acetone, ethanol, and methanol. The measurement results show that the SnO_2/ZSM-5 composite sensors have great influence on the responses of formaldehyde and acetone. Compared with SnO_2 sensor, the SnO_2/ZSM-5 composite sensors significantly improved the response values to formaldehyde and suppressed the response value to acetone, methanol and ethanol.

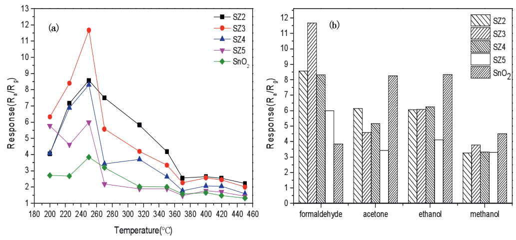

Fig.3 (a) Relationships between sensors response and operating temperature to formaldehyde;(b) Responses of SnO_2/ZSM-5 sensors and SnO_2 sensors to different gases in 40% RH.

The ZSM-5 zeolite plays an important role in improving the gas sensing properties of the SnO_2/ZSM-5 composites to formaldehyde. Three influences were brought by the ZSM-5 added.

Firstly, the polar gas molecules are more easily adsorbed in the polar centers of zeolites by using the adsorption characteristics of zeolites, which makes the gas molecules more easily contact with SnO_2.

Secondly, using the molecular sieve characteristics of zeolites, the larger gas molecules are not easily diffused from the channel of zeolite, the ZSM-5 zeolite channel is about 5.3×5.6Å, 5.1×5.5Å, and the molecular dynamic diameters of formaldehyde, acetone, methanol, and ethanol are 2.43Å, 4.60Å, 3.63Å, and 4.53Å, respectively.

Finally, the catalytic properties of ZSM-5 zeolites also play an important role in improving the gas sensing properties of SnO_2/ZSM-5 composites. The byproducts of the catalytic decomposition of these organic gas vapors on the surface of the ZSM-5 according to the following reactions:

$$HCHO + O_{2(zeolite)} \rightarrow H_2O + CO_2 \quad (1)$$

$$CH_3COCH_3 + 4O_{2(zeolite)} \rightarrow 3H_2O + 3CO_2 \quad (2)$$

$$CH_3CH_2OH + 3O_{2(zeolite)} \rightarrow 3H_2O + 2CO_2 \quad (3)$$

$$2CH_3OH + 3O_{2(zeolite)} \rightarrow 4H_2O + 2CO_2 \quad (4)$$

According to reactions (1-4), these four gas vapors would produce the water vapors on the surface of the ZSM-5 at elevated temperatures. These extra water vapors would in turn increase the relative humidity near the surface regions of the sensing composites and subsequently do a harm to the sensor response.

The response recovery curves of the SnO_2/ZSM-5 composites and SnO_2 sensors were measured at 40% RH ,250 °C operating temperature.The concentration of formaldehyde was from 2 ppm-100 ppm. It can be seen from the Fig.4 that SZ3 is the most sensitive materials of the four kinds of SnO_2/ZSM-5 composites. The response value of SZ3 to 2ppm formaldehyde is 3.87, When the formaldehyde concentration is 100ppm, the response value is reach to 63.47.

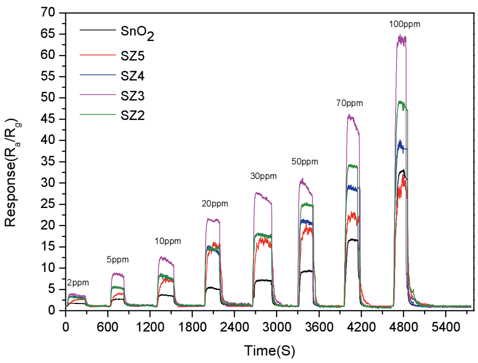

Fig.4 Transient response curves of the SnO_2/ZSM-5 composites and SnO_2 sensors to formaldehyde

Fig.5 (a) shows the repeatability of the SZ3 sensor to 10 ppm formaldehyde, Fig.5 (b) shows the stability of SZ3 sensor in 10 ppm formaldehyde concentrations for 45 days. It can be observed that the sensor response is highly repeatable and stable during the testing cycles indicating a significantly potential to be developed for a formaldehyde sensor.

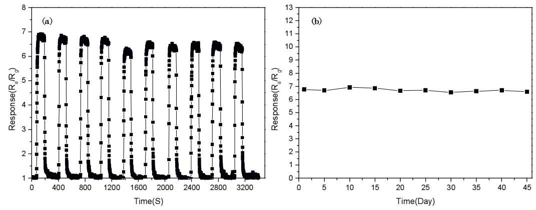

Fig.5 (a) Response and recovery behaviors of 10 cycles to 10 ppm formaldehyde at 47% RH for SZ3 sensor; (b) Stability of SZ3 sensor at 10 ppm formaldehyde concentrations for 45 days at 50% RH.

4 Conclusion

Four kinds of SnO_2/ZSM-5 composites were synthesised by electrospinning method, these composites sensors show a good sensitivey and selectivity to formaldehyde at 250°C. The increased response to formaldehyde could be due to the adsorptions of the polar gases such as formaldehyde by ZSM-5.This would enhance the formaldehyde adsorptions at the interface of SnO_2 nanoparticle/ZSM-5 thus leading to more formaldehyde participating in the redox reactions with the ionized oxygen on the surface of SnO_2.The suppression in the sensors response to ethanol, methanol and acetone due to the incorporation of ZSM-5.Under the catalytic property of ZSM-5, higher amount of water molecule were generated by the redox reactions of these vapors with the ionized oxygen on the surface of the SnO_2. The molecular sieve characteristics of the ZSM-5 also increase the diffusion resistance of the gas molecules with larger diameter such as acetone , which suppresses the response value.

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