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 SnO$_2$/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.
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

<table>
<thead>
<tr>
<th>Fiber</th>
<th>SnCl$_2$·2H$_2$O (mg)</th>
<th>ZSM-5 (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ2</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>SZ3</td>
<td>375</td>
<td>125</td>
</tr>
<tr>
<td>SZ4</td>
<td>480</td>
<td>120</td>
</tr>
<tr>
<td>SZ5</td>
<td>500</td>
<td>100</td>
</tr>
</tbody>
</table>

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

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:

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

$$\text{CH}_3\text{COCH}_3 + 4O_{\text{zeolite}} \rightarrow 3H_2O + 3CO_2 \quad (2)$$

$$\text{CH}_3\text{CH}_2\text{OH} + 3O_{\text{zeolite}} \rightarrow 3H_2O + 2CO_2 \quad (3)$$

$$2\text{CH}_3\text{OH} + 3O_{\text{zeolite}} \rightarrow 4H_2O + 2CO_2 \quad (4)$$

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 material 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.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.

4 Conclusion

Four kinds of SnO$_2$/ZSM-5 composites were synthesized by electrospinning method, these composites sensors show a good sensitivity 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 surface of SnO$_2$/ZSM-5 composites. The suppressions on 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 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 SnO$_2$. The molecular siev characteristics of the ZSM-5 also increase the diffusion resistance of the gas molecules with larger diameter such as acetone, which suppress the response value.

References


