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A Novel Alcohol Detector Based on ZrO_2-Doped SnO_2 Electrospun Nanofibers

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To overcome the interference of acetone when detecting alcohol, a novel alcohol detector based on zirconia-doped SnO_2 nanofibers were fabricated through electrospinning technique and calcination process. The samples have been characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and their gas sensing properties have also been investigated. When exposed to alcohol vapor, the nanofibers containing 15 mol% zirconia exhibit the best sensing properties. Moreover, the sensor holds the successful discrimination between acetone and alcohol, which makes our product a good candidate in fabricating highly selective sensors in practice.

I. Introduction

Chemical sensors for alcohol (C_2H_5OH) have attracted much attention due to increasing concern about environmental protection, industrial, and traffic safety.[1] While in the last 10 years, a great deal of efforts have been dedicated to developing efficient alcohol detectors. Metal-oxide semiconductors-based[2] and polymer-based[3] detectors are both in particular interest. Recently, SnO_2 as an II–VI compound semiconductor has been proven to be an excellent gas sensitive material for detection of both reducing and oxidizing gases.[4,5] Extensive studies on the SnO_2 sensors have been done to improve the sensor performances, such as adding catalysts, doping metals and metal oxides, decreasing grain size, controlling pore, and surface defects, etc.

Taking the advantages of small size, high density of surface sites and increased surface-to-volume ratios, many types of gas sensors based on SnO_2 nanostructures have been fabricated. In particular, one-dimensional (1D) nanostructure has been strongly proposed to be an effective platform for preparation of gas sensing materials because they can make it easy and fast to translate the gas recognition into an electrical signal and then transport electron effectively. Our group has fabricated several kinds of one component 1D metal oxide nanomaterials as alcohol sensors via electrospinning technique,[6,7] however, their sensitivities are relatively low. To enhance the sensitivity, adding certain amount of another kind of metal oxide component into electrospun metal oxide nanofibers is a meaningful object.[8] In addition to the sensitivity, selectivity is also an important factor in fabrication of gas sensors for practical applications. For detection alcohol, acetone (CH_3COCH_3) is usually an interfering gas for their similar chemical nature.

In this paper, we have focused on the fabrication of two components of metal oxide-based alcohol sensors. It was found that certain amount of zirconia-doped SnO_2 nanofibers by electrospinning technique and calcination process showed enhanced sensitivity for detection alcohol. Furthermore, we will specially focus on the selectivity properties of our sensors for the discrimination from acetone in this paper.

II. Experimental Procedure

All chemicals used in the experiment were analytical grade or better and used without further purification. In a typical procedure, 0.4 g $SnCl_2 \cdot 2H_2O$ was mixed with the 1:1 weight ratio of DMF and alcohol in a glove box under vigorous stirring for 10 min. Subsequently, 0.8 g PVP and a suitable amount of $ZrOCl_2 \cdot 8H_2O$ were added into the above solution under vigorous stirring for 30 min. Then the mixture was loaded into a glass syringe and connected to a high-voltage power supply. 10 kV was provided between the cathode (a flat foil) and anode (syringe) at a distance of 20 cm. Finally, the SnO_2 nanofibers doped with different amount of zirconia (5, 15, and 20 mol%) were obtained by calcination the as-spun nanofibers.

Fibers were characterized by means of scanning electron microscope (SEM, SSX-550, Shimadzu, Kyoto, Japan) transmission electron micrographs (TEM, Hitachi S-570, Tokyo, Japan), X-ray diffraction (XRD, Scintag XDS 2000 diffractometer with a Cu$K\alpha$ radiation, Scintag, CA). Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCALAB MKII (VG Scientific Ltd., East Grinstead, U.K.) using Al as the exciting source.

The as-prepared zirconia-doped SnO_2 nanofibers were mixed with deionized water in a weight ratio of 100:40 to form a paste. The paste was coated onto a ceramic tube on which a pair of gold electrodes was previously printed, and then a Ni–Cr heating wire was inserted in the tube to form a side-heated gas sensor. The electrical properties of the sensor were measured by CGS-1 intelligent test system (Beijing Elite Tech Co. Ltd., Beijing, China). The sensor response was measured between 150° and 400°C by comparing the resistance of the sensor in dry synthetic air (R_a) with that in target gases (R_g). The gas response is defined as the ratio of the sensor resistance in air and that in the test gas $R = R_a/R_g$. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of adsorption or the recovery time in the case of desorption.

III. Results and Discussion

Figure 1 shows the typical SEM images of the sintered products containing 5 mol% (Fig. 1(a)), 15 mol% (Fig. 1(b)), and 20

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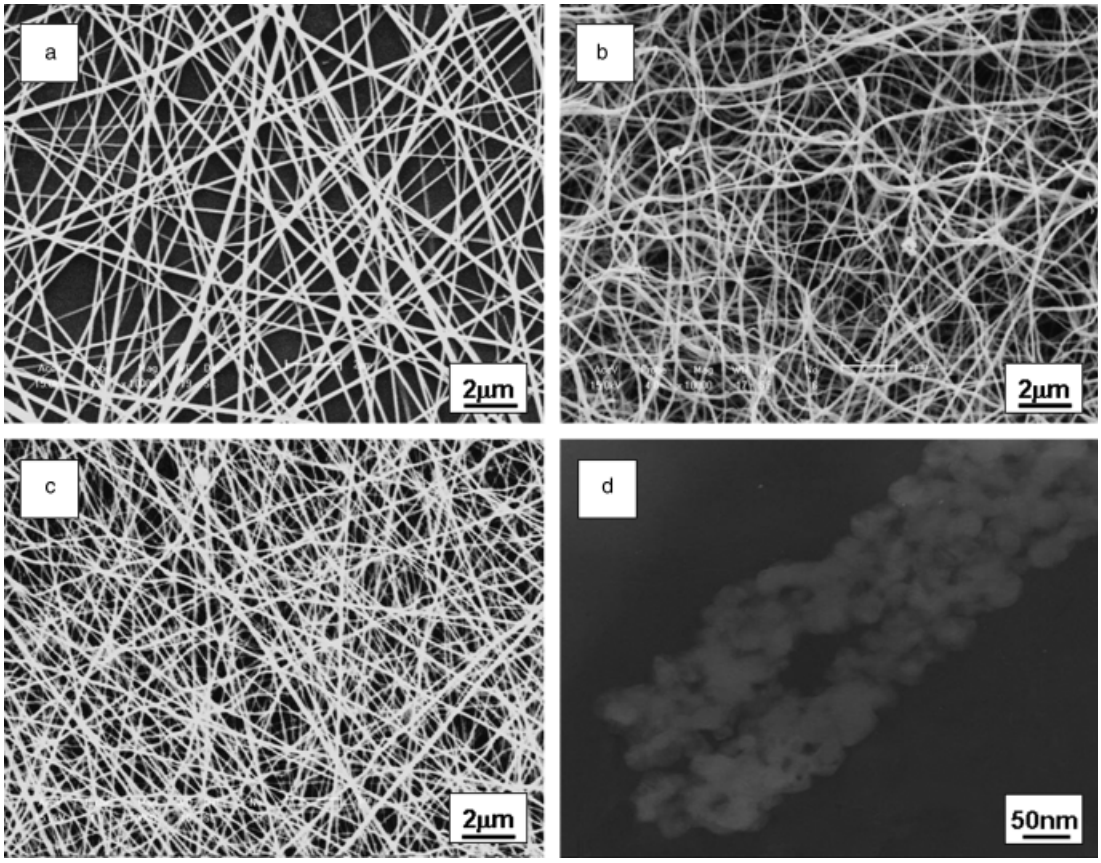

Fig. 1. (a), (b), (c) Scanning electron microscopy images of zirconia-doped SnO_2 nanofibers. The contents of zirconia are (a) 5 mol%, (b) 15 mol%, and (c) 20 mol%. (d) Transmission electron microscopy image of the 15 mol% zirconia-doped SnO_2 nanofibers.

mol% (Fig. 1(c)) of Zr. It indicats that a large good quantity of nanofibers with the diameter ranging from 100 to 150 nm can been obtained after pyrolysis. Figure 1(d) is the corresponding TEM images to 15 mol%, which illustrates that the as-prepared products are composed of nanocrystals and rough on surface.

Figure 2 gives the XRD patterns of zirconia-doped SnO_2 nanofibers. SnO_2 exhibits the tetragonal rutile structure in samples (JCPDS 41-1445) and the other weaker diffraction peaks are assigned to the tetragonal phase of ZrO_2 (JCPDS 17-0923).

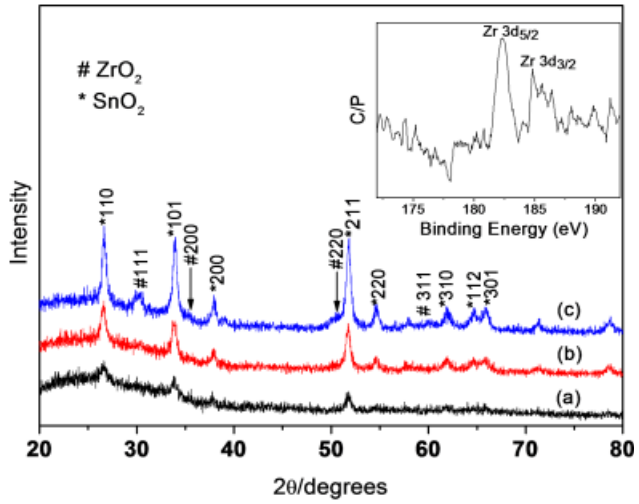

Fig. 2. X-ray diffraction of zirconia-doped SnO_2 nanofibers: (a) 5 mol%, (b) 15 mol%, and (c) 20 mol%. The inset is the X-ray photoelectron spectroscopy of Zr in the samples.

No characteristic peaks for impurity, such as SnO, ZrO, or other zirconium compounds, are observed. The XPS spectra of Zr in the samples is illustrated in Fig. 2 (inset). The Zr3d core level XPS spectrum also has two peaks of Zr3d3/2 and Zr3d5/2, which are centered at 184.8 and 182.3 eV with a spin–orbit separation of 2.5 eV and coincide with published values for Zr^{4+}.[9] All of these results give the insight that the nanofibers are composed of ZrO_2 and SnO_2.

The effect of the doping zirconia on the selectivity of SnO_2 nanofiber is studied by exposing the sensors to 50 ppm alcohol and 50 ppm acetone at 280°C, respectively. The results are shown in Fig. 3(a). When exposed to alcohol, the sensor exhibits enhanced response with zirconia content rising, and a maximum is obtained for the sample containing 15 mol% zirconia. While for acetone, there are few changes of response with zirconia content varying. Thus 15 mol% zirconia-doped SnO_2 nanofibers are chosen as the optimal sample for detection alcohol vapor in the present work.

Temperature has been found to be an important parameter for sensor response. Figure 3(b) depicts the response curves of the sensor based on zirconia-doped SnO_2 nanofibers to 50 ppm alcohol and 50 ppm acetone versus temperature. The response of the sensor to alcohol increase and reach maximum at 300°C, and then decreased rapidly with the temperature rising. Its response toward acetone also shows the similar trend. However, it can be seen that the response of the sensor based on 15% zirconia-doped SnO_2 nanofibers to alcohol reaches 13.3 and only 2.9 to acetone at 280°C. This means that the 15 mol% doped sample displays efficient selectivity in discrimination of alcohol and acetone at 280°C, which is based on the shift of the optimized operate temperature of the sensor to acetone and alcohol.

SnO_2 is a nonstoichiometric oxide having oxygen vacancies and electron donor states and its sensing mechanism to gases

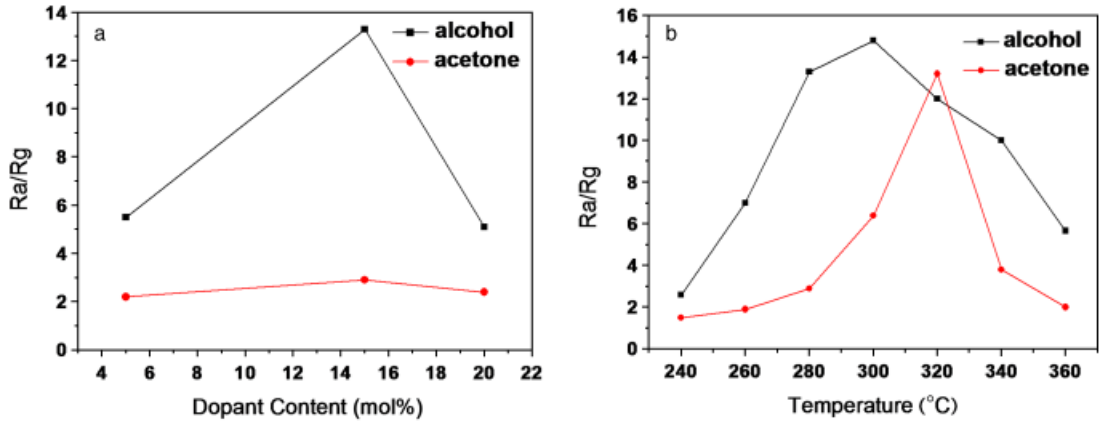

Fig. 3. (a) Responses for SnO_2 nanofibers with different contents of zirconia to 50 ppm alcohol and 50 ppm acetone at 280°C. (b) Responses variation of 15 mol% zirconia-doped SnO_2 nanofibers to 50 ppm alcohol and 50 ppm acetone versus temperature.

was clarified in previous works.[10] The most widely accepted model is based on the modulation of the depletion layer by oxygen absorption. Oxygen adsorbs on the exposed surface of the SnO_2 conduction band and ionizes to O^- or O^{2-}, forming depletion layers on the surface area of SnO_2. When the sensor is exposed to a reducing gas such as alcohol, the reducing gas reacts with the adsorbed oxygen and releases the trapped electrons back to the conduction band. There are resistance changes during the above process. Here by doping zirconia, the growth of SnO_2 nanograin is inhibited, which could lead to the increase of adsorption and sensitivity.[11] Moreover, it acts as a catalyst to the oxidation of alcohol to aldehyde, which is the intermediate of alcohol detection. So the dopant can lower markedly the activation energy of the reaction and accelerate the reaction, which facilitates the discrimination of alcohol and acetone.

In order to further understand the response of 15 mol% zirconia-doped SnO_2 nanofibers to alcohol, the response curves of the sensors versus alcohol concentration at 280°C are shown in Fig. 4(a). The response increases rapidly with increasing the concentration of alcohol (<1500 ppm). Above 1500 ppm, the increase of response turns slow with the alcohol concentration rising. Finally the sensor reaches saturation at about 6000 ppm. Moreover, the inset in Fig. 4(a) shows the linear calibration curve in the range of 1–200 ppm, which confirms that the sensor is very suitable for low concentration alcohol gas detection.

The as-prepared sensors exhibit quick response-recovery to 10 ppm alcohol at 280°C as shown in Fig. 4(b). The electrical signal from the sensors becomes stable within 5 s after being exposed to alcohol, and returns to the original values within 8 s after the tested vapor is replaced with air. The rapid response and recovery of the detector can be attributed to the 1D nanostructure of our electrospun nanofibers, which can facilitate fast mass transfer of alcohol molecules to and from the interaction region as well as improve the rate for charge carriers to traverse the barriers induced by molecular recognition along the fibers.[12] In addition, the dopant can produce more active centers to supports the catalytic conversion of alcohol into its oxidation products. This may be due to spill-over of activated fragments to the semiconductor surface to react with the adsorbed oxygen and is called chemical sensitization.[13]

IV. Conclusions

The zirconia-doped SnO_2 nanofibers have been synthesized via electrospinning technique and calcination process. The diameters of these nanofibers range from 100 to 150 nm. When the molar ratio of Zr/Sn is 15%, the as-prepared sensor shows efficient selective behavior to alcohol and other excellent sensing properties such as high sensitivity, quick response, and linear dependence of the sensitivity on the alcohol concentration (1–200 ppm). Then the good selectivity coupled with high response value make our product particularly candidate for fabricating alcohol sensors.

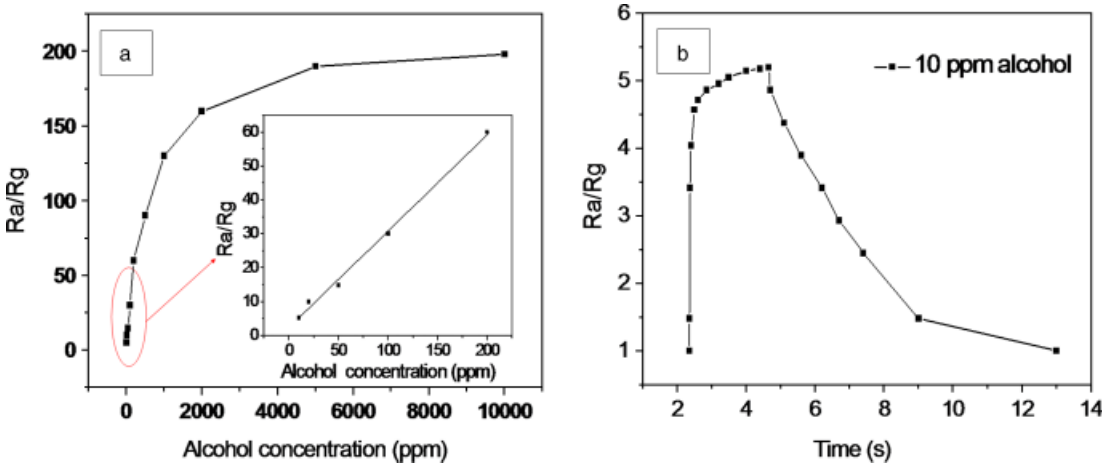

Fig. 4. (a) Response variation of 15 mol% zirconia-doped SnO_2 nanofibers versus alcohol concentration at 280°C. The inset shows response to alcohol in low concentration. (b) Response–recovery curves in a 10 ppm alcohol at 280°C.

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