Highly Responsive and Selective Ethanol Gas Sensor Based on Co₃O₄-Modified SnO₂ Nanofibers

Dong-dong Chen, Zhou Li, Xin Jin, Jian-xin Yi*

State Key Laboratory of Fire Science, Department of Safety Science and Engineering, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on April 24, 2017; Accepted on May 22, 2017)

SnO₂ nanofibers were synthesized by electrospinning and modified with Co₃O₄ via impregnation in this work. Chemical composition and morphology of the nanofibers were systematically characterized, and their gas sensing properties were investigated. Results showed that Co₃O₄ modification significantly enhanced the sensing performance of SnO₂ nanofibers to ethanol gas. For a sample with 1.2 mol% Co₃O₄, the response to 100 ppm ethanol was 38.0 at 300 °C, about 6.7 times larger than that of SnO₂ nanofibers. In addition, the response/recovery time was also greatly reduced. A power-law dependence of the sensor response on the ethanol concentration as well as excellent ethanol selectivity was observed for the Co₃O₄/SnO₂ sensor. The enhanced ethanol sensing performance may be attributed to the formation of p-n heterojunctions between the two oxides.

Key words: SnO₂ nanofibers, Heterojunction, Electrospinning, Impregnation, Gas sensors

I. INTRODUCTION

Resistance-type gas sensors based on semiconductor metal oxides such as SnO₂, ZnO, and TiO₂ have been widely investigated due to their high sensitivity, fast response, and low cost. Among them, SnO₂ is widely regarded as one of the most promising sensing materials for detection of various gases. However, SnO₂-based gas sensors are still limited by their poor selectivity and relatively long response/recovery time for practical applications.

In order to obtain better selectivity and faster response/recovery speed, much effort has been made on the design of material microstructure and surface modification. Various shapes of SnO₂ materials on the nanoscale, including flowers [1], spheres [2], rods [3], and fibers [4] have been fabricated. In particular, SnO₂ nanofibers are of great interest because of their large surface-to-volume ratio. Furthermore, their gas-sensing property can also be effectively enhanced by forming heterojunctions with other semiconductor metal oxides, such as Co₃O₄ [5, 6], NiO [7, 8], CuO [9], and In₂O₃ [10]. Among these oxides, Co₃O₄ has attracted much attention due to its excellent catalytic performance and synergetic effect with SnO₂. Jeong et al. synthesized Co₃O₄-coated SnO₂ hollow nanospheres via galvanic replacement, and obtained highly improved selectivity to xylene and methylbenzenes [5]. Wang et al. modified SnO₂ nanospheres with Co₃O₄ via a hydrothermal method, and significantly enhanced the response to ammonia gas [11]. However, these synthesis methods are difficult for wide-spread use because of the complexity. In contrast, impregnation has been widely adopted as a facile and low cost route for preparation of nano-sized catalysts, which may also be used for synthesis of heterojunction sensing materials.

In this work, SnO₂ nanofibers were prepared by electrospinning, and modified with Co₃O₄ by impregnation. The results showed that gas sensors based on Co₃O₄/SnO₂ nanofibers were highly responsive and selective to ethanol gas. Furthermore, significant reduction in both the response and recovery time was also observed relative to that for the SnO₂ nanofibers. The gas-sensing performance was discussed in relation to the p-n heterojunction.

II. EXPERIMENTS

All reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. Pristine SnO₂ nanofibers were prepared via electrospinning. Typically, 0.4 g SnCl₂·2H₂O, 5.6 mL anhydrous ethanol, and 4.7 mL N,N-dimethylformamide (DMF) were mixed and stirred for 30 min under 1000 r/min. 0.8 g polyvinyl pyrrolidone (PVP, M₉₆=1.3×10⁶) was then added under stirring. The obtained transparent solution was transferred to a plastic syringe. A voltage of 15 kV was applied for electrospinning and the feeding rate was kept constant at 0.4 mL/h using a syringe pump. The as-spun fibers were dried at 80 °C, and then calcined at 600 °C for 3 h to obtain SnO₂ nanofibers.

*Author to whom correspondence should be addressed. E-mail: yjx@ustc.edu.cn, Tel: +86-551-63607817

DOI:10.1063/1674-0068/30/cjcp1704080 474 ©2017 Chinese Physical Society
Appropriate amounts of SnO$_2$ nanofibers were soaked in 0.1 mol/L cobalt nitrate solution followed by filtering. The filtered powders were dried at 80°C for 2 h, and then heated at 600°C for 3 h to obtain Co$_3$O$_4$/SnO$_2$ nanofibers. These procedures were repeated to obtain another sample with different Co$_3$O$_4$ amounts. SnO$_2$ nanofibers subjected to this impregnation treatment for 0, 1, and 2 times are denoted as SCo-0, SCo-1, and SCo-2, respectively.

Crystal structure was examined by powder X-ray diffraction (XRD, TTR III) with Cu Kα1 radiation. Morphology and microstructure of the nanofibers were studied by scanning electron microscope (JSM-6700F) and transmission electron microscopy (JEM-2011) equipped with an energy-dispersive X-ray spectrometer (EDX). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 spectrometer using Al Kα as the exciting source.

To prepare the sensor, nanofibers were dispersed in ethanol under ultrasonic vibration for 10 min. The obtained paste was coated on an alumina tube and then heat-treated at 400°C for 2 h. The alumina tube has been equipped with a pair of Au electrodes, which was each connected with two platinum wires. A Ni-Cr alloy coil was inserted into the alumina tube as a heater.

The sensing properties of the nanofibers were examined with a WS-30A (Weisheng Electronics Co. Ltd., China) system and an electrometer (Agilent 34461A). The testing method was similar to that described in our previous work [7]. Measurements were conducted in an 18 L chamber in a static atmosphere. Appropriate amounts of certified analyte gas (Nanjing Specialty Gas Co., Ltd.) were injected with a syringe, which led to changes in the electrical resistance of the sensor. For ethanol and acetone, vapors were obtained by vaporizing their liquid samples with an evaporator inside the chamber. The sensor response was defined as $S=R_{\text{air}}/R_{\text{gas}}$ ($R_{\text{air}}$: resistance in air atmosphere, $R_{\text{gas}}$: resistance during exposure to the target gas). The time taken by the sensor to reach 90% of the total resistance change was defined as the response time in the case of response or the recovery time in the case of recovery.

### III. RESULTS AND DISCUSSION

FIG. 1 shows the XRD patterns of the as-prepared samples. For pristine SnO$_2$, a single-phase tetragonal rutile structure (JCPDS No.41-1445) was obtained. For Co$_3$O$_4$/SnO$_2$ composites, all peaks could be indexed to SnO$_2$, and neither presence of Co$_3$O$_4$ nor shift of the diffraction peaks was observed. Under the present synthesis conditions, Co$_3$O$_4$ would be formed by thermal decomposition of Co(NO$_3$)$_2$·6H$_2$O [12]. The absence of Co$_3$O$_4$ diffraction peaks is explained as follows. As the concentration of cobalt nitrate solution used was relatively low and the impregnation time was as short as 2 min, only a small amount of Co$_3$O$_4$ with small particle size would be formed, which is consistent with the SEM-EDX results discussed below. Similar phenomena have also been observed in other composite materials prepared by impregnation methods [4, 13, 14]. On the other hand, FIG. 1 also shows that the diffraction peaks became broadened for the Co$_3$O$_4$/SnO$_2$ composites, suggesting larger crystalline size. According to the Debye-Scherrer equation, the crystallite size was estimated to be 9.3 nm for SCo-0, which increased to 33.6 and 48.0 nm for SCo-1 and SCo-2, respectively. The grain growth can be attributed to the repeated calcinations at 600°C after the impregnation.

XPS was used to analyze the composition and chemical state of the samples, wherein the binding energy for the C 1s peak at 284.8 eV was used as a reference for energy calibration (FIG. 2). Sn and O peaks were observed for all the samples, and Co peaks were found for the impregnated samples. The Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ peaks appeared at 495.0 and 488.6 eV, respectively, which agreed well with other reports for SnO$_2$ [15]. Co 2p$_{3/2}$ and Co 2p$_{1/2}$ doublets for SCo-1 and SCo-2 were observed at 796.5 and 781.0 eV, respectively, which was consistent with those of Co$_3$O$_4$ [16]. The Co/(Sn+Co) ratio was determined to be 6.9 at% for SCo-1 and 9.9 at% for SCo-2 (Table I), indicating an increase of Co loading amount with the increase of impregnation times. For the O 1s spectra, each peak was asymmetric and could be deconvoluted into two peaks at ~531.4 and ~530.3 eV, corresponding to the adsorbed oxygen (O$_{\text{ads}}$) and lattice oxygen (O$_{\text{latt}}$), respectively. As can be seen from Table I, the peak area ratio for adsorbed oxygen to total O is decreased monotonically with increasing impregnation time, indicating that oxygen adsorption was depressed by the presence of Co$_3$O$_4$.

SEM images in FIG. 3 shows that the length and the diameter of SnO$_2$ nanofibers were ~1 μm and 100–200 nm, respectively. Similar morphology was observed for the SCo-1 and SCo-2 nanofibers. TEM analysis further indicated that the particle size was around 10–50 nm (FIG. 4). Some small pores were present in the nanofibers, which would be favorable for achiev-
FIG. 2 (a) Survey XPS spectrum and high resolution spectra for (b) Sn 3d, (c) Co 2p, and (d) O 1s of pristine and Co$_3$O$_4$ modified SnO$_2$ nanofibers.

TABLE I Compositions determined from XPS for pristine and Co$_3$O$_4$ modified SnO$_2$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$O_{ads}/%$</th>
<th>$O_{lat}/%$</th>
<th>M/$%$</th>
<th>Sn/$%$</th>
<th>Co/$%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCo-0</td>
<td>29.1</td>
<td>70.9</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCo-1</td>
<td>24.9</td>
<td>75.1</td>
<td>93.1</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>SCo-2</td>
<td>24.1</td>
<td>75.9</td>
<td>90.1</td>
<td>9.9</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 3 SEM photographs of the as-prepared samples of (a) SCo-0, (b) SCo-1, (c) SCo-2.

ing high gas accessibility of the materials. EDX analysis revealed a Co/(Sn+Co) ratio of 3.7 at% for SCo-2 nanofibers, corresponding to $\sim$1.2 mol% Co$_3$O$_4$. The Co content is much lower than that measured by XPS, which is also consistent with the fact that Co$_3$O$_4$ was formed on the surface of SnO$_2$. Direct observation of Co$_3$O$_4$ particles was not successful, owing to the low content of Co$_3$O$_4$ as well as its small particle size prepared by impregnation.

FIG. 5(a) presents the response of the as-prepared samples to 100 ppm ethanol at different temperatures. For all the samples, the response first increased with temperature, reached a maximum at 300 °C, and then decreased. The response increased significantly with the Co$_3$O$_4$ loading. A response of 38.0 was obtained at 300 °C for SCo-2, 6.7 times higher than that of SCo-0. Table II shows that the ethanol response of SCo-2 nanofibers is higher than that of some other SnO$_2$-based sensors [17–19]. As shown in FIG. 5(b), the gas response of the sensors varied linearly with the ethanol concentration on a log-log scale, indicating a power-law type relationship. The distinctly larger slope observed for the SCo-2 sensor suggests a more pronounced enhancement of the response at higher ethanol concentra-
Based on Co$_3$O$_4$-modified SnO$_2$ Nanoﬁbers

Assuming a value of 1.2 as the lowest response [20], the detection limit was estimated by extrapolating the regressed linear line in FIG. 5(b) to be 2.3 and 1.5 ppm for SCo-0 and SCo-2, respectively. Further investigation of gas-sensing performance was focused on SCo-2 due to its higher response and lower detection limit.

FIG. 6 presents the continuous response curves of SCo-0 and SCo-2 nanoﬁbers to 100 ppm ethanol gas at 300 °C. It can be seen that the dynamic response-recovery features for both samples were well repeated, and the sensor response could restore to the initial baseline after each cycle. The response and recovery time for SCo-2 were found to be 5 and 23 s, respectively, which were remarkably reduced compared with the respective values (10 and 62 s) for SCo-0.

The cross sensitivity of SCo-2 nanoﬁbers was examined in the temperature range of 200–400 °C (FIG. 7). The sensor exhibited negligible response to methane, propane, and carbon monoxide, and minor response to hydrogen at temperatures above 300 °C. The response to ethanol was over 28 times higher than that to the interferent gases, which clearly demonstrated excellent ethanol selectivity for SCo-2.

It is widely accepted that the gas sensing mechanism of metal oxide semiconductor is based on the adsorption and desorption of gases on the surface of materials [21]. In air atmosphere, oxygen molecules are adsorbed on the material surface, and form O$_2^-$, O$^-$ and O$^{2-}$ ions by capturing electrons from the material. Then an electron depletion layer and a potential barrier are formed on the surface, leading to increase of resistance. When ethanol is present in the atmosphere, adsorbed oxygen species will react with ethanol and the captured

FIG. 4 TEM pictures of the as-prepared samples of (a) SCo-0, (b) SCo-1, (c) SCo-2.

FIG. 5 (a) Response of as-prepared samples to 100 ppm ethanol gas at different temperatures. (b) Log-log plot for the dependence of response on the ethanol concentration.

TABLE II The 100 ppm ethanol gas sensing properties of SnO$_2$-based ethanol sensors.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Morphology</th>
<th>$T/°C$</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$ [17]</td>
<td>Mesoporous</td>
<td>280</td>
<td>4.6</td>
</tr>
<tr>
<td>SnO$_2$ [18]</td>
<td>Nanoﬁbers</td>
<td>260</td>
<td>11.0</td>
</tr>
<tr>
<td>Co$_3$O$_4$/SnO$_2$ [19]</td>
<td>Nanospheres</td>
<td>240</td>
<td>6.5</td>
</tr>
<tr>
<td>Co$_3$O$_4$/SnO$_2$ (this work)</td>
<td>Nanoﬁbers</td>
<td>300</td>
<td>38.0</td>
</tr>
</tbody>
</table>

FIG. 6 Dynamic response curves of SCo-0 and SCo-2 to 100 ppm ethanol at 300 °C.

DOI:10.1063/1674-0068/30/cjcp1704080 ©2017 Chinese Physical Society
FIG. 7 Response of SCo-2 to 100 ppm various gases at different temperatures.

electrons will be released back to the material. As a result, the electron depletion layer becomes thinner and the resistance decreases.

Generally speaking, better surface oxygen adsorption, smaller grain size, and formation of p-n heterojunction are beneficial to achieving higher gas sensing performance [7, 22]. The present work showed that Co$_3$O$_4$/SnO$_2$ nanofibers were associated with depressed surface oxygen adsorption (Table I) and larger grain size, which may deteriorate the gas sensing properties. Therefore, the remarkable enhancement of ethanol response for SnO$_2$ nanofibers by Co$_3$O$_4$ decoration may mainly result from formation of p-n heterojunctions between the two oxides, which changes the surface potential barrier and makes the material more sensitive [20].

IV. CONCLUSION

SnO$_2$ and Co$_3$O$_4$/SnO$_2$ nanofibers were synthesized via electrospinning and impregnation. When compared with pristine SnO$_2$ nanofibers, Co$_3$O$_4$/SnO$_2$ exhibited greatly enhanced response to ethanol and significantly reduced response/recovery time. A response of 38.0 to 100 ppm ethanol gas and a response/recovery time of 5 and 23 s was observed for SCo-2 at 300 °C. Furthermore, excellent ethanol selectivity against interference of methane, propane, hydrogen, and carbon monoxide was also observed for SCo-2. The improved ethanol sensing performance may be ascribed to formation of p-n heterojunctions between SnO$_2$ and Co$_3$O$_4$.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.U1432108) and the Fundamental Research Funds for the Central Universities (No.WK2320000034).