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Influence of Fabricating Process on Gas Sensing Properties of ZnO Nanofiber-Based Sensors *

XU Lei(徐磊), WANG Rui(王瑞)**, LIU Yong(刘雍), DONG Liang(董亮)
School of Textiles, Tianjin Polytechnic University, Tianjin 300160

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ZnO nanofibers are synthesized by an electrospinning method and characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Two types of gas sensors are fabricated by loading these nanofibers as the sensing materials and their performances are investigated in detail. Compared with the sensors based on traditional ceramic tubes with Au electrodes (traditional sensors), the sensors fabricated by spinning ZnO nanofibers on ceramic planes with Ag-Pd electrodes (plane sensors) exhibit much higher sensing properties. The sensitivity for the plane sensors is about 30 to 100 ppm ethanol at 300 °C, while the value is only 13 for the traditional sensors. The response and recovery times are about 2 and 3 s for the plane sensors and are 3 and 6 s for the traditional sensors, respectively. Lower minimum-detection-limit is also found for the plane sensors. These improvements are explained by considering the morphological damage in the fabricating process for traditional sensors. The results suggest that the plane sensors are more suitable to sensing investigation for higher veracity.

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Increasing demands for more sensitive gas sensors for practical applications in environmental protection and safety have led to an upsurge of research devoted to the development of novel sensing materials.[1,2] Most traditional sensing films consist of thin films or nanoparticles/nanopowders,[3–7] which naturally have their own characteristics. Sensing thin films need complex depositing process, such as metal organic chemical vapor deposition (MOCVD), dc and rf sputtering and these films often have many challenges for their weak mechanical strength and poor physical and chemical stability.[8] Sensing nanoparticles/nanopowders are easy for synthesis and doping, but usually suffer from low sensitivity and long response/recovery times.[9]

Over the past decade, materials with special structures and morphologies have received considerable attention due to their remarkable performance in gas sensors.[10] Particularly, mesoporous materials exhibit high sensitivity and excellent selectivity because of their ordered pore distributions, high pore volumes and high surface areas.[11] One-dimensional (1D) nanomaterials own much shorter response/recovery times due to their small size, high density of surface sites, increasing surface-to-volume ratios and anti-aggregation characteristics.[12] Many researchers have turned their focus on these novel materials for the new generation sensing materials, which should have high sensitivity, rapid speed, good accuracy, reproducibility, durability, easy processing and low cost. For many experimental groups (especially Chinese groups), their investigations are mainly based on the traditional gas sensors with ceramic tubes.[13–16] These sensors have been used in scientific research and industrial production for at least 40 years, and hundreds of papers are published based on this type of sensors each year.[17] The reason for this condition is that nanosensors are still hard to fabricate with current technology and their repeatability is also low.[17] Accordingly, the traditional sensors have become the best choice in practice. However, the fabrication of traditional sensors can not be combined with material synthesis and some actions such as grinding and coating in the sensor fabrication will unavoidably damage the structure and morphology of sensing materials and thus decrease the sensor performance accordingly. Thus it is foreseen that the detailed comparison of gas sensors with a same sensing material and different fabricating processes can provide some useful information for future investigation in gas sensors.

In this study, we fabricate two types of sensors with different processes by loading ZnO nanofibers as the sensing materials. ZnO is a typical sensing material and ZnO nanofibers have exhibited many excellent sensing properties in sensing investigations.[18] The performance comparison reveals that the plane sensors, which are fabricated by spinning ZnO nanofibers on ceramic substrates directly, have higher sensitivity, shorter response/recovery times, and lower minimum-detection-limit than the traditional sensors (based on ceramic tubes). These differences are explained by the morphological damage in the fabricating process.

Zinc acetate, poly (vinyl alcohol) (PVA, MW=75,000), Tritaon-X100 were supplied by Beijing Chemical Co. (China). All the chemicals were analytical grade and used as received without further purification.

The electrospinning process in the present ex-

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**Email: wangruitjpu@yahoo.cn

periment is similar to those described previously for ZnO nanofiber synthesis.[19] Briefly, 3 g of zinc acetate aqueous solution (16.7 wt%) was dropped slowly into an aqueous solution containing 7.6 g of poly (vinyl alcohol) (PVA, MW=75,000) with 0.01 g of Tritaon-X100 added. After stirring for 12 h, a viscous gel was obtained. Then, the as-obtained gel was loaded into a glass syringe and connected to a high-voltage power supply. An electric field of 18 kV was applied between the cathode (a flat aluminum foil) and anode (syringe) at a distance of 20 cm. Then calcination (600℃ in air for 5 h) was used to remove the organic constituents of PVA and convert the precursor into crystalline ZnO.

X-ray powder diffraction (XRD) data were collected on an X'Pert MPD Philips diffractometer (Cu $K\alpha$ X-radiation at 40 kV and 50 mA). Scanning electron microscopy (SEM) images were recorded on an SHIMADZU SSX-550 (Japan) instrument.

To fabricate traditional sensors, the as-calcined nanofibers were mixed with deionized water (resistivity=18.0 MΩcm^{-1}) in a weight ratio of 100:25 and grounded for about 3 min to form a paste. The paste was coated on ceramic tubes on which gold electrodes were previously printed and then Ni-Cr heaters were inserted in the tubes to form the side-heated gas sensors.[13–16]

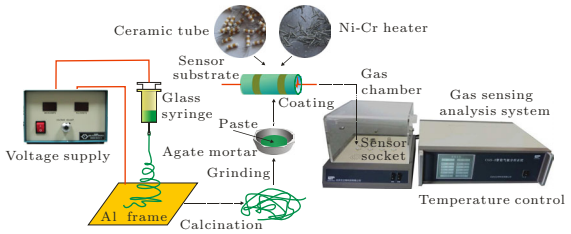

Fig. 1. Schematic illustration of the experimental process for employing ZnO nanofibers to fabricate traditional sensors.

Traditional sensor measurement was performed on a CGS-8 (Chemical gas sensor-8) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China).[20–21] The sensors were pre-heated at different operating temperatures for about 30 min. When the resistances of all the sensors were stable, saturated target gas was injected into the test chamber (20 L in volume) by a micro-injector through a rubber plug. The saturated target gas was mixed with air (relative humidity was about 25%) by two fans in the analysis system. After the sensor resistances reached a new constant value, the test chamber was opened to recover the sensors in air. All the measurements were performed in a laboratory fume hood. The sensor resistance and sensitivity values were acquired by the analysis system automatically. The operating temperature of traditional sensors was measured by a radialization power-based temperature measurement.[22] The experimental process for traditional sensors is illustrated in Fig. 1.

To fabricate plane sensors, the ceramic plane substrates (with a mask) (6 mm × 3 mm, 0.5 mm in thick) with Ag-Pd electrodes were placed on the aluminum foil in the electrospinning process. There were four pairs of Ag-Pd interdigitated electrodes (both the width and distance were 0.15 mm) on the ceramic substrate and the electrodes could be calcined at 800℃ without any resistivity change. After spinning, the mask was removed and the substrates were calcined at 600℃ for 5 h.

Plane sensor measurement was performed on a CGS-1T (Chemical gas sensor-1 temperature) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China). The analysis system offered the external temperature control (from room temperature to about 600℃), which could adjust the sensor temperature directly. The other measuring details were similar as that in traditional sensor measurement. The experimental process for plane sensors is illustrated in Fig. 2.

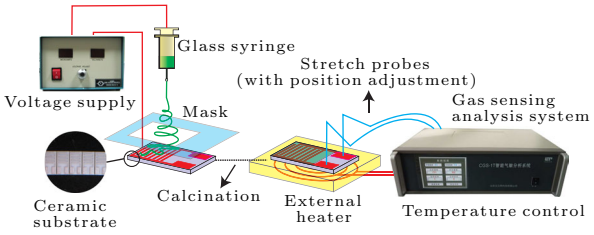

Fig. 2. Schematic illustration of the experimental process for employing ZnO nanofibers to fabricate plane sensors.

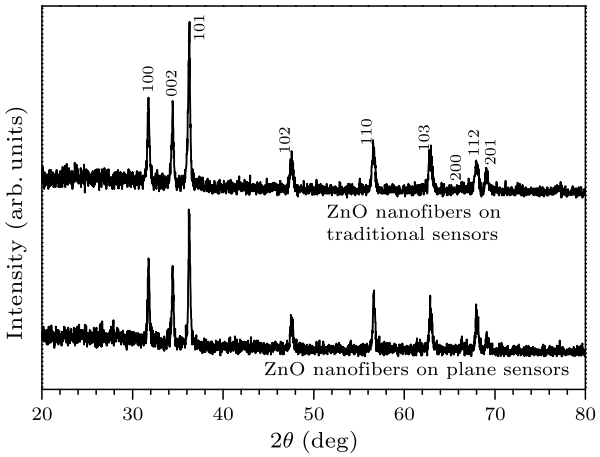

Fig. 3. XRD patters of ZnO nanofibers on traditional sensors and plane sensors.

The sensitivity value was defined as Ra/Rg, where Ra was the sensor resistance in air and Rg was a mixture of target gas and air. 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. The minimum-detection-limit was defined as the gas concentration for the sensitivity down to 3.

Figure 3 shows the XRD patterns of the ZnO nanofibers on traditional sensors and plane sensors, respectively. All the diffraction peaks can be in-

dexed as a Wurtzite structure with lattice constants of $a = 3.24$ Å and $c = 5.19$ Å, which together with the intensity distribution are consistent with those of the standard card for the hexagonal ZnO crystal (Joint Committee for Powder Diffraction Studies (JCPDS) card #36-1451).[23] No obvious difference can be found between the two samples, which is because of the same synthesis process.

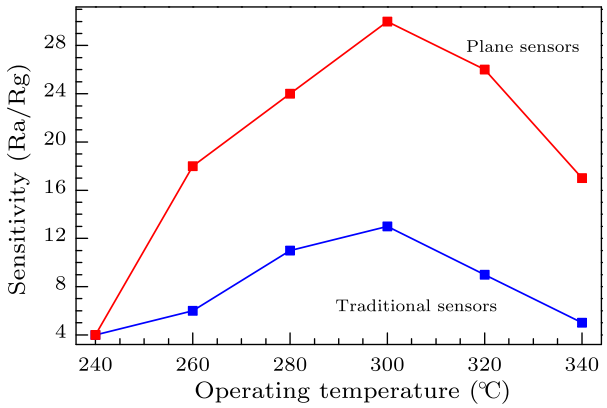

Fig. 4. Sensitivities of traditional sensors and plane sensors to 100 ppm ethanol at different temperatures.

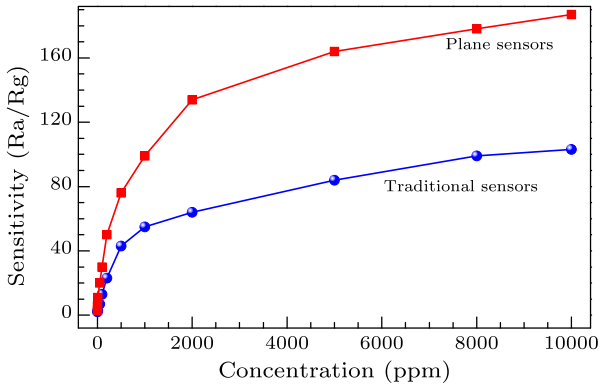

Fig. 5. Sensitivities of traditional sensors and plane sensors to different concentrations of ethanol at 300℃.

Gas sensing experiments were performed at different temperatures to find out the optimum operating condition for ethanol detection. The sensitivities of traditional sensors and plane sensors to 100 ppm ethanol at different temperatures are shown in Fig. 4. The sensitivities for each sample are found to increase with increasing the operating temperature, which attain their maximum at 300℃ and then decrease with a further rise of the operating temperature. This behavior can be explained from the kinetics and mechanics of gas adsorption and desorption on the surface of ZnO or similar semiconducting metal oxides.[24] When the operating temperature is too low, the active of nanofibers is consequently small, leading to a very small sensitivity. When the operating temperature increased too much, some observed ethanol molecules may escape before their reaction due to their high active, thus the sensitivity will decrease correspondingly. Both the optimal operating temperatures (corresponding to the maximum sensitivity values) of traditional sensors and plane sensors are 300℃, which is due to the same nanofibers loaded in the sensors.

Figure 5 shows the sensitivities of traditional sensors and plane sensors to different concentrations of ethanol at 300℃. The plane sensors exhibit much higher sensitivities than that of traditional sensors to the same ethanol concentration in all the measurements. The sensitivities are only about 1.2, 3, 13 and 55 to 3, 10, 100 and 1000 ppm ethanol for the traditional sensors, while are about 3, 11, 30 and 99 for the plane sensors, respectively. The minimum-detection-limit is about 10 ppm for the traditional sensors and 3 ppm for the plane sensors.

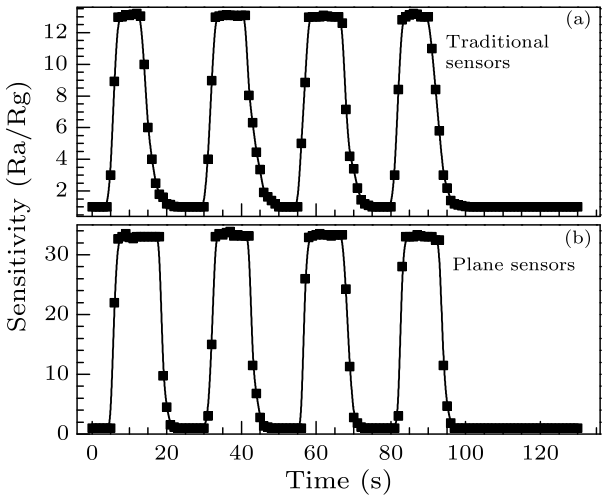

Fig. 6. Response and recovery characteristics of traditional sensors and plane sensors to 100 ppm ethanol at 300℃.

Figure 6 shows the response and recovery characteristics of these two types of sensors to 100 ppm ethanol at 300℃. For traditional sensors, the response and recovery times are found to be about 3 and 6 s, respectively. However, plane sensors show much quicker reaction speeds compared with traditional sensors. The response and recovery times for plane sensors are decreased to 2 and 3 s, respectively, indicating the rapid speeds of this type of sensors. Additionally, the unchanged sensitivity values and reaction speeds of both types of sensors indicate the high stability and good repeatability of the ZnO nanofibers.

The qualitative mechanism to explain the gas sensing properties of metal-oxide based chemical sensors was presented in many former papers.[1,2] Briefly, the oxygen vacancy in ZnO nanofibers acts as an electron donor to provide electrons to conduction band of ZnO and makes the nanofibers to be an n-type MOS. When the ZnO nanofibers are surrounded by air, oxygen molecules will adsorb on the fiber surface to generate chemisorbed oxygen species (O^- is believed to be dominant),[1,2] and resultin a high resistance. When reducing ethanol is introduced at a moderate temperature (the optimizing operating temperature), these

nanofibers are exposed to the traces of the reducing gas. By reacting with the oxygen species on the ZnO surface, ethanol will reduce the concentration of oxygen species on the ZnO surface and thus increase the conductivity of ZnO nanofibers. The reaction between surface oxygen species and ethanol can be simply described as

$$C_2H_5OH + O^- \leftrightarrow CO_2 + H_2O + e.$$

ZnO has proven to be a sensing material for the detection of both reducing (e.g., ethanol, CO, CH_4 and H_2) and oxidizing gases (e.g., Cl_2, O_2 and NO_X).[25] However, pure ZnO often shows relatively low sensitivities and long response/recovery times for the detection. Thus various technologies (such as adding catalysts or doping metals and metal oxides) have been employed for its sensing improvement.[25] The present sensors exhibit high sensitivity and quick response/recovery speeds without any catalysts or dopants, which is attributed to the nanofiber structure. The 1D nanostructure of ZnO nanofibers possesses a large surface-to-volume ratio, which can absorb more ethanol molecules on the fiber surface.[26] Simultaneously, the nanofibers synthesized by electrospinning own high length-to-diameter ratio, which may form a net-like structure on the sensor surface. This net-like structure will further enhance the gas adsorption and lead to a high sensitivity value.[27] Moreover, 1D nanostructures can facilitate fast mass transfer of the analyte molecules to and from the interaction region as well as require charge carriers to transverse the barriers introduced by molecular recognition along the 1D nanostructures.[28]

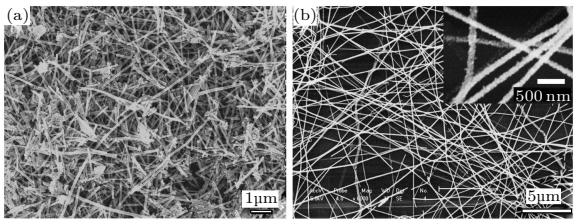

Fig. 7. SEM images of ZnO nanofibers on traditional sensors (a) and plane sensors (b), the insert is a high-resolution SEM image on plane sensors.

To explain the different performances between these two types of sensors with the same sensing material, two SEM images, which are the nanofibers on traditional sensors and plane sensors respectively, are shown in Fig. 7. The nanofiber morphology is totally destroyed during the grinding and coating processes in the traditional sensor fabrication, as shown in Fig. 7 (a). All the nanofibers are cracked into short rod-like fibers with lengths of several micrometers. In addtion, some aggregation growths are also observed among these cracked nanofibers and this will lead to the decreased sensing performances.[29] In contrast, the nanofibers on the plane sensors retain all the primordial morphology due to the scatheless fabrication (even in the low-resolution SEM image of Fig. 7(b)). All the nanofibers with lengths of several ten micrometers form a net-like structure, which thereby can be considered as the ideal morphology to show high performance. Furthermore, abundant large pores with loose structure for the nanofibers on plane sensors can make gas molecules pass through easily, which will decrease the response/recovery times effectually.[28] All these factors will lead to the higher sensing properties of the plane sensors eventually. The insert in Fig. 7 (b) is a high-resolution SEM image of ZnO nanofibers on plane sensors, which shows that the average diameter of these nanofibers is about 140 nm.

In summary, ZnO nanofibers are synthesized through an electrospinning method. Two types of gas sensors, which are the traditional sensors (based on ceramic tubes) and plane sensors (based on ceramic planes) respectively, are fabricated by loading these nanofibers as the sensing materials. Compared with the traditional sensors, the plane sensors exhibit much higher sensitivity, shorter response/recovery speeds and lower minimum-detection-limit and these differences are explained by considering the morphological damage from the fabricating process for traditional sensors. These experimental results suggest that plane sensors are more suitable for the sensing investigation of novel materials with special structures and morphologies. In addition, our investigation may also provide some useful information for the improvement of sensor performances.

References

[1] Janata J et al 1994 *Anal. Chem.* **66** 207
[2] Huang X J et al 2007 *Sensors Actuators* B **122** 659
[3] Qiu W et al 2009 *Chin. Phys. Lett.* **26** 080701
[4] Li L J et al 2010 *Chin. Phys. Lett.* **27** 086105
[5] Zhong Z et al 2010 *Chin. Phys. Lett.* **27** 096101
[6] Zhu J et al 2009 *Chin. Phys. Lett.* **26** 014204
[7] Liu L et al 2009 *Chin. Phys. Lett.* **26** 090701
[8] Lee S M et al 2003 *Microelectronics J.* **34** 115
[9] Neri G et al 2008 *Sensors Actuators* B **132** 224
[10] Franke M E et al 2006 *Small* **2** 36
[11] Liu Y, Koep E and Liu M 2005 *Chem. Mater.* **17** 3997
[12] Wan Q et al 2004 *Appl. Phys. Lett.* **84** 3654
[13] Qi Q et al 2008 *Sensors Actuators* B **134** 166
[14] Xu J et al 2007 *Sensors Actuators* B **120** 694
[15] Ge J P et al 2006 *Sensors Actuators* B **113** 937
[16] Liang Y X et al 2004 *Appl. Phys. Lett.* **85** 666
[17] Huang J and Wan Q 2009 *Sensors* **9** 9903
[18] Qiu Y and Yang S 2007 *Adv. Funct. Mater.* **17** 1345
[19] Greiner A et al 2007 *Angew. Chem. Int. Ed.* **46** 5670
[20] Liu L et al 2010 *Sensors Actuators* B **150** 806
[21] Zhang H, Li Z et al 2010 *Sensors Actuators* B **147** 111
[22] Zhang T, Qi Q, Liu K X, Liu L, Zhang L and Xu B K 2006 *Trans. Nanoferrous Met. Soc. Chin.* **16** 780
[23] Grasset F et al 2008 *Adv. Mater.* **20** 1710
[24] Yamazoe N et al 1979 *Surf. Sci.* **86** 335
[25] Barsan N et al 2007 *Sensors Actuators* B **121** 18
[26] Wu W et al 2010 *Nanoscale Res. Lett.* **5** 1471
[27] Li D and Xia Y 2004 *Adv. Mater.* **16** 1151
[28] Kolmakov A and Moskovits M 2004 *Annu. Rev. Mater. Res.* **34** 151
[29] Sahm T et al 2004 *Sensors Actuators* B **98** 148