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Improved ethanol, acetone and H_2 sensing performances of micro-sensors based on loose ZnO nanofibers

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Both one-dimensional nanostructures and porous nanostructures are benefit to the sensing enhancement of semiconducting functional materials. The present paper shows an effective route to combining the advantages of these two nanostructures for a novel type of ZnO nanomaterials. Basically, a pore-forming material is employed in an electrospinning method, and the products are characterized by X-ray powder diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM). The obtained materials are loose ZnO nanofibers, which own both porous and one-dimensional nanostructures. Micro-sensors are fabricated by sputtering and etching techniques, and the as-prepared nanofibers are used as the functional materials in them. The sensors show improved sensing properties both in sensitivity and response-speeds. The sensitivity is enhanced from 4 to 8 and the response time is shortened from 14 to 10 s when the sensors are exposed to 100 μL/L ethanol at 260°C. Similar results are also observed in acetone and H_2 sensing tests. These enhancements are based on the one-dimensional and porous nanostructures of the nanofibers.

micro-sensors, one-dimensional nanostructures, porous nanostructures, semiconductors, gas sensors

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Gas sensors are widely applied in the fields of air quality control, environmental protection, and national security, with economic impact in medicine, agriculture, industrial production, and in the automotive and aerospace industries [1]. Chemical gas sensors, which are mostly based on semiconductors such as ZnO and SnO_2, play an important role in gas sensor field for their small size, good reproducibility, and low cost [2]. Traditional chemical gas sensors are fabricated by handmade coating [3], thus lack consistency and repeatability. Therefore, micro-sensors have received considerable attention due to their remarkable mechanical and electronic properties in recent years [4]. Especially, with the coming age of the internet of things, interest in micro-sensors has been greatly stimulated for their potential applications in sensing integrate circuits.

The sensing mechanism of chemical gas sensors is based on the reaction between the adsorbed oxygen species on the sensor surface and the gas molecules to be detected, and this reaction is strongly dependent on the morphology and structure of the materials [5]. Accordingly, many scientific and technological efforts have been made to synthesize semiconductors with various nanostructures and to reveal the corresponding sensing properties of them. In recent decade, it has been proved that one-dimensional nanostructures and porous nanostructures can help gas absorption, thus benefit to high sensitivity and quick response [6]. However, the materials with both these two characteristics have rarely been reported.

ZnO is a chemically and thermally stable n-type II-VI compound semiconductor with a large band gap energy (3.37 eV at room temperature) and a strong exciton binding energy (60 meV). It has been extensively studied for optoelectronics, field-emission devices, as well as chemical sensors [7,8]. In this paper, we use a simple electrospinning method to prepare loose ZnO nanofibers by use block copolymer P123 ($EO_{20}PO_{70}EO_{20}$) in the precursor as the

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pore-forming material. Then we fabricate some micro-sensors by sputtering and etching techniques. Effectually improved sensing performances have been obtained based on the sensors. And some theoretical explanations are also provided for experimental phenomena.

1 Experimental

1.1 Fabrication of sensor substrates

Micro-sensors were fabricated by micro-electronics techniques. The designs of signal electrodes and heating electrodes are shown in Figure 1(a) and (b) respectively, and the fabricating process is shown in Figure 1(c). Briefly, the fabrication of the sensor substrates was achieved according to the following steps: (a) sputtering platinum (thickness of 2000 Å) as metal electrodes on the top surface of SiN_x-Si-SiN_x wafers; (b) masking signal electrode patterns transfer to the wafers by photolithography and then etching the top platinum layer by reactive ion etching; (c) sputtering platinum (thickness of 2000 Å) as metal electrodes on the bottom surface of SiN_x-Si-SiN_x wafers; (d) masking heating electrode patterns transfer to the wafers by photolithography and then etching the bottom platinum layer by reactive ion etching; (e) removing the photoresist and solidifying the substrates by calcining substrates at 600°C in air for 4 h.

1.2 Preparation of materials

Poly(vinyl pyrrolidone) (PVP, MW=1300000, the pore-forming material), zinc nitrate ($Zn(NO_3)_2{\cdot}6H_2O$), and block copolymer P123 ($EO_{20}PO_{70}EO_{20}$) were used as the precursory materials. For the preparation of precursor solution, 0.412 g PVP powder was dissolved in 4.243 g ethanol and vigorously stirred for 4 h at room temperature. 1.887 g $Zn(NO_3)_2{\cdot}6H_2O$ was mixed with 3.245 g deionized water, followed by magnetic stirring for 1 h. After the dissolution, the aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ was added into the PVP solution in advance with a weight ratio of 1/3, stirring to yield a homogeneous mixture. At last, 0.080 g P123 was dissolved in the mixture, followed by magnetic stirring for 6 h.

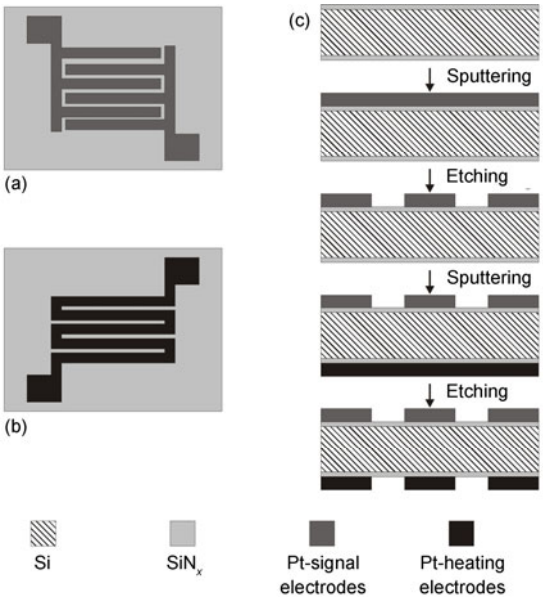

Figure 1 (a) Design of signal electrodes (the electrode width is 20 μm); (b) design of heating electrodes (the electrode width is 20 μm); (c) fabricating process of the sensor substrates.

Electrospinning of loose ZnO nanofibers was conducted with a similar set-up which has been detailed in a previous study [9]. The spinning solution obtained was delivered to a syringe pump at a constant flow rate of 1.0 mL/h, and then electrospun by applying 20 kV at an electrode distance of 17 cm. A piece of flat aluminum foil was employed to collect the precursory nanofibers.

1.3 Measurement and characterization

The length and width of the sensor substrates were 3 and 4 mm, the sensor substrate is shown in Figure 2(a). To employ loose ZnO nanofibers as the functional material in the micro-sensors, many sensor substrates were fixed on the aluminum foil by double-sided glue and then electrospinning for about 10 h. After that, the organic constituents (such as PVP) were selectively removed from the precursory nanofibers by calcining them at 600°C for 5 h, and the micro-sensors with crystal nanofibers were obtained. The synthetical process of the nanofibers is shown in Figure 2(b).

Sensor measurement was performed using a chemical gas sensor (CGS-8, Beijing Elite Tech Co., Ltd, Beijing, China) intelligent gas sensing system (Figure 2(c) and (d)) [10]. The sensors were pre-heated at different operating temperatures for about 10 min. When the resistance of each sensor was stable, suitable volume of target vapor or liquid was injected into the test chamber (20 L in volume for CGS-8 in this case) by a syringe through a rubber plug. For a gas prepared by vapor sources, the source volume was calculated by $Q = CV$, where Q was the volume value, C was the target concentration, and V was the chamber volume. If a liquid was used as the gas source, the volume was calculated by $Q = (CVM) / (22.4dp)$, where Q was the liquid volume, C was the target concentration, V was the chamber volume, M was the molecular weight, d was the density, p was the purity. After the sensor resistance reached a constant value again, the test chamber was opened to recover the sensor in air. The sensor resistance and sensitivity were acquired by the analysis system automatically.

Sensitivity value (S) was designated as $S = Ra/Rg$, where Ra was the sensor resistance in air (base resistance) and Rg was a mixture of target gas and air. The time taken by the sensor resistance to change from Ra to $Ra - 90\% \times (Ra - Rg)$ was defined as response time when the target gas was introduced to the sensor, and the time taken from Rg to Rg

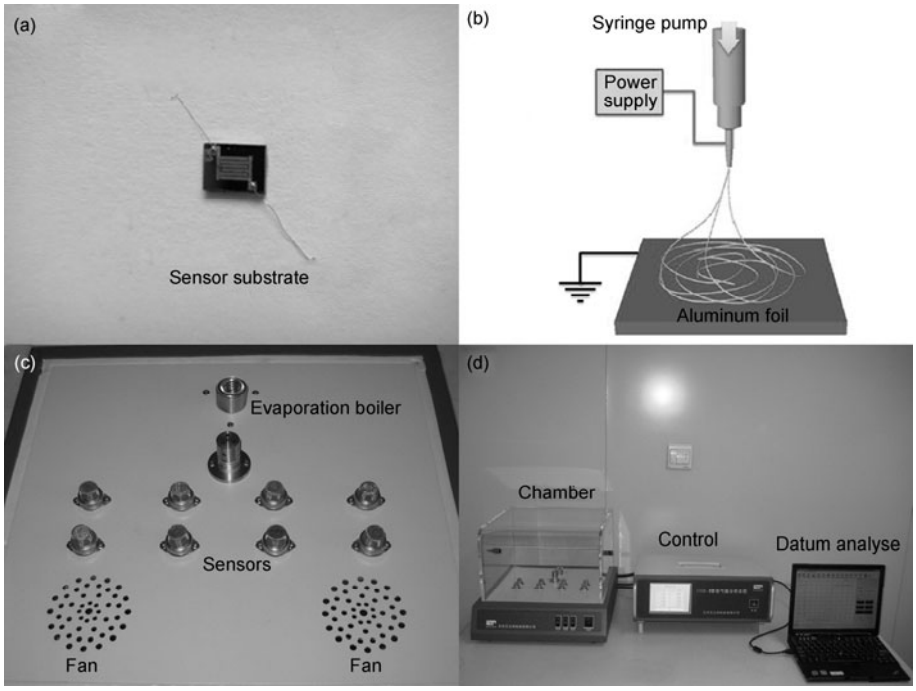

Figure 2 (a) A photograph of a sensor substrate and a coin; (b) fabricating process of the loose ZnO nanofibers; (c) a photograph of eight micro-sensors in an analysis system; (d) a photograph of the gas sensing analysis system.

+ 90%×(*Ra*–*Rg*) was defined as recovery time when the ambience was replaced by air.

The crystal structures of the products were determined by X-ray powder diffraction (XRD) using an X-ray diffractometer (Siemens D5005, Munich, Germany). The material compositions were analyzed by energy dispersive X-ray (EDX) spectroscopy (SSX-550, Shimadzu). The morphologies of the electrospun nanofibers were viewed by transmission electron microscopy (TEM, Model JEM-2000EX, JEOL) with an accelerating voltage of 200 kV.

2 Results and discussion

To reveal the effect of the pore-forming material on the sensing performance of ZnO nanofibers, we also synthesized ZnO nanofibers by the same method except the addition of P123. The obtained nanofibers are designated as common ZnO nanofibers, and the samples with P123 in the precursors are designated as loose ZnO nanofibers in this paper. The EDX and XRD results shown in Figure 3 indicate that the two types of nanofibers own the same composition and crystal-structure. Only Zn and O can be found in the samples according to EDX patterns. And all the diffraction peaks in the XRD patterns from these nanofibers can be indexed as hexagonal ZnO with lattice constants a = 3.25 Å and c = 5.21 Å, which are consistent with the values in the standard card (JCPDS file no. 36-1451).

Fiber morphologies are tested by TEM analysis, and Figure 4(a) and (b) are the corresponding images of common and loose ZnO nanofibers. The two samples with

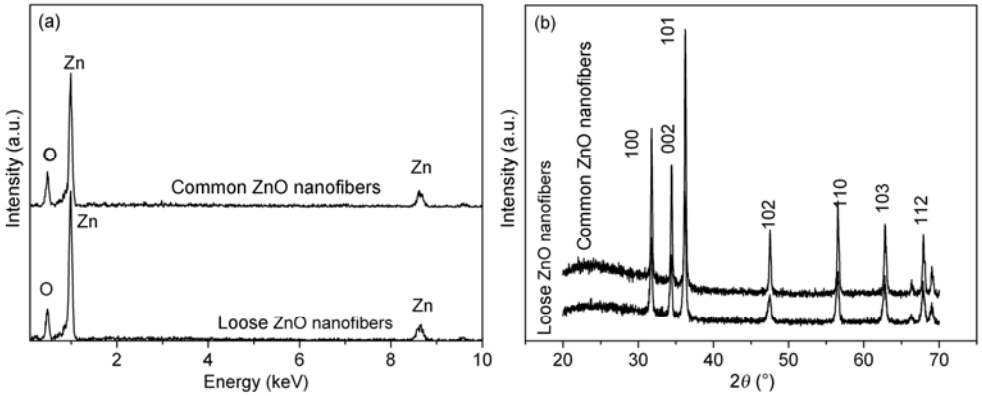

Figure 3 (a) EDX and (b) XRD patterns of common and loose ZnO nanofibers.

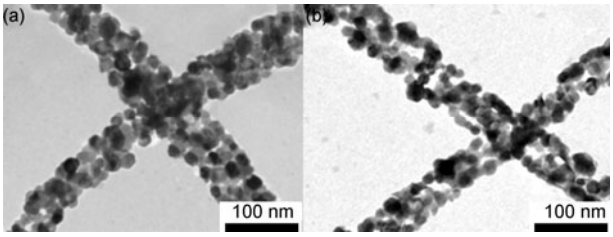

Figure 4 TEM images of (a) common and (b) loose ZnO nanofibers.

similar diameters (about 80 nm) show very different micro-structures. It can be found that after adding P123 in the precursors, the nanofibers become coarse and loose, and many pores can be easily observed. This characteristic will make the sensor absorb more gas molecules, therefore enhance the sensor performance consequentially.

Micro-sensors were exposed to ethanol (C_2H_5OH), acetone (CH_3COCH_3), and H_2 at different temperatures to reveal their gas sensing performances. The sensors exhibit various sensing responses in the tests, as shown in Figure 5. For each curve, the sensitivity increases and reaches its maximum, and then decreases rapidly with further increasing the temperature. The optimum operating temperatures (corresponding to the maximum sensitivity) of the sensors are 260°C to ethanol and acetone, and 300°C to H_2. The two types of sensors show same optimum operating temperature values, but their sensitivities are quite different. Therefore, we studied their sensing properties at each optimum temperature in detail.

The comparison of the sensor response speeds to ethanol at 260°C is shown in Figure 6(a). For the micro-sensors fabricated from common ZnO nanofibers, their sensitivity quickly rises when the sensors are surrounded by ethanol, the final sensitivity is about 4 and the response time is found to be about 14 s. The sensors with loose ZnO nanofibers show much larger sensitivity (about 8), which is twice as large as that of common ZnO nanofiber sensors. However,

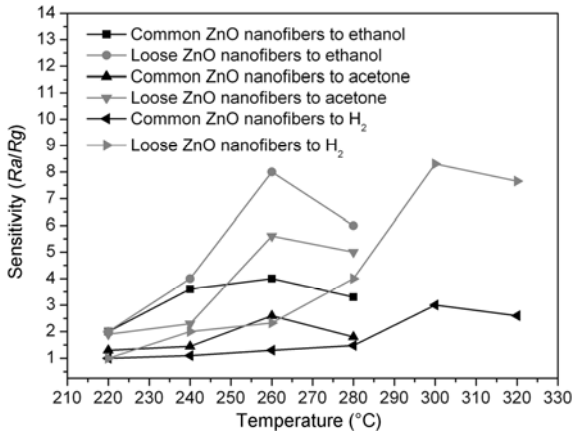

Figure 5 Sensitivities of the micro-sensors to ethanol, acetone, and H_2 at different working temperatures.

their response time is surprisingly decreased to 10 s. Normally, larger sensitivity means bigger resistance change, which often needs longer times to response. The sensors with loose ZnO nanofibers exhibit larger sensitivity but shorter response time, indicating the addition of P123 in the electrospinning is beneficial to the gas sensing of the nanofibers. The sensors show similar recovery times, which are about 12 s. We also tested the sensor sensitivities to different concentrations of ethanol at 260°C. And the results in Figure 6(b) show the sensors with loose ZnO nanofibers own much better sensitivities in all the tests. For instance, the sensitivities are about 2.2, 8, 15, and 18 for the sensors with loose ZnO nanofibers to 10, 100, 500, and 1000 μL/L ethanol, but are only 1.3, 4, 8.3, and 11 for the sensors with common ZnO nanofibers.

Similar sensing improvements are also observed in the sensor tests to acetone and H_2, as shown in Figures 7 and 8, respectively. For the tests of acetone, the response times of the sensors with common and loose ZnO nanofibers are 9 and 7 s, respectively. The sensitivities of the sensors with common ZnO nanofibers to 10, 100, 500, and 1000 μL/L

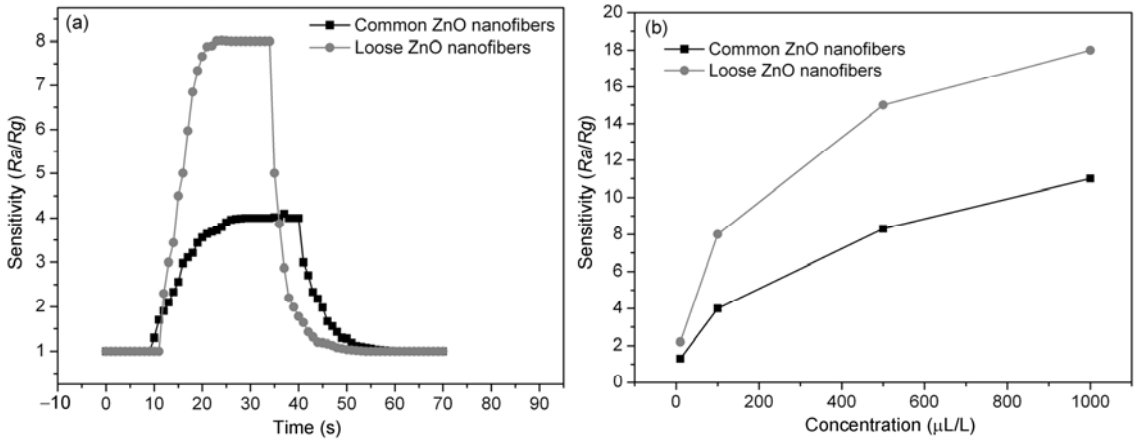

Figure 6 (a) Response-recovery curves of the sensors fabricated from common and loose ZnO nanofibers to 100 μL/L ethanol at 260°C; (b) sensitivities of the sensors fabricated from common and loose ZnO nanofibers to different concentrations of ethanol at 260°C.

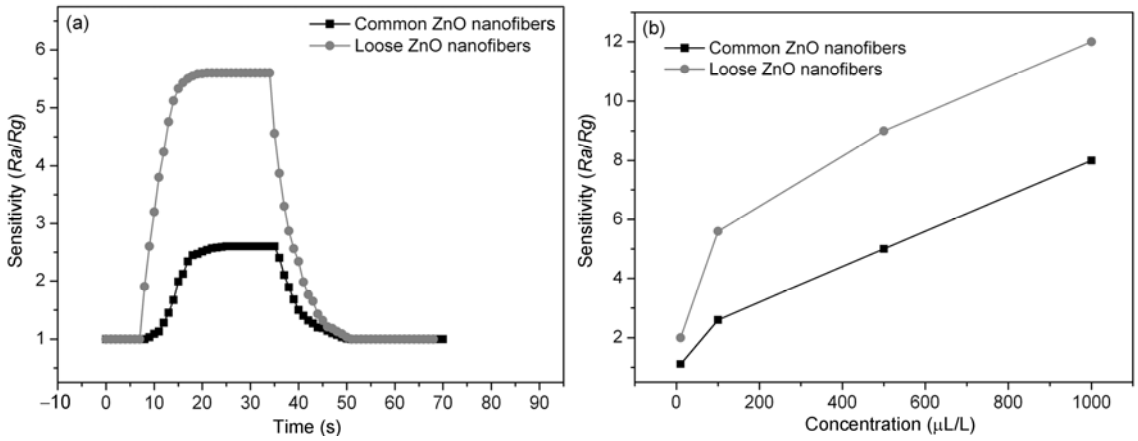

Figure 7 (a) Response-recovery curves of the sensors fabricated from common and loose ZnO nanofibers to 100 μL/L acetone at 260°C; (b) sensitivities of the sensors fabricated from common and loose ZnO nanofibers to different concentrations of acetone at 260°C.

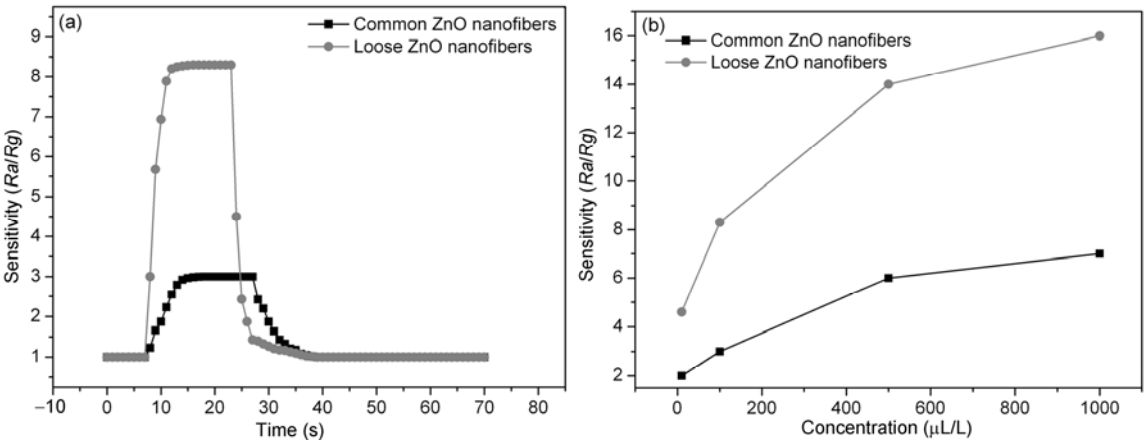

Figure 8 (a) Response-recovery curves of the sensors fabricated from common and loose ZnO nanofibers to 100 μL/L H_2 at 300°C; (b) sensitivities of the sensors fabricated from common and loose ZnO nanofibers to different concentrations of H_2 at 300°C.

acetone are 1.1, 2.6, 5, and 8, and the corresponding values are 2, 5.6, 9, and 12 for the sensors with loose ZnO nanofibers. The recovery times of the sensors are about 16 s.

In the H_2 sensing tests at 300°C, the sensitivity improvement brought about by the loose surface of the nanofibers is the largest. The sensitivity is only 3 for the sensors fabricated from common ZnO nanofibers to 100 μL/L H_2, but it is enhanced to 8.3 by loading the loose ZnO nanofibers. The response times are also reduced from 8 to 5 s. The recovery times are about 10 s.

From above results, we can figure that by adding pore-forming material in the electrospinning precursor, the nanofibers will become loose. And the sensitivity and response speed can be improved evidently. The recovery speed does not change. The following discussion will focus on the possible reasons for these experimental phenomena.

The base sensing mechanism of ZnO is similar as that of other semi-conducting metal oxides such as SnO_2 and Fe_2O_3, and the theoretical analyse has been clarified in many previous works [11,12]. Basically, the change in resistance of oxide gas sensors is primarily caused by the adsorption and desorption of the gas molecules on the surface of sensing films. The higher resistance of sensors in air (*Ra*) is due to the oxygen adsorbs on the ZnO surface and thus decrease the carrier concentration and electron mobility accordingly. And the decreased resistance of sensor in target gas (*Rg*) is because of the reducing gases (such as ethanol, acetone, and H_2 in this paper) can react with the adsorbed oxygen molecules and release the trapped electrons back to the conduction band, thereby increase the conductivity eventually.

Normally, pure ZnO exhibits responses to many gases, but its sensitivity is quite low [7]. Thus many dopants are selected to improve its sensing performance [7]. However, both the common and loose ZnO nanofibers show very high sensitivity and short reacting times. This is based on the one-dimensional nanostructure of the nanofibers prepared by electrospinning [13]. The large surface-to-volume ratio of the nanofibers and the congruence of the carrier screening length with their lateral dimensions make them highly sensitive and efficient transducers of surface chemical processes into electrical signals. And the fabricating process of the micro-sensors will not damage the fiber structure, thus

many web-like structures can be naturally formed by the one-dimensional nanostructures on the sensor surface, which make them highly sensitive and efficient transducers of surface chemical processes into electrical signals [9]. Those advantages can work together and lead to significant gain in high sensitivity of the as-prepared sensors.

P123 is widely used to synthesize porous materials with high surface-to-volume ratio such as SBA-15. Adding this pore-forming material in the electrospinning precursor, the nanofibers can turn to loose. The sensing enhancement from this loose morphology can be explained by two aspects [14,15]. Firstly, this morphology is useful to gas adsorption because more active sites are provided on the surface of the ZnO nanofibers, which is a vital factor for high sensitivity. On the other hand, gas molecules can transfer more easily in the nanofibers with this loose nanostructure, thus even the sensitivity rises, the response time decreases instead. The un-changed recovery time is due to the pores on the nanofibers are concave, and this characteristic may counteract the accelerating affection of desorption by the loose structure [16]. Moreover, it should be noted that although P123 are used to form many porous materials, there is no ordered pore distributions can be found in the ZnO nanofibers. This is because a standing process is obligatory for the preparation of porous materials by P123 [17]. However, this standing process is inconsistent with the electrospinning method, thus can not be used in our experiment [18].

3 Conclusions

In conclusion, loose ZnO nanofibers are synthesized by adding P123 in the electrospinning precursor, and the fiber sensing properties can be effectively enhanced by this way. The sensing enhancements are observed in the sensing tests for ethanol, acetone, and H_2. And the possible theoretical explanation is also provided. This method is simple and effective, thus can be widely used in the electrospinning syntheses of semiconductor nanofibers.

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