



SnO₂ nanoparticle-coated In₂O₃ nanofibers with improved NH₃ sensing properties



Qi Qi^a, Pei-Pei Wang^a, Jun Zhao^a, Liang-Liang Feng^a, Li-Jing Zhou^a, Rui-Fei Xuan^{a,b}, Yi-Pu Liu^a, Guo-Dong Li^{a,*}

^a State Key Lab of Inorganic Synthesis & Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

^b College of Materials Science and Engineering, China University of Mining and Technology, Xuzhou 221116, PR China

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ABSTRACT

SnO₂ nanoparticles and In₂O₃ nanofibers are synthesized via a sol–gel process and an electrospinning method, respectively. Excellent sensing materials for NH₃ detection are achieved by coating SnO₂ nanoparticles on In₂O₃ nanofibers. When the as-prepared sensors were exposed to 1 ppm NH₃ at room temperature, the response is 21, and the response and recovery times are 7 and 10 s, respectively. With this method, NH₃ can be detected down to a concentration of 0.1 ppm, and the corresponding response is about 2. The selectivity and stability of the sensors are satisfactory for gas sensing. And the surface coating is proved to be an effective method for the sensing enhancement of one-dimensional nanomaterials.

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1. Introduction

Metal semiconducting oxides have attracted great attention and been widely employed in chemical sensors due to the advantages such as high sensitivity, low cost and easy fabrication [1,2]. Based on the variation of electrical properties of an active element, most oxides sensors operate on a thick [3] or thin film form [4], caused by the adsorption or desorption of an analyte on the surface of the film. Thus, many oxides with various surface characteristics and sensing properties were reported in the past fifty years [1]. To improve the performance of sensors, doped nanoparticles were studied intensely in spite of the aggregation of nanoparticles [5]. In this decade, it is found that the formation of semiconductor nanostructures, such as one-dimensional or porous structures, can enhance their responses greatly [6]. And dopants have been used in these oxides to improve the performance of gas sensors [7]. However, most of the dopants are introduced into the precursors as additives. It means that the dopants are distributed both on the film surface and in its interior [8]. While, the inner dopants can not join the sensing reactions, the doping efficiency should be quite low [9].

Herein, we present a simple and effective surface doping method for one-dimensional nanomaterials. In₂O₃ nanofibers synthesized by electrospinning are used as the base sensing

materials in our experiment. In₂O₃ is one of the most attractive gas sensing oxides for the versatile and controllable sensing properties as well as excellent chemical stability [10]. Electrospinning is an easy and cost-efficient technique for producing multi-functional nanofibers from various polymers, polymer blends, composites, sol–gels, ceramics, etc [11]. Electrospun nanofibers/nanowebs have remarkable characteristics such as large surface-to-volume ratios and natural web-like structures [12]. SnO₂ nanoparticles are the most applied sensing materials which have been used to fabricate gas sensors to C₂H₅OH, ammonia (NH₃), H₂, CH₄ and H₂O [13–16]. This material can be employed as a base material as well as an additive. The SnO₂ nanoparticle-coated In₂O₃ nanofibers in this paper show improved and excellent NH₃ sensing properties at room temperature. Surface doping method has been used in nanoparticle sensors and thin film sensors [8,16,17], but rarely been reported for the combination of nanofibers and nanoparticles. The results in this paper not only demonstrate the potential application of the obtained nanofibers for NH₃ detection, but also present an effective method for the sensing improvement of one-dimensional nanomaterials.

2. Experimental

2.1. Synthesis of materials and fabrication of sensors

All chemicals (analytical grade reagents) were purchased from Beijing Chemicals Co. Ltd. and used as received without further

* Corresponding author. Tel.: +86 431 85168318; fax: +86 431 85168624.

E-mail addresses: ljd@jlu.edu.cn, lifind@21cn.com (G.-D. Li).

purification. Deionized water with a resistivity of $18.2\text{ M}\Omega\text{ cm}^{-1}$ was used in all experiments. SnO_2 nanoparticles were synthesized by a sol-gel method [18]. In a typical synthesis process, 5 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added to an aqueous solution consisting of 0.5 g of citric acid and 100 mL of deionized water. After dissolved completely, about 8 mL of 0.5 M aqueous ammonia was added as a precipitator under strongly stirring to obtain $\text{Sn}(\text{OH})_4$ precipitation. Then the resultant product was centrifuged, and washed with deionized water for 10 times in order to eliminate the chloride ions. The precipitate was dried under an infrared lamp, and then ground using an agate pestle and mortar to obtain $\text{Sn}(\text{OH})_4$ powders. 0.05 g of $\text{Sn}(\text{OH})_4$ powders were mixed with 10 g of deionized water and heated to 60°C and then stirred for 2 h to obtain a homogeneous sol solution. In_2O_3 nanofibers were prepared by an electrospinning method [19]. Typically, 0.42 g of $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ was added to 8.8 g of mixed solvent contained *N,N*-dimethylformamide (DMF)/ethanol with the weight ratio of 1:1 and stirred for 2 h, and then 1.2 g of PVP was added to the above solution with stirring for another 6 h. Electrospinning of In_2O_3 nanofibers was conducted with a similar set-up which has been detailed in a previous study [19]. The as obtained spinning solution was delivered to a hypodermic syringe at a constant flow rate of 1.0 mL/h, and then electrospun by applying 20 kV at an electrode distance of 25 cm. A piece of aluminum foil was used as the cathode and several sensor substrates were placed on it. Sensor substrates were fabricated by radio-frequency (RF) sputtering Pt arrays on SiO_2/Si chips as signal electrodes. The thickness of SiO_2 layer and Pt array were about 300 and 100 nm, respectively. The precursor solution was directly electrospun on sensor substrates with interdigitated Pt electrode arrays. The sensor length and width were 3 and 2 mm, respectively. A photograph of a sensor's substructure is shown in Fig. 1. After being electrospun for 2 h, the sensor substrates were calcined at 500°C for 2 h in air, and then dipped by the sol solution with different times. After each step, the substrate was dried on a mildly heated hot plate before the next step. Finally, the sensors

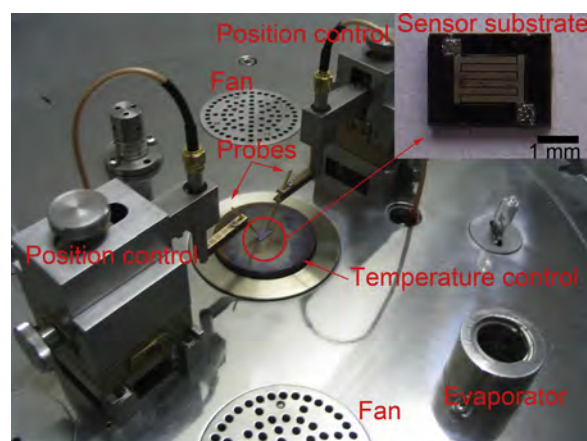


Fig. 1. A photograph of the gas sensing analysis system, and the inset shows a sensor substrate.

were calcined at 600°C for 1 h in air followed by annealing at 300°C for 10 min in hydrogen atmosphere to obtain the SnO_2 -coated In_2O_3 sensors.

2.2. Characterization of materials and measurement of sensors

X-ray diffraction (XRD) analysis was conducted on a Scintag XDS-2000 X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) spectra were performed on a SHIMADZU SSX-550 (Japan). Transmission electron microscope (TEM) images were obtained on a HITACHI S-570 microscope with an accelerating voltage of 200 kV. N_2 adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP2020 system. Surface area was evaluated using a Brunauer-Emmett-Teller (BET) method.

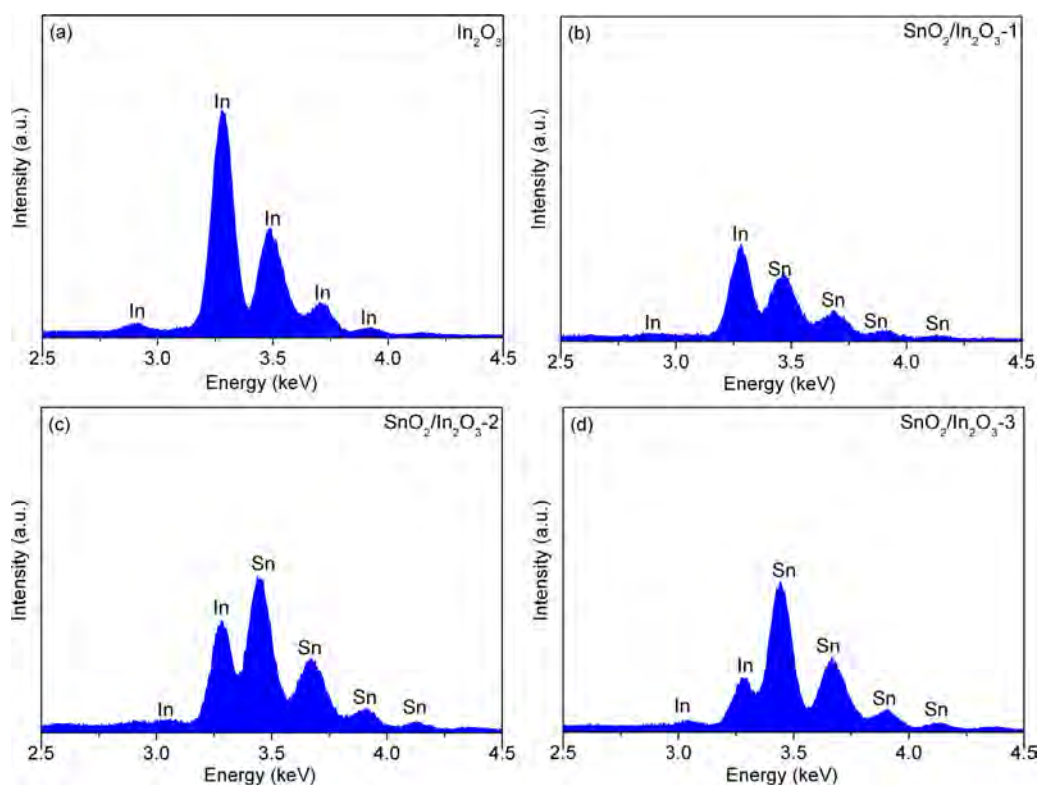


Fig. 2. EDS spectra of (a) In_2O_3 nanoparticles, (b) $\text{SnO}_2/\text{In}_2\text{O}_3$ -1 nanofibers, (c) $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofibers, and (d) $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofibers.

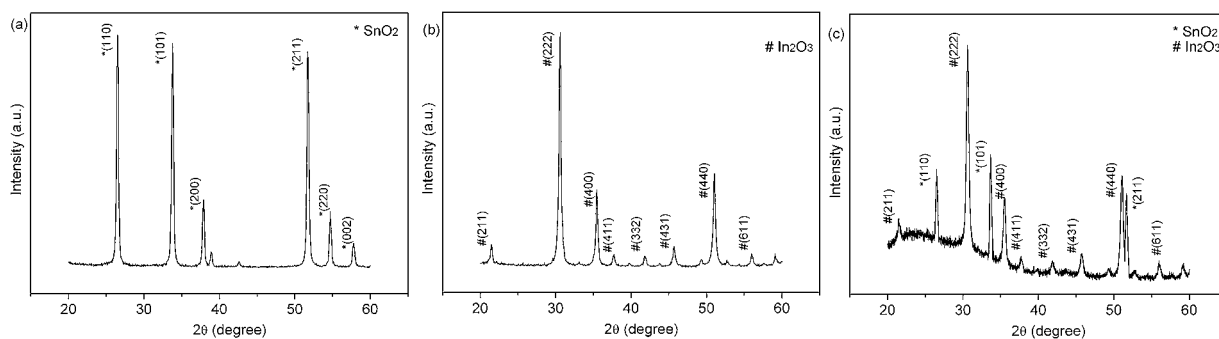


Fig. 3. XRD patterns of (a) SnO₂ nanoparticles, (b) In₂O₃ nanofibers, and (c) SnO₂/In₂O₃-2 nanofibers.

Sensing measurement was performed on a CGS-1TP (Chemical Gas Sensor-1 Temperature Pressure) intelligent gas sensing analysis system (Beijing Elite Tech Co., Ltd, China) [20,21]. The analysis system offered an external temperature control, which could adjust the sensor temperature with a precision of 1 °C. In this case, the operating temperature was remained at 25 °C (defined as the room temperature). Two probes were pressed on sensor electrodes, and the electrical signals were collected through the probes and analyzed by the system automatically. The testing value was DC 5 V. The gas ambience was controlled by a DGD-III (Dynamic Gas Distributing-III) system (Beijing Elite Tech Co., Ltd, China). High purity NH₃ gas (99.999%) and synthetic air (20% relative humidity (RH) at 25 °C) were used as the analyte and carrier gases, respectively. The carrier gas was used for diluting NH₃ gas concentration. The flow rates were controlled by the DGD-III system automatically. There was a high-speed gas-switching device in the system, which could switch the sensors between target gases and air within a second. R_a and R_g were the sensor resistance in air (base resistance) and a mixture of target gas and air, respectively. The time taken by the sensor resistance to change from R_a to $R_a - 90\% \times (R_a - R_g)$ was defined as response time when the target gas was introduced to the sensor, and the time taken from R_g to $R_g + 90\% \times (R_a - R_g)$ was defined as recovery time when the target gas was replaced by air.

3. Results and discussion

Four thin film sensors of different doping times (0, 1, 4, and 6) were fabricated. And EDS spectra were executed to study the component of the as obtained nanofibers. It is revealed that the as prepared nanofibers are composed of In, O and Sn. The In:O mol ratio is about 2:3 for un-doped sample [22]. The atomic percentage of SnO₂ in the composite products is about 0%, 7.5 at%, 16 at% and 21 at% for the samples with 0, 1, 4, and 6 doping times, respectively (Fig. 2(a–d)) [23]. Correspondingly, the four sensors are denoted as In₂O₃ nanofiber sensors, SnO₂/In₂O₃-1 nanofiber sensors, SnO₂/In₂O₃-2 nanofiber sensors, and SnO₂/In₂O₃-3 nanofiber sensors.

Fig. 3(a) shows the XRD pattern of SnO₂ nanoparticles, which is in agreement with that SnO₂ (JCPDS 41-1445) [24]. The XRD pattern of In₂O₃ nanofibers in Fig. 3(b) matches very well with that of cubic In₂O₃ (JCPDS 06-0416) [21]. Both of these two patterns are clearly presented in the XRD pattern of (SnO₂)₁₆In₂O₃ nanofibers (Fig. 3(c)). It is indicated that the SnO₂ nanoparticle-coated In₂O₃ nanofibers are consist of SnO₂ and In₂O₃.

Fig. 4(a) and (b) are the TEM images of SnO₂ nanoparticles and In₂O₃ nanofibers, respectively. For SnO₂ nanoparticles, the particle size is about 10–20 nm. The In₂O₃ nanofibers are composed of regular In₂O₃ nanoparticles with diameter of 15–30 nm.

The morphologies of the samples are observed by SEM, and the results of In₂O₃ nanofibers, SnO₂/In₂O₃-1 nanofibers, SnO₂/In₂O₃-2 nanofibers, and SnO₂/In₂O₃-3 nanofibers are shown in Fig. 5. All of

the samples are mainly composed of nanofibers with lengths of several 10 μm and diameters ranging from 30 to 80 nm. The nanofibers form a web-like micro-structure on the sensor substrates naturally, and the pores in this structure are beneficial for the adsorption and desorption of gas molecules. With the increasing of doping times, the pores are stifled by SnO₂ nanoparticles. In Fig. 5(d), most porous morphologies are disappeared [25,26].

The porous features of the samples were characterized by N₂ adsorption–desorption isotherms (Fig. 6). SnO₂ nanoparticles show a low BET surface area of 33 m² g⁻¹, and this is mainly caused by the aggregation of the nanoparticles [4]. The BET surface area of In₂O₃ nanofibers is around 15 m² g⁻¹, which is because of their imperforate exteriors [11]. The coated sample of SnO₂/In₂O₃-2 nanofibers own a much higher BET surface area, and the result is 102 m² g⁻¹. The enhanced surface area can be explained by considering the anti-aggregation of the nanoparticles and modified fiber exterior of this sample [6,9]. The SnO₂/In₂O₃-3 nanofibers show a lower surface area of 42 m² g⁻¹, which is consisted with the morphologic change in Fig. 5.

All of the sensors are exposed to different concentrations of NH₃ at room temperature to test their sensing performances. The sensor resistances (R_a) in air are 64.4, 54.7, 33.2, and 30.4 MΩ for In₂O₃ nanofiber sensors, SnO₂/In₂O₃-1 nanofiber sensors, SnO₂/In₂O₃-2

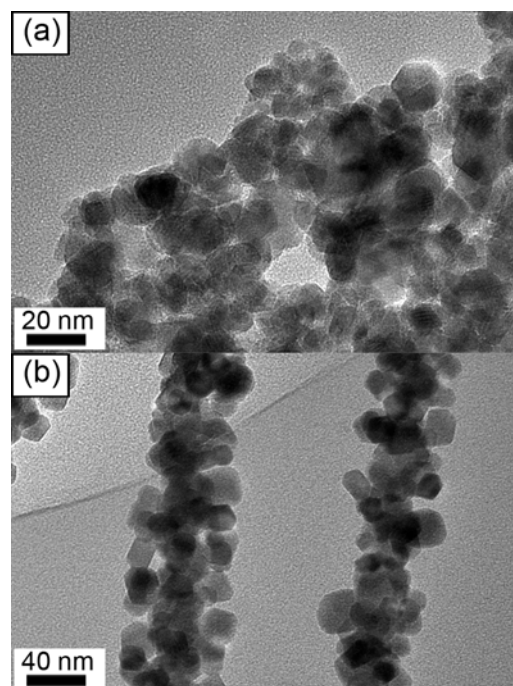


Fig. 4. TEM images of (a) SnO₂ nanoparticles and (b) In₂O₃ nanofibers.

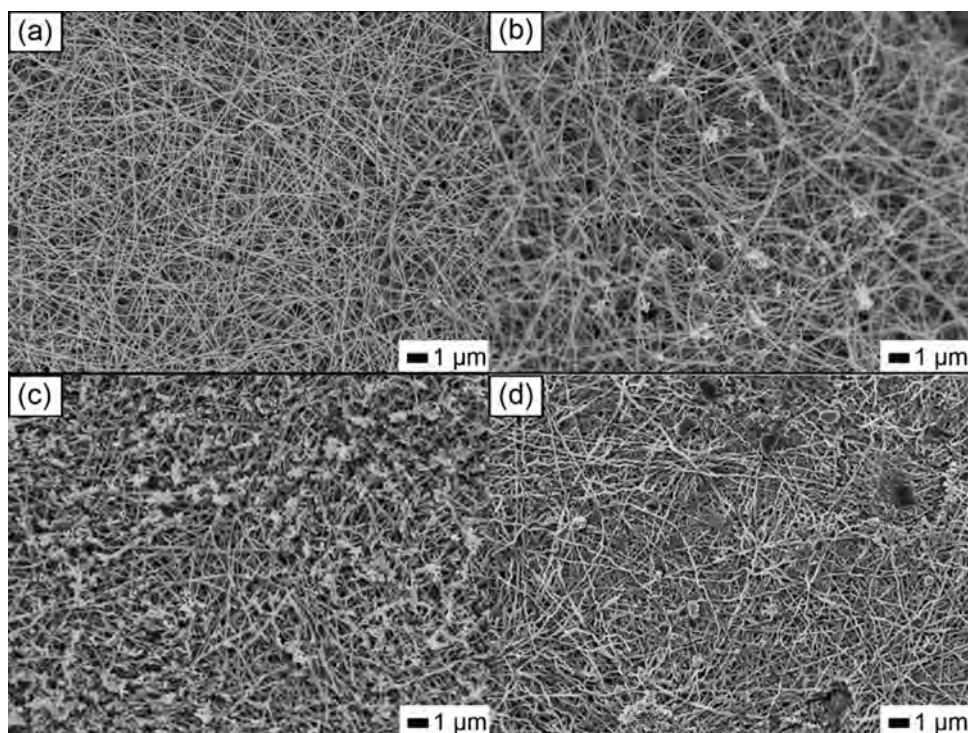


Fig. 5. SEM images of (a) In_2O_3 nanofibers, (b) $\text{SnO}_2/\text{In}_2\text{O}_3$ -1 nanofibers, (c) $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofibers, and (d) $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofibers.

nanofiber sensors, and $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofiber sensors, respectively. As shown in Fig. 7, In_2O_3 nanofiber sensors show very low responses. With suitable SnO_2 coating, the response can be enhanced evidently. $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors own the highest response in all of the tests. For instance, the responses are 6, 21, 53, 145, 273 and 480 for $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors to 0.1, 1, 10, 100, 1000, and 10,000 ppm NH_3 , while the values are only

1.3, 4, 7, 11, 18 and 34 for In_2O_3 nanofiber sensors. It should also be noted that the $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofiber sensors show very low response, even lower than that of the In_2O_3 nanofiber sensors. The corresponding responses are decreased to only 2, 3, 5, 9, 12, and 26. The response enhancement brought about by SnO_2 coating can be explained by the increased adsorption efficiency [9], and the decreased responses of $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofiber sensors may due

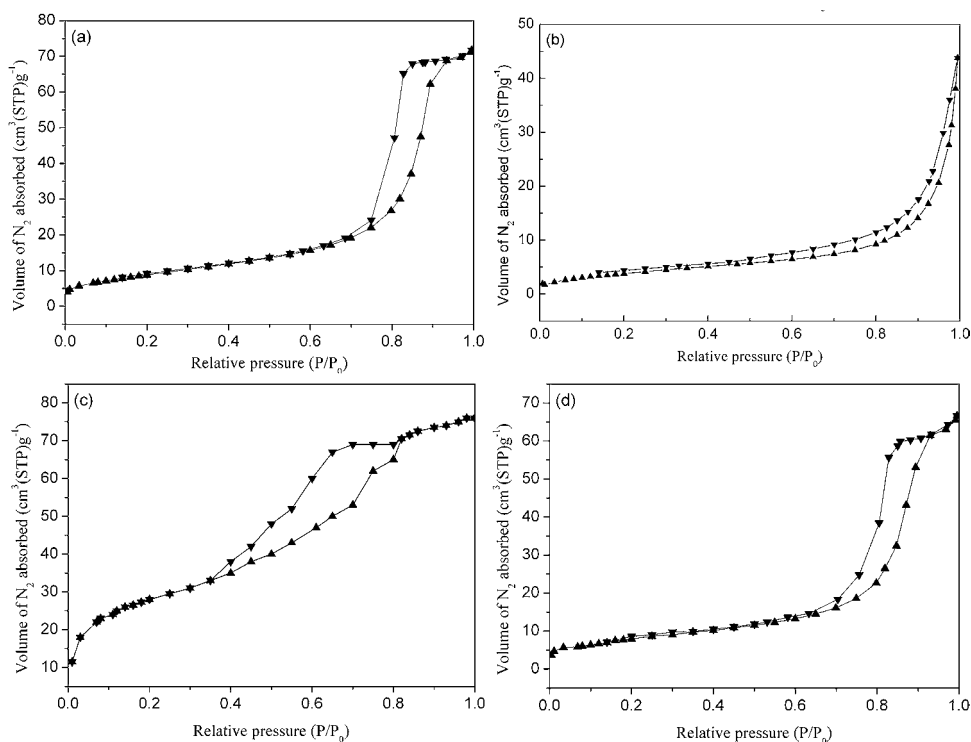


Fig. 6. Nitrogen adsorption–desorption isotherms of (a) SnO_2 nanoparticles, (b) In_2O_3 nanofibers, (c) $\text{SnO}_2/\text{In}_2\text{O}_3$ -2, and (d) $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofibers.

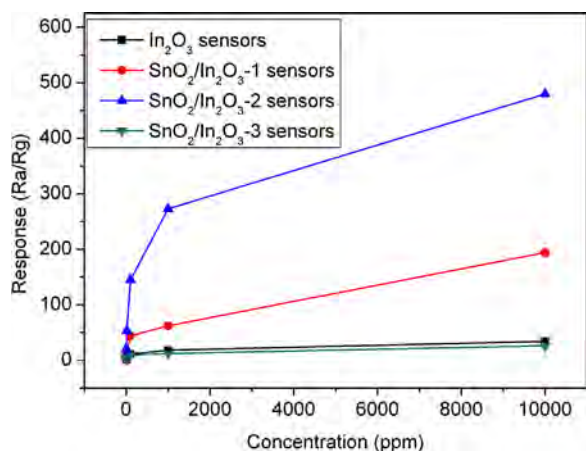


Fig. 7. Responses of In_2O_3 nanofiber sensors, $\text{SnO}_2/\text{In}_2\text{O}_3$ -1 nanofiber sensors, $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors, and $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofiber sensors to different concentrations of NH_3 at room temperature.

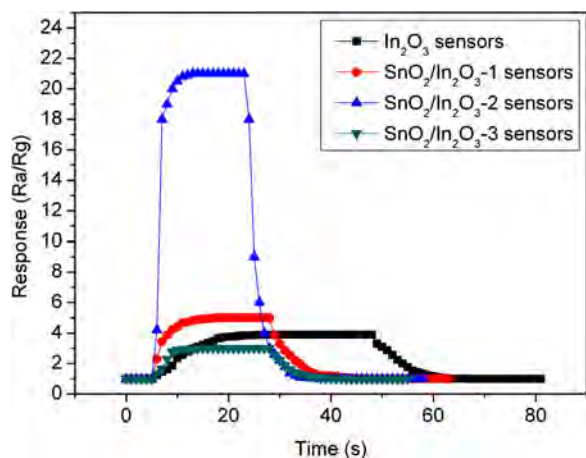


Fig. 8. Response-time curves of In_2O_3 nanofiber sensors, $\text{SnO}_2/\text{In}_2\text{O}_3$ -1 nanofiber sensors, $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors, and $\text{SnO}_2/\text{In}_2\text{O}_3$ -3 nanofiber to 1 ppm NH_3 at room temperature.

to the disappeared porous structure of this sample, as shown in Fig. 5(d) [27].

Response-time curves are used to evaluate the response and recovery speeds of gas sensors. As shown in Fig. 8, the response of In_2O_3 nanofiber sensors is the smallest one among these four sensors, at the same time, the response and recovery times are the longest. The response and recovery times of In_2O_3 nanofiber sensors are about 16 and 15 s, respectively. And the corresponding values are only about 7 and 10 s for that of the $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors. It means that SnO_2 -coating can enhance both the responses and reacting speeds of In_2O_3 nanofibers to NH_3 .

The $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors are also exposed to 1 ppm different gases to test their selectivity. As shown in Fig. 9, the sensors show much lower responses to H_2S (about 4) and $\text{C}_2\text{H}_5\text{OH}$ (about 3), and are almost insensitive (the responses are about 1) to H_2 , C_2H_2 , C_6H_6 , O_2 , CH_4 , and CO . It is considered that higher energy (higher temperature) is needed for the In_2O_3 nanofibers to react with those gases and give higher response [28].

The stability of $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors is concerned for the lower mechanical property of surface doping [29]. The sensor responses were tested every 10 days for 90 days. As shown in Fig. 10, only a very small degradation can be found in the first 10 days, and the signals keep constant in the following 80 days. Thus a good

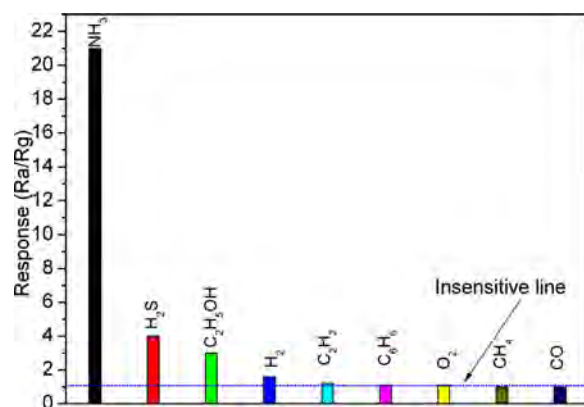


Fig. 9. Responses of $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors to 1 ppm different gases at room temperature.

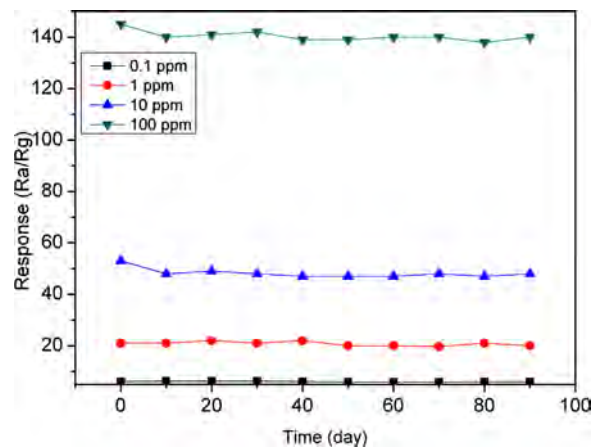
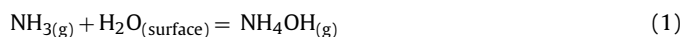


Fig. 10. Stability of $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors in 90 days.

stability is obtained and the surface doping has been proved to meet the demands of sensor application accordingly.

Both In_2O_3 and SnO_2 are semiconducting oxides and the change in resistance is primarily caused by the adsorption and desorption of the gas molecules on the surface of the sensing material. At room temperature, there exists oxygen adsorption on the surface of the In_2O_3 nanofibers, while the oxygen-reaction is not employed to detect NH_3 [30]. The decrease of resistance at room temperature can be explained by the surface reaction of NH_3 with physisorbed H_2O or by proton conductivity via NH_4^+ cations [30]. The reaction between NH_3 and surface adsorbed H_2O can be simply described as:



Ammonium hydroxide NH_4OH produced during the surface reaction is volatile in nature. The large surface-to-volume ratio and web-like micro-structures of the In_2O_3 nanofibers are benefit for the volatility of NH_4OH molecules [27]. The SnO_2 nanoparticles coating on the fiber surface can provide more absorbing sites for gas molecules [31–35]. Thus the sensors with high response and quick response/recovery properties are obtained. This mechanism has been discussed by Sberveglieri and Patil previously [30,36]. To prove it, the $\text{SnO}_2/\text{In}_2\text{O}_3$ -2 nanofiber sensors were also tested at various RH levels (at 25°C) and AC conditions. As shown in Fig. 11, the response decreases at both 1% RH and 54% RH. The lower response at 1% RH may due to the deficient water-molecules for NH_3 reaction. The decreased value at 54% RH can be understood by the affected initial resistance (R_a) and final resistance (R_g) [18]. The

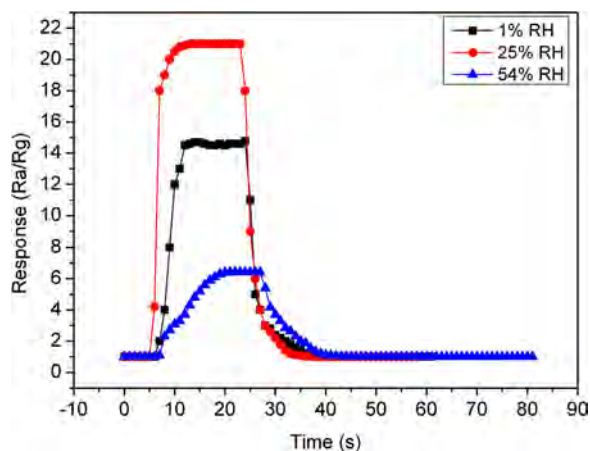


Fig. 11. Response-time curves of SnO₂/In₂O₃-2 nanofiber sensors to 1 ppm NH₃ at 1%, 25%, and 54% RH (room temperature).

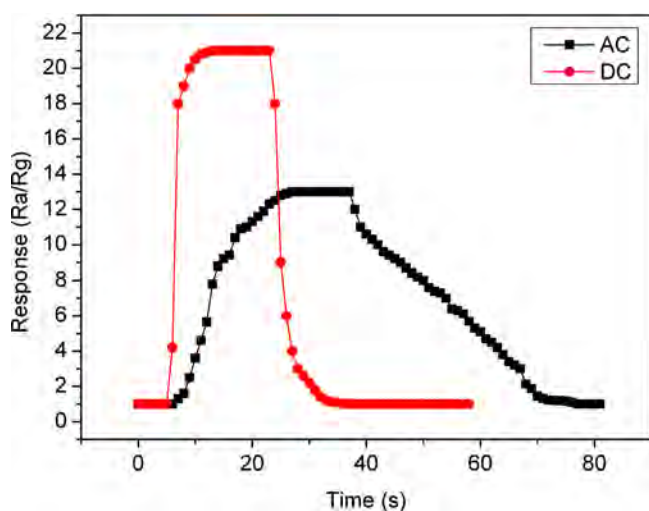


Fig. 12. Response-time curves of SnO₂/In₂O₃-2 nanofiber sensors to 1 ppm NH₃ at AC 1 V, 1 kHz and DC 5 V (room temperature).

sensor performance at AC 1 V, 1 kHz is shown in Fig. 12. Much lower response and longer response and recovery times are observed, which are related to the un-suitable sensor substrates (substrate size, electrode number, electrode width, electrode length, and electrode distance) or testing parameters (voltage and frequency) [37].

4. Conclusions

In conclusion, SnO₂ nanoparticles coated In₂O₃ nanofibers with excellent NH₃ sensing properties at room temperature are synthesized via a sol-gel process and a simple electrospinning method. The response increases from 4 to 21 to 1 ppm NH₃, meanwhile, the response time decreases from 16 to 7 s, and the recovery time decreases from 15 to 10 s, respectively. The higher surface area of the sample and the higher sensing performance can be found. The results provide a possible platform to design high performance gas sensors with one-dimensional nanomaterials.

Acknowledgments

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Biographies

Qi Qi received his Ph.D. degree in the field of microelectronics and solid state electronics in 2010 from Jilin University. Now, he is carrying out a postdoctoral research related to the synthesis of 1D sensing materials in college of chemistry, Jilin University.

Pei-Pei Wang received her B.S. degree from the college of chemistry, Northeast Dianli University, China in 2010. She entered the Ph.D. course in September 2012, Jilin University. She is majored in the synthesis of sensing nanocomposites.

Jun Zhao received her B.Sc. degree from Changchun Institute of Technology, China in 2006. She is currently undertaking her Ph.D. in college of chemistry, Jilin University. She is majored in gas sensing materials with controlled structure.

Liang-Liang Feng received her B.S. degree from department of chemistry, Zhoukou Normal University in 2011. Now, she is a postgraduate student in college of chemistry, Jilin University. She is majored in the synthesis of nanomaterials.

Li-Jing Zhou received her B.Sc. degree in 2009 from Heibei North University, China. Presently, she is a Ph.D. student in college of chemistry, Jilin University. She is now engaged in the synthesis of sensing materials.

Rui-Fei Xuan is a master student at College of Materials Science and Engineering, China University of Mining and Technology in China, and he now is studying in State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University in China. His research interest is the synthesis of metal oxide materials.

Yi-Pu Liu is an undergraduate student at College of Chemistry, Jilin University in China. Her research interest is the synthesis of advanced functional materials.

Guo-Dong Li received his Ph.D. degree in the field of Chemistry in 2001 from Jilin University. He was appointed a full professor in College of Chemistry, Jilin University in 2006. Now, he is interested in the field of sensing functional materials and chemical sensors.