A Novel Low-concentration Isopropanol Gas Sensor Based on Fe-doped ZnO Nanoneedles

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***Abstract*—This work reports a highly sensitive Fe doped ZnO nanoneedles based gas sensor for detection at low concentrations. Pure and Fe doped ZnO were synthesized via a hydrothermal method and spray-coated onto an alumina substrates. The sensing properties were investigated under different temperatures and concentrations. Fe doping significantly increased the sensing performance of ZnO nanoneedles. The 5 at% Fe doped sensor showed the best response to isopropanol and the optimal working temperature is 275°C. The sensor showed a high response to 250 ppb isopropanol, together with high stability under different humidity levels.**

Keywords- ZnO; Fe doping; gas sensor; isopropanol; lung cancer.

I. INTRODUCTION

To realize the early detection of lung cancer via e-nose, sensors with high response to low concentrations of Volatile Organic Compounds (VOCs) biomarkers are necessary. Metal oxide sensor is a good candidate for the sensors in e-nose [1][2]. Isopropanol is one of the important biomarkers of lung cancer. The concentration of isopropanol in the breath of lung cancer patients can come up to over 270 ppb, with an average concentration of 438 ppb [3]. In this work, we present a sensor that can detect ppb level isopropanol as low as to 250 ppb with good stability in humidity.

In Section Ⅱ, we will introduce the method we use to synthesize the sensing materials, characterizing the as-synthesized powders and making the sensing test. In Section Ⅲ, the results of characterization and sensing test are shown. We conclude our work in Section IV.

II. MATERIALS AND METHODS

The ZnO nanoneedles are synthesized via a simple hydrothermal method. 3×10^{-3} mol of $Zn(NO_3)\bullet 2H_2O$ were dissolved into 44 ml of deionized water. Meanwhile, 1 g of Cetyltrimethylammonium Bromide (CTAB) was dissolved in 22 ml of ethanol. After that, 3×10^{-2} mol of NaOH was added into the $Zn(NO_3)_2$ solution, then the two different solutions were mixed, followed with the addition of 10 ml ethylenediamine. The solution was treated at 100°C for 2 h in an oven. The obtained powder was washed and dried in an oven overnight. To prepare the Fe-doped ZnO needles, $Fe(NO_3)_3$ solutions with different concentrations were slowly added into the $Zn(NO_3)_2$ solution before the addition of NaOH. The doping contents of Fe were 1%, 3% and 5% by atom ratio, which are written as 1 at%, 3 at% and 5 at% Fe-ZnO. The sensors are prepared on alumina substrate with gold interdigitated electrodes by spraying.

The as-synthesized powders are characterized by Scanning Electron microscopy (SEM) [4], Energy-dispersive X-ray spectroscopy (EDS) [5] and X-ray diffraction (XRD) [6]. The gas sensing test is carried out in a home-made system. The gas flow is controlled at 1 L/min by 3 flow meters. Before the sensing test, all the sensors were pre-heated at 350°C for 1 week. The response of the sensors was defined as $S=(R_a-R_g)/R_g$. In the equation, S refers to the response of the sensor, Ra represents the electrical resistance in air, R_g represents the electrical resistance the target gas. The response and recovery time were respectively defined as the time needed to reach 90% of the maximum response and the time needed to recover to 110% of the baseline.

III. RESULTS AND DISCUSSION

The XRD of the samples indicated that all the samples are ZnO or Fe-doped ZnO without any other impurities. The main peak of Fe-ZnO has a small shifting to the left with the increase of the amount of Fe, indicating that the Fe^{3+} was doped into the ZnO. The SEM picture of pure and different Fe-doped ZnO are shown in Figure 1. All the samples have needle like nanostructure. The Fe doping changed the structure of ZnO, making the needles become smaller.

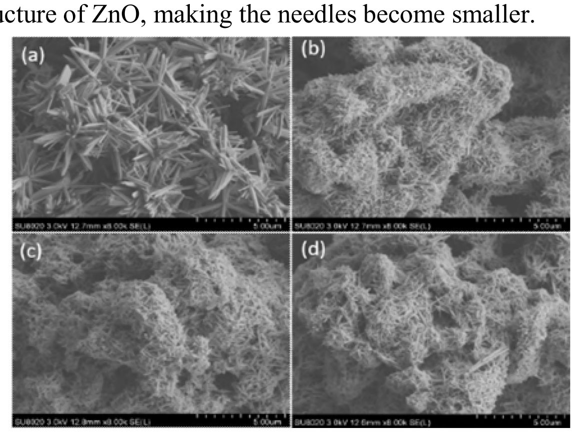

Figure 1. SEM image of (a) pure ZnO needles; (b) 1 at% Fe-doped ZnO; (c) 3 at% Fe-doped ZnO; (4) 5 at% Fe doped ZnO.

Fig. 2 (a) and (b) exhibited the resistance change and gas sensing performance of Fe-ZnO to different concentrations of isopropanol at 275°C with 50% Relative Humidity (RH). The resistance of the four sensors decreased significantly with the presence of isopropanol, which indicated that the Fe-doped ZnO remains n-type. The response of 5 at% Fe-doped ZnO nanoneedles can reach 23.6 when the concentration of isopropanol is 5 ppm. When the concentration of isopropanol decreased to 250 ppb, the response still can reach around 4.7. The response and recovery time of 5 at% Fe-doped ZnO to 5 ppm ZnO is calculated as 51 s and 762 s respectively. Fig. 2 (c) shows the response to 5 ppm isopropanol at different temperature. It can be seen that the Fe doping not only increases the response, but also decreases the optimal operating temperature. Fig. 2 (d) is the response to 5 ppm isopropanol under different RH. From 25% to 100%, the response of 5 at% Fe-ZnO is not affected by RH a lot. In Table 1, we compared the results with some other works.

For the gas sensing mechanism, we consider that the isopropanol reacted with both the adsorbed oxygen ions and the Fe^{3+} doped in the ZnO.

IV. CONCLUSION

ZnO and Fe-doped ZnO nanoneedles were synthesized via a simple one-step hydrothermal method. The Fe doping changed the morphology of ZnO. The Fe-doped ZnO retains the n-type semiconductor property. The 5 at% Fe-doped ZnO showed the best sensing performance to isopropanol at 275°C with fast response. The improvement of sensing properties is considered as the adjustment of the band structure by the doping of Fe.

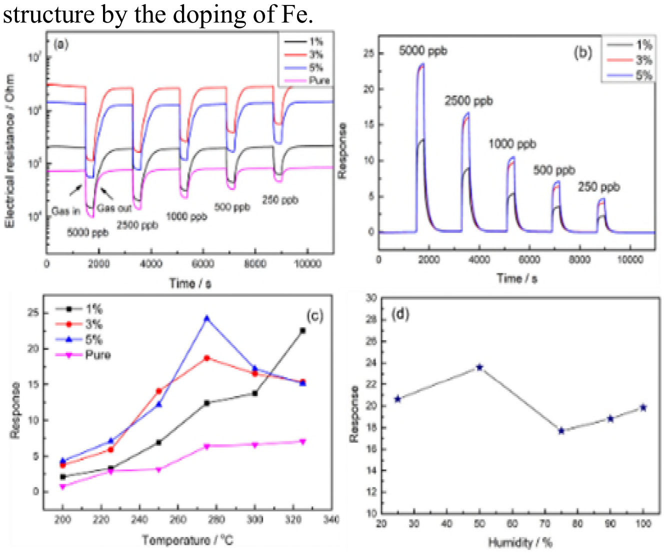

Figure 2. (a) Electrical resistance change (b) response of pure and Fe doped ZnO nanoneedles to isopropanol. (c) Response to 5 ppm isopropanol under different operating temperature (d) Response of 5 at% Fe-doped ZnO under different RH%

TABLE I. COMPARISON OF THE GAS SENSING RESULT OF ISOPROPANOL SENSORS BETWEEN THIS WORK AND SOME PREVIOUS WORKS

Material	Temperature (°C)	Concentration (ppm)	Response	Ref
CdO-ZnO	248°C	1000	174.8	[4]
$ZnO-ZrO_2$	350°C	100	33.4	[5]
$Pd@Co_3O_4$-ZnO	240°C	1	1.8	[6]
Fe-ZnO	275°C	5	23.6	This work

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REFERENCES

[1] J. Kaur, K. Anand, K. Anand and R. Singh, "WO_3 nanolamellae/reduced graphene oxide nanocomposites for highly sensitive and selective acetone sensing." J Mater Sci, vol. 53, pp. 12894-12907, 2018.

[2] H. Duan et al., "Controllable synthesis of Ho-doped In_2O_3 porous nanotubes by electrospinning and their application as an ethanol gas sensor." J Mater Sci, vol. 53, pp. 3267–3279, 2018.

[3] R. Machado et al., "Detection of Lung Cancer by Sensor Array Analyses of Exhaled Breath." American Journal of Respiratory and Critical Care Medicine, vol. 171, pp. 1286-1291, 2005.

[4] X. Geng, C. Zhang, Y. Luo and M. Debliquy, "Flexible NO_2 gas sensors based on sheet-like hierarchical ZnO_{1-x} coatings deposited on polypropylene papers by suspension flame spraying." Journal of the Taiwan Institute of Chemical Engineers, vol. 75, pp. 280-286, 2017.

[5] C. Zhang, X. Geng, H. Liao, C. Li and M. Debliquy, "Room-temperature nitrogen-dioxide sensors based on ZnO_{1-x} coatings deposited by solution precursor plasma spray. Sensors and Actuators B: Chemical, vol 242, pp. 102-111, 2017.

[6] Y. Luo, C. Zhang, B. Zheng, X. Geng and M. Debliquy, "Hydrogen sensors based on noble metal doped metal-oxide semiconductor: A review." International Journal of Hydrogen Energy, vol 42, pp. 20386-20397, 2017,

[7] X. Cai et al., "Isopropanol sensing properties of coral-like ZnO–CdO composites by flash preparation via self-sustained decomposition of metal-organic complexes." Sensors and Actuators B: Chemical, vol. 198, pp. 402-410, 2014.

[8] Q. Jin, W. Wen, S. Zheng and J. Wu, "Enhanced isopropanol sensing of coral-like $ZnO–ZrO_2$ composites." Nanotechnology, vol. 31, pp. 402-410, 2014.

[9] Y. Sun et al., "Electrospinning preparation of $Pd@Co_3O_4$-ZnO composite nanofibers and their highly enhanced VOC sensing properties." Materials Research Bulletin, vol. 109, pp. 255-264, 2019.

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