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Electrospun zinc oxide nanospheres for ultrasensitive room-temperature gas sensors*

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Zinc oxide (ZnO) nanospheres with excellent sensing ability towards formaldehyde were successfully synthesized using a single-capillary electrospinning method. Structural and electrical characteristics of the as-synthesized ZnO nanospheres were systematically investigated. The scanning electron microscope (SEM) images clearly display a novel structure of ZnO with pores distributed on the surface of the nanospheres. The results demonstrate that the ZnO nanospheres possess excellent formaldehyde gas-sensing properties. At room temperature, the response of ZnO nanospheres to formaldehyde with concentration of 100 ppm is determined to be 126.3. In addition, the ZnO nanosphere sensors exhibit short response time of 30 s and short recovery time of 2 s. These excellent gas-sensing properties make the ZnO nanospheres a promising material for the application in environmental monitoring devices.

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Zinc oxide (ZnO) is one of the most important n-type semiconductors and has received considerable attention for potential optoelectronic applications. ZnO has many desirable properties, including a wide bandgap (3.3 eV) and large exciton binding energy (60 meV) at room temperature[1-3]. Recently, various techniques have been developed to improve the optical and electrical properties of ZnO-based gas sensors owing to their low cost, non-toxicity and high stability performance[4]. In general, it is necessary to operate ZnO-based gas sensors at high temperatures or under ultraviolet (UV) irradiation because of their large bandgap. However, this prevents the miniaturization of the gas sensor[5]. When detecting certain gases, explosion and combustion are often a concern, which limits the application of the prepared sensors. Metal oxide semiconductors usually display catalytic properties in the oxidation of reducing gases or volatile organic compounds (VOCs) at high temperatures, leading to the changes in the depletion layer thickness on the metal oxide surface. Therefore, a gas sensor which can operate at room temperature must be designed. To date, a few different-dimensional ZnO-based gas sensors have been designed and fabricated that operate at reduced temperatures. The design strategies for these materials have included increasing the surface area of the sensor, reducing the size of the material and using composite materials[3,6]. In addition, numerous methods have been developed for fabricating ZnO-based gas sensors, such as the hydrothermal method, oil bath method and solid phase synthesis. However, electrospun sensors have high sensitivity with shorter response and recovery times compared with sensors prepared by the methods mentioned above for the high surface-to-volume ratio, high porosity and other outstanding properties[7].

In general, spinning technology is often used to prepare nanofibers. In this paper, we report the development of a ZnO nanosphere-based sensor with excellent formaldehyde sensing performance. The porous ZnO nanospheres were successfully fabricated via single-capillary electrospinning and calcination methods. The gas-sensing properties of the as-synthesized materials towards formaldehyde are also studied. The results demonstrate that the sensor based on ZnO nanosphere exhibits good response and selectivity towards formaldehyde at room temperature.

All chemical reagents were of analytical-grade purity and used without further purification. In a typical process for ZnO nanosphere synthesis, 0.26 g $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 5 mL dimethylformamide. Meanwhile, 0.36 g polyvinylpyrrolidone was dissolved in 2.5 mL ethanol. These two solutions were then mixed and stirred for 6 h at room temperature to obtain a clear and homogeneous solution. The mixture was transferred into a syringe with an attached spinneret and connected to a high-voltage power supply of 22 kV. The final nanospheres were obtained after calcination in a tube furnace at 500 °C for 2 h with heating rate of 2 $°C \cdot min^{-1}$. The as-calcined nanospheres were then characterized.

Morphological and structural investigations of the ZnO nanospheres were performed using a field emission scanning electron microscope (FESEM, Hitachi S-4800) and a Bruker D8 Advance Diffraction diffractometer in

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the 2θ range from 10° to 80°, with Cu Kα radiation (λ=0.154 05 nm) at 40 kV and 40 mA. The gas-sensing properties of the samples were characterized using a WS-60A gas-sensing measurement device (Weisheng Electronics Science and Technology Co. Ltd. China). The response (R) is defined as I_a/I_g, where I_a and I_g are the currents of the sensor in air and in an environment containing the target gas, respectively. Various gases were tested under controlled conditions at room temperature (~300 K). The response time is defined as the time for the sensor to achieve 90% of its final current, and the recovery time is the time for the sensor to return 90% of the current variation when exposed to air.

Fig.1 shows the X-ray diffraction (XRD) pattern of ZnO nanosphere annealed at 500 °C for 3 h in air. Well-defined diffraction peaks are observed which correspond to the (100), (002), (101) (102) and (110) planes of ZnO at 31.701°, 34.341°, 36.271°, 47.631° and 56.561°, respectively. The positions of the diffraction peaks indicate that the ZnO nanospheres are polycrystalline with a hexagonal wurtzite structure, which are matched to the JCPDS file (No.36-1451). The ZnO nanospheres exhibit a large (101) peak intensity and the smallest full-width at half-maximum value, indicating high crystallinity. By applying the Debye-Scherrer relation, the average crystallite size is calculated to be 9.67 nm.

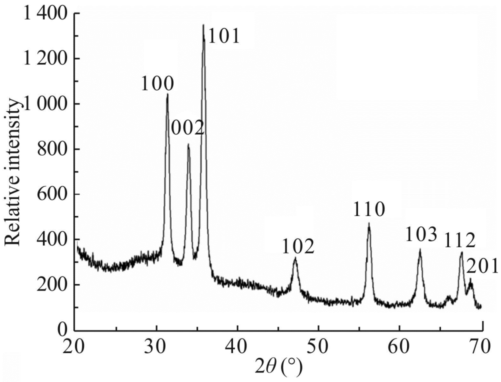


Fig.1 XRD pattern of ZnO nanosphere

The surface morphologies of ZnO nanospheres with and without annealing are shown in Fig.2. The scanning electron microscope (SEM) images display that the nanospheres are very homogeneous and composed of small nanoparticles, which is consistent with the XRD analysis. The nanospheres spontaneously aligned with another to form a porous sponge-like structure with a loose structure, which is considered to be beneficial to gas diffusion and gas detection[8]. From Fig.2, we can see that the shape of the product is transformed from nanowires to nanospheres after calcination at 500 °C. This phenomenon can be attributed to the calcination in the air. After stirring for 6 h, the precursor is very uniform, and zinc nitrate uniformly disperses in the nanowire. With increasing temperature, polyvinyl pyrrolidone (PVP) is gradually melted and zinc nitrate begins to decompose. When the content of zinc nitrate is small, the nanowire fractures and aggregates, the adjacent two or three small zinc oxide become more mobile and very possibly unitetogether to form one particle[9]. These nanospheres with rough surface have a higher surface. Meanwhile, PVP is decomposed into some new organicmolecules, and they stick to the particles, as shown in Fig.2(b).

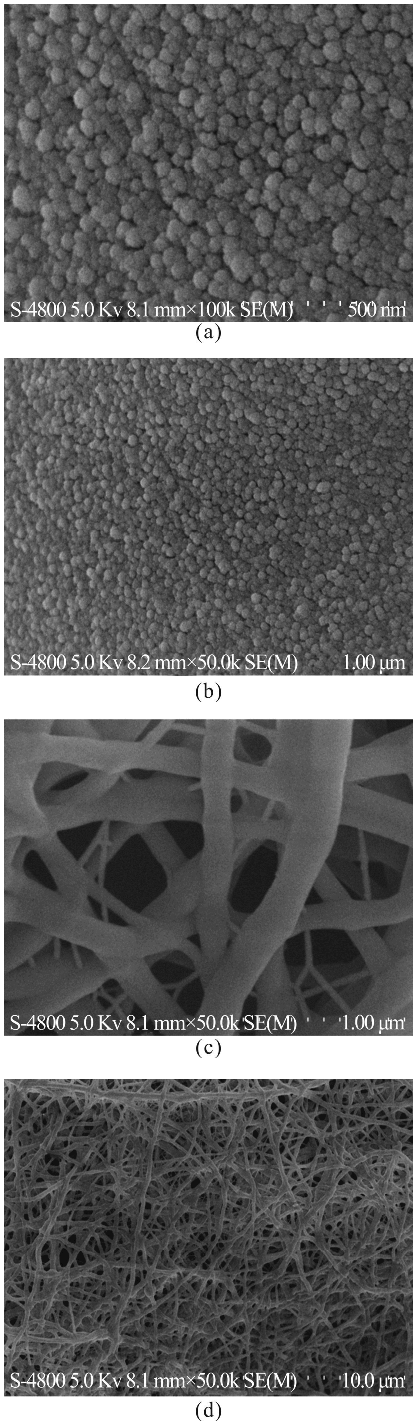
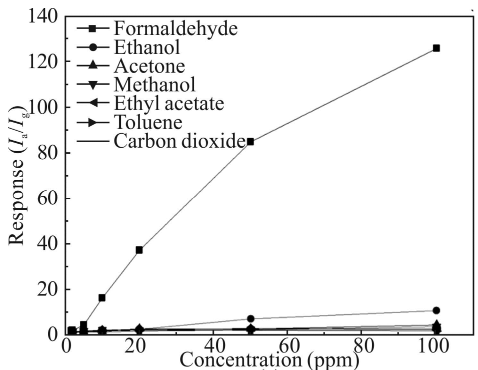


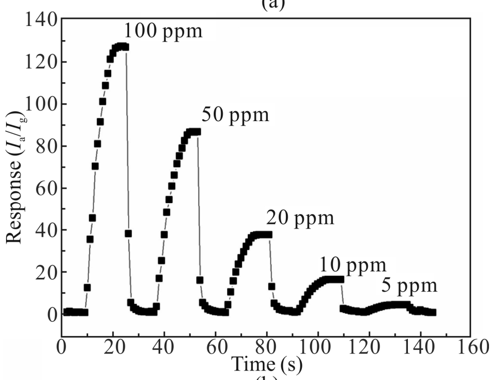
Fig.2 SEM images of (a,b) ZnO nanospheres (after annealing) and (c,d) nanofiber (before annealing)

The gas-sensing properties of the as-prepared ZnO sensor are investigated at room temperature. The response values of the sensor to different gas concentrations at room temperature are shown in Fig.3(a). The gas response of the ZnO nanospheres to formaldehyde is considerably higher than those to other gases, especially when the gas concentration reaches 100 ppm. The response values for various gases are different at room temperature, which may be caused by the intrinsic characteristics of the materials. Previous studies[10,11] have demonstrated that the energies of adsorption, desorption, and the reaction of materials with gases differ depending on their chemical nature, resulting in varying response values at the same operating temperature. The higher response toward formaldehyde can be attributed to the small size of the ZnO nanospheres and their correspondingly large surface area. It is well known that gas-phase chemical reactions can occur on the nanostructure surface. Therefore, the area of the electron depletion layer in the crystalline structure is an important factor governing the operation of the sensor[12]. Decreasing the crystalline size increases the proportion of the electron depletion layer in the crystalline structure. Thus, the ZnO nanospheres have more free electrons than that can be released upon exposure to formaldehyde gas. Therefore, the resistance of the ZnO nanospheres decreases significantly upon formaldehyde adsorption.

Fig.3(b) shows the response-recovery characteristics of the formaldehyde sensor towards the target gas at varying concentrations at room temperature. The results show that the formaldehyde sensor exhibits quick response and recovery properties. For the ZnO nanofiber sensor, the acquired response and recovery times are only 30 s and 2 s, respectively. The results show faster response rate than others reported by literatures[13,14]. Furthermore, the sensor exhibits a strong response to formaldehyde at a concentration of 500 ppm at room temperature. This report is the first regarding the gas sensing properties of ZnO-based sensors.



(a)



(b)

Fig.3 (a) Response versus different concentrations of gas for the ZnO nanofiber; (b) Dynamic response-recovery features of the ZnO sensor for 5—100 ppm formaldehyde at room temperature

In summary, we successfully synthesized ZnO nanospheres by the electrospinning method. The prepared ZnO nanospheres exhibit an excellent sensing ability towards formaldehyde at room temperature. The results demonstrate that the sensor based on ZnO nanosphere has a short response time of 30 s and a recovery time of only 2 s. The results shown herein demonstrate the excellent potential for applications in the efficient detection of formaldehyde in the environment and broader applications for low power consumption sensors.

References

[1] C. Soci, A. Zhang, B. Xiang, S.A. Dayeh, D.P.R. Aplin, J. Park, X.Y. Bao, Y.H. Lo and D. Wang, Nano Lett. **7**, 1003 (2007).

[2] P. Yang, X. Xiao, Y. Li, Y. Ding, P. Qiang, X. Tan, W. Mai, Z. Lin, W. Wu, T. Li, H. Jin, P. Liu, J. Zhou, C.P. Wong and Z.L. Wang, ACS Nano **7**, 2617 (2013).

[3] Y. Zhang, C. Liu, F. Gong, B. Jiu and F. Li, Materials Letters **186**, 7 (2017).

[4] S. Ameen, M.S. Akhtar, H.-K. Seo, Y.S. Kim and H.S. Shin, Chem. Eng. J. **187**, 351 (2012).

[5] B. Gong, T. Shi, W. Zhu, G. Liao, X. Li, J. Huang, T. Zhou and Z. Tang, Sens Actuators B: Chem. **245**, 821 (2017).

[6] S.L. Zhang, S.T. Nguyen, T.H. Nguyen, W. Yang and J.S. Noh, J. Am. Ceram. Soc. **100**, 5629 (2017).

[7] Ding Wang, Minglu Zhang, Zhenlu Chen, Huijun Li, Aiying Chen, Xianying Wang and Junhe Yang, Sensors and Actuators B-Chemical **250**, 533 (2017).

[8] E. Comini and G. Sberveglieri, Materials Today **13**, 28 (2010).

[9] Y. K. Du, P. Yang, Z. G. Mou, N. P. Hua and L. Jiang, J Appl. Polym. Sci. **99**, 23 (2006).

[10] S.T. Navale, D.K. Bandgar, S.R. Nalage, G.D. Khuspe, M.A. Chougule, Y.D. Kolekar, S. Sen and V.B. Patil, Ceramics International **39**, 6453 (2013).

[11] B. Huang, C. Zhao, M. Zhang, Z. Zhang, E. Xie, J. Zhou and W. Han, Appl. Surf . Sci. **349**, 615 (2015).

[12] J. Zhang, S. Wang, Y. Wang, M. Xu, H. Xia, S. Zhang, W. Huang, X. Guo and S. Wu, Sens Actuators B: Chem. **139**, 369 (2009).

[13] ZHENG Xuan , MING An-jie, YE Li, CHEN Feng-hua, SUN Xi-long, LIU Wei-bing, LI Chao-bo, OU Wen, WANG Wei-bing and CHEN Da-peng, Optoelectronics Letters **12**, 308 (2016).

[14] Yanying Cao, Yi He, Xiaoxin Zou and Guo-Dong Li, Sensors and Actuators B-Chemical **252**, 232 (2017).