Synthesis, characterization and acetone sensing performance of ZnFe₂O₄ hollow spheres/RGO composites

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Abstract

ZnFe₂O₄ hollow spheres and ZnFe₂O₄ hollow spheres / RGO composites with different RGO contents were successfully synthesized using a one-pot solvothermal method. The morphology and microstructure of the as-prepared samples were characterized through multiple techniques. The gas-sensing experiments include the effects of operating temperature and RGO mixing mass on the gas-sensing response, the selectivity and the response of the sensor based on 0.5 wt% ZnFe₂O₄/RGO to acetone in various concentrations. The experimental results reveal that the mixing of graphene into ZnFe₂O₄ hollow spheres can improve the performance of the sensors to low-ppm-level acetone vapor, and the sensor based on 0.5 wt% ZnFe₂O₄/RGO exhibits good sensitivity and selectivity to 0.8-10 ppm acetone vapor at 200°C. So, the sensor based on 0.5 wt% ZnFe₂O₄/RGO may be applied to detect diabetes mellitus via quantitative measuring of the acetone from respiratory gases of patients if the response is improved further and the operating temperature is further optimized.

Keywords: ZnFe₂O₄, RGO, composite, gas sensing, acetone

1. Introduction

Acetone, as a volatile organic compound, is chemically active and extremely flammable. It also behaves toxicity, and the long-term exposure to the gas will pose a threat to human health. Furthermore, acetone is also a fat metabolite in the body. According to the related literature⁽¹⁻²⁾, the concentration of acetone in the exhaled gas of healthy people is less than 0.9 ppm, while the content of acetone in exhaled gases of diabetic patients is higher than that of healthy people (the acetone content is higher than 1.8 ppm), can help diagnose diabetes. So, it is

necessary to study novel micro/nano-materials, which can be applied in high-performance gas sensors to detect or monitor the concentration of acetone.

Single metal oxide has been widely studied as gas sensitive material, such as ZnO⁽³⁾, WO₃⁽⁴⁾, α -Fe₂O₃⁽⁵⁾, SnO₂⁽⁶⁾, In₂O₃⁽⁷⁾ and TiO₂⁽⁸⁾. However, the response and recovery characteristics of single-phase gas sensitive materials to VOCs or other reducing gases still need to be enhanced. Multioxides, such as ABO₃, are more selective and sensitive to certain gases than the single oxide. Zinc ferrite (ZnFe₂O₄), a typical spinel ferrite, is a kind of semiconductor with a narrow band gap width (~ 1.9 eV), which possesses a variety of excellent characteristics and attracts much attention in the field of gas sensing. In recent years, the preparation methods of ZnFe₂O₄ gas-sensitive materials mainly include co-precipitation⁽⁹⁻¹⁰⁾, sol-gel method⁽¹¹⁾ and template method⁽¹²⁾, etc., which can prepare ZnFe₂O₄ nanomaterials with different morphologies, such as nanorods and hollow spheres, and are mostly used to detect reducing gases.

As a carbon-based new material, graphene possesses a high specific surface area and a unique structure in which sp² hybrid carbon atoms are tightly packed in a two-dimensional honeycomb lattice. Its applications in thermal, electrical and mechanical fields show the superiority of graphene over traditional materials. Liu et al.⁽¹³⁾ solvothermally synthesized graphene-ZnFe₂O₄ composite and investigated the effects of graphene mixing on the gas sensing performance of acetone vapor. It was found that 0.125 wt% graphene-ZnFe₂O₄ showed the best sensing performance to acetone at 275 °C. However, the operating temperature still needs to lower further for achieving low power consumption and practical application.

Herein, in order to further study the gas sensing performance of graphene-ZnFe₂O₄ composite, we prepared

ZnFe₂O₄ hollow spheres and ZnFe₂O₄ hollow spheres/RGO composites via a one-pot solvothermal method. The morphology, structure and acetone sensing performance were discussed. Moreover, the optimum RGO mixing ratio and operating temperature are 0.5 wt% and 200 °C, respectively.

2. Experimental details

2.1 Synthesis of ZnFe₂O₄ hollow spheres and ZnFe₂O₄ hollow spheres/RGO composite

Firstly, 0.5 mmol of Zn(CH₃COO)₂·2H₂O and 1 mmol Fe(NO₃)₃·9H₂O were dissolved in the mixed homogeneous solution of isopropanol and glycerol. Then the above-mixed solution was added into the Teflon-lined autoclave (100 mL), which was subsequently heated at 180 °C for 12 h and naturally cooled to room temperature. The precursors were obtained by centrifugation and drying. Subsequently, the as-prepared powders were annealed at 400 °C for 2 h in the air with a heating rate of 5 °C·min⁻¹. Ultimately, the ZnFe₂O₄ hollow spheres were obtained.

The preparation of them was similar to synthesis of ZnFe₂O₄ nanospheres. The difference between the two processes is as follows: The GO aqueous dispersion solution was further ultrasonic dispersed, then the mixture of Zn(CH₃COO)₂·2H₂O and Fe(NO₃)₃·9H₂O dissolved in the same mixed organic solvents was added into the GO aqueous dispersion solution. Subsequently, it is necessary to magnetically stirrer the mixture with low speed for 1 h to obtain the desired products: 0.1 wt % ZnFe₂O₄/RGO, 0.25 wt% ZnFe₂O₄/RGO, 0.5 wt % ZnFe₂O₄/RGO, 1 wt% ZnFe₂O₄/RGO.

2.2 Characterization methods and measurement of the gas sensing performance

The surface morphologies and elemental analysis of ZnFe₂O₄/RGO powders were measured by a field-emission scanning electron microscope (S4800 II, Hitachi, Japan). The microstructure of samples was detected by a transmission electron microscope (JEM-2100, Japan).

The obtained pure ZnFe₂O₄ and ZnFe₂O₄/RGO powders were mixed with a certain amount of deionized water to form a paste and were coated on the surface of sensor substrates to fabricate the thin sensing films. Subsequently, the sensor substrates were dried to obtain ZnFe₂O₄/RGO gas sensors. After the aging for 12 h at 300 mA current, a series of pure ZnFe₂O₄ and ZnFe₂O₄/RGO

gas sensors were finally obtained. The gas sensing tests were carried out in a homemade testing system. The temperature of sensors was measured via a domestic digital thermometer, and the temperature was controlled by adjusting the applied voltage. In the study, the sensor response is calculated as: $S = R_{\text{air}} / R_{\text{target gas}}$, where R_{air} and $R_{\text{target gas}}$ is the resistances of the sensors in air and target gas atmosphere, respectively.

3. Results and discussions

3.1 Morphologies and microstructure properties

Fig. 1 shows FE-SEM images of pure ZnFe₂O₄ hollow spheres and ZnFe₂O₄/RGO. The as-synthesized ZnFe₂O₄ powders are spherical and the diameter of spheres is 800-1000 nm. It can also be seen from Fig. 1 (a) that the pure ZnFe₂O₄ hollow spheres are composed of small-size nanosheets. Moreover, the diameter of ZnFe₂O₄/RGO powders has no change when the RGO content increases from 0.1 to 1wt%, as shown in Fig. 1 (b), (c), (d), and (e). However, when the RGO content exceeds 0.25 wt%, there are a part of ZnFe₂O₄ hollow spheres which are composed of small-size nanoparticles, the variation may be resulted from that more aqueous solution are introduced into the organic solvent as the increase of RGO content.

Fig. 1. FE-SEM images of (a) pure ZnFe₂O₄ hollow spheres and (b-e) ZnFe₂O₄/RGO (RGO contents are 0.1 wt%, 0.25 wt%, 0.5 wt% and 1 wt%, respectively).

TEM images of pure ZnFe_2O_4 hollow spheres and 0.5 wt% - $\text{ZnFe}_2\text{O}_4/\text{RGO}$ samples are shown in Fig. 2, which further indicates the as-synthesized pure ZnFe_2O_4 and $\text{ZnFe}_2\text{O}_4/\text{RGO}$ powders are both hollow sphere structure. Furthermore, when RGO is introduced in the ZnFe_2O_4 hollow nanomaterial, the surface of ZnFe_2O_4 spheres become more regular, which is consistent with the results shown in SEM images. Moreover, RGO sheets are not enough obvious to be observed, which may owing to the smaller sheet size of graphene.

Fig. 2. TEM images of (a) pure ZnFe_2O_4 hollow spheres and (b) $\text{ZnFe}_2\text{O}_4/\text{RGO}$.

3.2 Gas sensing performance

Fig. 3 shows the responses of five $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensors to 100 ppm acetone vapor at 150 - 225 °C. The responses of all the five sensors obtain a certain enhancement when the operating temperature increases from 150 °C to 200 °C. The variation should be attributed to the low surface activation energy of sensing layer under low temperature. When the operating temperature is 200 °C, 0.5 wt% $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensor can reach the highest value of 70.4. When the temperature is further increased, the responses decrease quickly, which is ascribed that the excessive temperature leads to the fast diffusion of acetone molecules on the surface of sensing materials. Thus, the optimal operating temperature is chosen as 200 °C.

Fig. 3. The responses of ZnFe_2O_4 and four $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensors to 100 ppm acetone vapor at 150 - 225 °C.

Subsequently, the dynamic response/recovery curves of all five $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensors to 0.8 - 10 ppm acetone vapor at 200 °C are tested, as shown in Fig. 4. It could be observed that the significant enhancement of the response when the mass fraction of RGO increases from 0 to 0.5 wt%. Especially, the sensor based on 0.5 wt% - $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensor shows the best sensing performance. The response to 10 ppm acetone vapor is 8.18, and the response to 0.8 ppm is 1.50. However, the response starts to decrease with the further increase of RGO content.

Fig. 4. Dynamic response/recovery curves of ZnFe_2O_4 and four $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensors to 0.8 - 10 ppm acetone vapor at 200 °C.

Herein, ethanol, methanol and formaldehyde are selected to measure the selectivity of 0.5 wt% - $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensor at 200 °C. The responses to 10 ppm acetone, ethanol, methanol and formaldehyde are 8.18, 2.76, 2.05 and 1.31, respectively. Hence, 0.5 wt% - $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensor has a good selectivity to 10 ppm acetone vapor.

4. Conclusions

In summary, we found that the response of the sensors based on ZnFe_2O_4 to low-ppm-level acetone vapor can be improved by mixing graphene. The RGO mass fractions of as-synthesized $\text{ZnFe}_2\text{O}_4/\text{RGO}$ are 0.1, 0.25, 0.5 and 1wt%. With the introducing of the RGO, the sphere size has no obvious change whereas the surface structure was modified. The 1 wt% - $\text{ZnFe}_2\text{O}_4/\text{RGO}$ sensor exhibits fine sensitivity and good selectivity to 10 ppm acetone vapor at 200 °C, the response of 1 wt% - $\text{ZnFe}_2\text{O}_4/\text{RGO}$ and pure ZnFe_2O_4 sensor to 10 ppm acetone are 8.18 and 3.40, respectively. This sensor shows a good potential for the detection of acetone vapor in practical application. It may be applied to detect diabetes mellitus via measuring the acetone vapor if

the response is improved further and the operating temperature is lower as well as the amount relation of sensing response versus concentration of acetone is found.

References

- (1) Marco Righettoni, Antonio Tricoli, and Sotiris E. Pratsinis : “Si:WO₃ sensors for highly selective detection of acetone for easy diagnosis of diabetes by breath analysis”, *Analytical Chemistry*, Vol. 82, No. 9, pp. 3581-3587, 2010
- (2) Luís F. da Silva, Ariadne C. Catto, Waldir Avansi Jr., Laecio S. Cavalcante, Valmor R. Mastelaro, Juan Andres, Khalifa Aguir, and Elson Longo : “Acetone gas sensor based on α -Ag₂WO₄ nanorods obtained via a micro-wave-assisted hydrothermal route”, *Journal of Alloys and Compounds*, Vol. 683, pp. 186-190, 2016
- (3) Xin Geng, Chao Zhang, Yifan Luo, and Marc Debliquy : “Flexible NO₂ 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
- (4) Elisabeth M. Preiß, Andreas Krauß, Ville Kekkonen, Nicolae Barsan, and Helmut Seidel : “Characterization of WO₃ thin films prepared by picosecond laser deposition for gas sensing”, *Sensors and Actuators B: Chemical*, Vol. 248, pp. 153-159, 2017
- (5) Shuai Liang, Jianping Li, Fei Wang, Jilong Qin, Xiaoyong Lai, and Xingmao Jiang : “Highly sensitive acetone gas sensor based on ultrafine α -Fe₂O₃ nanoparticles”, *Sensors and Actuators B: Chemical*, Vol. 238, pp. 923-927, 2017
- (6) Byeong-Guk Kim, Dong-Gun Lim, Jae-Hwan Park, Young-Jin Choi, and Jae-Gwan Park : “In-situ bridging of SnO₂ nanowires between the electrodes and their NO₂ gas sensing characteristics”, *Applied Surface Science*, Vol. 257, No. 10, pp. 4715-4718, 2011
- (7) Xiumei Xu, Dawei Wang, Jing Liu, Peng Sun, Yue Guan, Heng Zhang, Yanfeng Sun, Fengmin Liu, Xishuang Liang, Yuan Gao, and Geyu Lu : “Template-free synthesis of novel In₂O₃ nanostructures and their application to gas sensors”, *Sensors and Actuators B: Chemical*, Vol. 185, pp. 32-38, 2013
- (8) Jawad Nisar, Zareh Topalian, Abir De Sarkar, Lars Österlund, and Rajeev Ahuja : “TiO₂-based gas sensor: a possible application to SO₂”, *ACS Applied Materials and Interfaces*, Vol. 5, No. 17, pp. 8516-8522, 2013
- (9) Mahmoud Goodarz Naseri, Elias B. Saion, Mansor Hashim, Abdul Halim Shaari, and Hossein Abasstabar Ahangar : “Synthesis and characterization of zinc ferrite nanoparticles by a thermal treatment method”, *Solid State Communications*, Vol. 151, No. 14, pp. 1031-35, 2011
- (10) Jayvant Y. Patil, Digambar Y. Nadargi, Jyoti L. Gurav, I.S. Mulla, and Sharad S. Suryavansh : “Glycine combusted ZnFe₂O₄ gas sensor: Evaluation of structural, morphological and gas response properties”, *Ceramics International*, Vol. 40, No. 7, pp. 10607-10613, 2014
- (11) Archana Singh, Ajendra Singh, Satyendra Singh, Poonam Tandon, B.C. Yadav, and R.R. Yadav : “Synthesis, characterization and performance of zinc ferrite nanorods for room temperature sensing applications”, *Journal of Alloys and Compounds*, Vol. 618, pp. 475-483, 2015
- (12) Baojun Liu, Xinyong Li, Qidong Zhao, Yang Hou, and Guohua Chen : “Self-templated formation of ZnFe₂O₄ double-shelled hollow microspheres for photocatalytic degradation of gaseous o-dichlorobenzene”, *Journal of Materials Chemistry A*, Vol. 5, No. 19, pp. 8909-8915, 2017
- (13) Feng Liu, Xiangfeng Chu, Yongping Dong, Wangbing Zhang, Wenqi Sun, and Liming Shen : “Acetone gas sensors based on graphene-ZnFe₂O₄ composite prepared by solvothermal method”, *Sensors and Actuators B: Chemical*, Vol. 188, pp. 469-474, 2013