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High response and excellent selectivity acetone sensor based on γ-Fe_2O_3 hollow microspheres

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ABSTRACT

The γ-Fe_2O_3 hollow microspheres were synthesized by a simple solvothermal method and a subsequent two-step annealing process. The sensor based on γ-Fe_2O_3 hollow microspheres exhibited an ultra-fast response time (1s), high response (232.7), and excellent selectivity to 100 ppm acetone at the optimum operating temperature (173 °C). The excellent gas sensing performance could be attributed to the large specific surface area (182.6 m^2g^{-1}) and a large number of oxygen vacancies, which would enhance the adsorption of oxygen molecules on the surface of the material. Moreover, the sensor achieves a response of 5.64 to 1 ppm acetone, which enables the prepared γ-Fe_2O_3 hollow microspheres a promising candidate for clinical detection of diabetic ketosis.

1. Introduction

Acetone is considered a marker for the clinical detection of diabetes mellitus. Non-invasive and painless detection of diabetes can be achieved by detecting acetone in the exhaled breath of diabetic patients. The threshold of acetone concentration in exhaled gas for clinical detection of diabetes is 1.8 ppm [1]. Therefore, the development of a miniaturized acetone gas sensor with low cost, high sensitivity, excellent selectivity, low detection limit, and fast response is of great significance for the clinical detection of diabetes mellitus. As a promising magnetic material, γ-Fe_2O_3 has been widely used as high-density magnetic material, catalyst, water treatment, and pigment. Meanwhile, owing to the advantages of low cost and high sensitivity, γ-Fe_2O_3 can be used as a sensing material to detect polluting gases and volatile organic compound gases (VOCs). For example, Zhang et al. prepared a high-sensitivity H_2S sensor based on γ-Fe_2O_3 (R_{air}/R_{gas} = 520.73, 97 ppm) [2]. Song et al. prepared hollowed-out hierarchical γ-Fe_2O_3 microrods to 100 ppm acetone with a response of 125.5 [3]. In this work, γ-Fe_2O_3 hollow microspheres were synthesized by the solvent thermal method, and their gas sensing properties were investigated.

2. Experimental

2.1. Synthesis of Fe_2O_3 hollow microspheres

Ferric nitrate monohydrate ($Fe(NO_3)_3{\cdot}9H_2O$, 99.8 %), glycerinum ($C_3H_8O_3$), and ethanol absolute (C_2H_5OH) were purchased from Beijing Chemical Works. All chemicals were used without further treatment. In a typical synthesis, 0.271 g of $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in a mixed solution of 10 mL of glycerol and 70 mL of isopropanol, stirred magnetically for 10 min, and then poured the homogeneous clear solution into a 100 mL Teflon-lined stainless steel autoclave and reacted at 190 °C for 12 h. After the autoclave was cooled to room temperature, the product was centrifuged and washed several times with deionized water and ethanol, and then dried at 70 °C for 12 h. The product was then calcined in a tube furnace at 350 °C for 2 h in an N_2 and air atmosphere at a heating rate of 1 °C min^{-1}, respectively. A reddish-brown powder was obtained.

2.2. Characterization

The crystal structure and chemical states of the sample were investigated via X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The morphologies of the sample is observed by scanning electron microscopy (SEM). The specific surface area and pore

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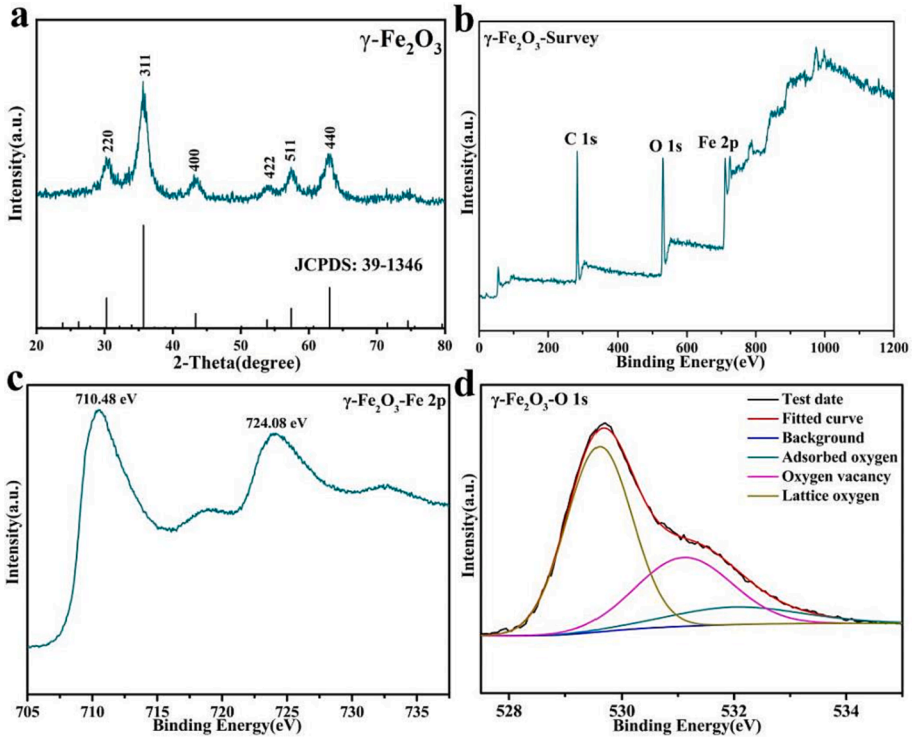

Fig. 1. (a) XRD pattern, (b) XPS survey spectra, (c) High resolution Fe 2p spectra, and (d) high resolution O 1s spectra of the γ-Fe_2O_3 hollow microspheres.

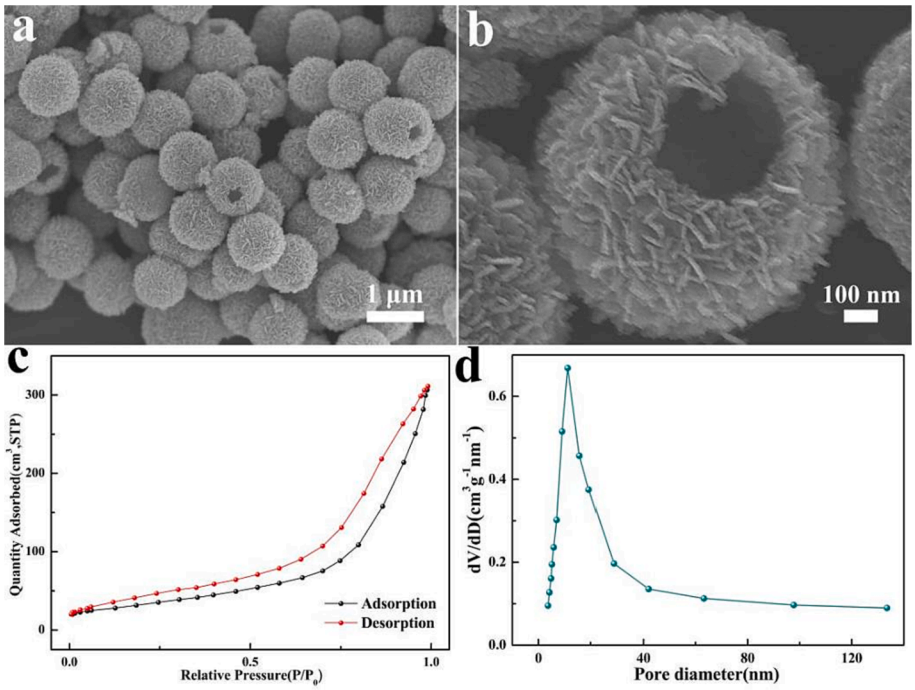

Fig. 2. FESEM images of γ-Fe_2O_3 hollow microspheres: (a) Low magnification; (b) high magnification. (c) Nitrogen adsorption–desorption isotherms and (d) Pore size distribution plot of γ-Fe_2O_3 hollow microspheres.

size distribution of the sample were analyzed by Brunauere Emmette Teller (BET) and Barrett-Joyner-Halenda (BJH), respectively. The performances of the gas sensor were carried out by a CGS-8 intelligent gas sensing analysis system. The response of the sensor was defined as $S = R_a/R_g$. R_a and R_g represent the resistance of the sensor in air and the target gas, respectively. The response and recovery time are defined as the time it takes for the sensor to complete 90 % of the total resistance change during the response and recovery process.

3. Results and discussion

3.1. Characterization

It can be seen from XRD characterization (Fig. 1**a**) that all the

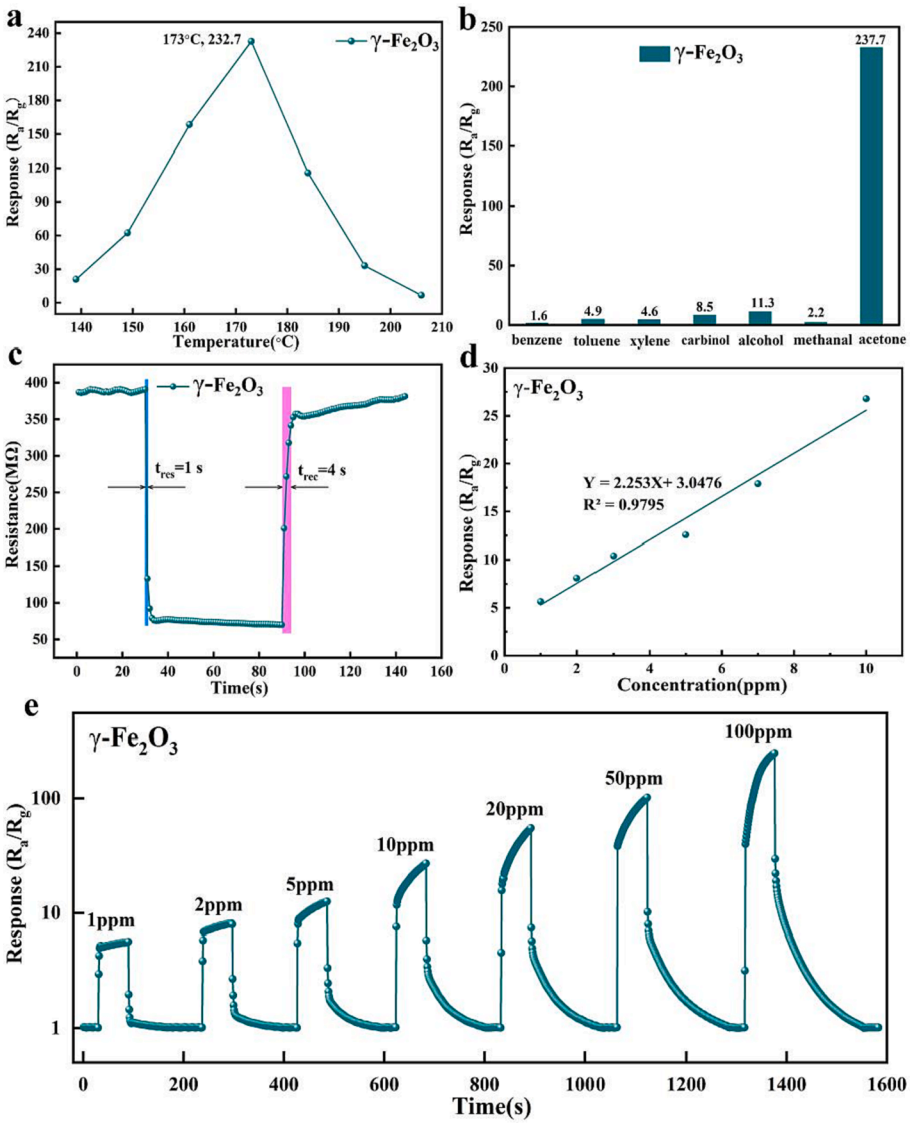

Fig. 3. (a) Responses of the γ-Fe_2O_3 sensor to 100 ppm acetone at different operating temperatures, (b) Responses of the γ-Fe_2O_3 sensor to 100 ppm various tested gases at 173 °C. (c) The resistance transient curve of the γ-Fe_2O_3 sensor to 100 ppm acetone at 173 °C. (d) Responses of the sensor based on γ-Fe_2O_3 hollow microspheres as a function of acetone concentration (1–10 ppm) at 173 °C. (e) Concentration-dependent response curves of the γ-Fe_2O_3 sensor to 1–100 ppm acetone at 173 °C.

apparent diffraction peaks correspond well to the standard card of γ-Fe_2O_3 (JCPDS Card No. 39-1346), indicating that the synthesized material is γ-Fe_2O_3 with high purity and good crystallinity [4]. The XPS spectrum indicates that only C, Fe and O were observed, where C was introduced as a reference standard (Fig. 1**b**). Fig. 1**c** shows that the two peaks in the Fe 2p spectrum located at 710.48 and 724.08 eV corresponding to Fe $2p_{3/2}$ and $Fe2p_{1/2}$ can be attributed to Fe^{3+}. The XPS spectrum of O 1s shown in Fig. 1**d** can be further decomposed into three individual peaks with binding energies at 529.58, 531.08, and 532.18 eV, which can be attributed to lattice oxygen, oxygen vacancies, and chemisorbed oxygen, respectively. The percentage of oxygen vacancies is 31.2 %, which facilitates the adsorption of oxygen molecules on the surface of the material and therefore improves its gas sensing performance [5]. The SEM images (Fig. 2**a and b**) show that the morphologies of the prepared γ-Fe_2O_3 sample are uniform hollow microspheres with a diameter of about 0.8–1 μm. The BJH characterization result indicates that the prepared γ-Fe_2O_3 hollow nanospheres have a mesoporous structure (Fig. 2**c**) with a pore size of about 11.2 nm. the BET characterization result shows that the γ-Fe_2O_3 hollow nanospheres have a large specific surface area (182.6 m^2g^{-1}), which can facilitate the adsorption of gas molecules on the surface of the material (Fig. 2**d**).

3.2. Gas sensing characteristics

To determine the optimum operating temperature of the γ-Fe_2O_3 sensor, the responses to 100 ppm acetone gas were tested in the range of 140–210 °C and the results were shown in Fig. 3**a**. The response of the γ-Fe_2O_3 sensor reaches its maximum value (232.7) when the operating temperature is 173 °C. Therefore, 173 °C is considered to be the optimum operating temperature for the γ-Fe_2O_3 sensor. This "increase-maximum-decrease" phenomenon can be explained by the following processes. As the operating temperature increases, the acetone molecules gain enough energy to overcome the activation energy barrier and react with the adsorbed oxygen. However, when the temperature is too high, the adsorption capacity of the gas decreases, resulting in a decrease in the response. All subsequent gas sensing performance tests are carried out at 173 °C. Fig. 3**b** shows the cross-response properties of the γ-Fe_2O_3 sensor for several VOC gases with a concentration of 100 ppm. It is clear that the prepared γ-Fe_2O_3 hollow nanospheres show the highest response to acetone. Fig. 3**c** shows the resistance transient curve of the γ-Fe_2O_3 sensor to 100 ppm acetone at 173 °C. It can be seen that the response and recovery time are 1 and 4s, indicating that the γ-Fe_2O_3 sensor can achieve rapid detection of acetone.

When the sensor was exposed to lower concentrations of acetone (1–10 ppm), the relationships between the concentrations of acetone

Table 1
The acetone sensing performances of gas sensors based on similar materials reported in the literature.

Sensing Materials	Conc/ ppm	Response	Res/rec time (s)	Temp/ °C	Ref.
γ-Fe_2O_3 microrods	100	125.5	0.9/15	220	[3]
α/γ-Fe_2O_3 micro flowers	1500	160	95/25	320	[6]
alpha-Fe_2O_3 hollow spheres	100	46.6	1/12	220.4	[7]
3D α-Fe_2O_3	50	19.14	7/8	220	[8]
γ-Fe_2O_3 hollow microspheres	100	232.7	1/4	173	This work

Conc.: Concentration; Res: Response; Temp: Temperature; Ref: Reference.

and the corresponding responses are shown in Fig. 3**d**. The concentration–response curve can be fitted as $Y = 2.253X + 3.0476$, where Y is the response of the sensor and X is the concentration of the tested acetone gas. The correlation coefficient R^2 was 0.9795, indicating a good linear relationship. The response of the sensor to 1 ppm acetone is 5.64, but the clinical threshold for diagnosing diabetes is 1.8 ppm, thus satisfying the need for clinical diagnosis of diabetes. The acetone concentration-dependent response curve of the γ-Fe_2O_3 sensor exhibits good reproducibility and reversibility (Fig. 3**e**). To evaluate the sensing performances of γ-Fe_2O_3 hollow microspheres, we listed the acetone sensing performances of γ-Fe_2O_3 hollow microspheres and several similar materials (Table 1), indicating that our sensor has the best sensing performances to acetone [6–8].

3.3. Gas sensing mechanism

γ-Fe_2O_3 is a typical *n*-type semiconductor where the main carriers are free electrons. When the γ-Fe_2O_3 sensor is exposed to air, O_2 molecules adsorbed on the surface of the material captures the free electrons from the conduction band to convert into adsorbed oxygen negative ions (O_2^- and O^-), thus reducing the concentration of conducting electrons and exhibiting a high resistance state [7]. When the γ-Fe_2O_3 sensor is exposed to an acetone atmosphere, the adsorbed acetone gas molecules react with the adsorbed oxygen ions to produce carbon dioxide and water vapor [9,10]. During this process, free electrons trapped by oxygen molecules are released into the conduction band, which will result in a narrowing of the electron depletion layer and therefore a decrease in the resistance of the sensor.

4. Conclusions

In this work, γ-Fe_2O_3 hollow microspheres were prepared by a combination of a solvothermal method and a two-step calcination treatment. The prepared γ-Fe_2O_3 sensor shows a fast response/recovery time (1/4 s) and achieves a high response of 232.7 to 100 ppm acetone. It also has an ideal response (5.64) to low concentration (1 ppm) of acetone, which is completely adequate for the clinical diagnosis of diabetes.

CRediT authorship contribution statement

Qixuan Qin: Investigation, Conceptualization, Methodology, Writing – original draft. **Xindong Zhang:** Supervision, Data curation, Writing – review & editing. **Nan Zhang:** Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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References

[1] S. Lv, J. Fan, F. Liu, Y. Zhang, L. Jiang, S. Ouyang, C. Zhang, C.G. Wang, P. Sun, L. J. Wang, G.Y. Lu, YSZ-based mixed potential type acetone gas sensor attached with $CuSb_2O_6$ sensing electrode for ketosis diagnosis, Sens. Actuators B Chem. 370 (2022), 132408.
[2] C.X. Zhang, S. Zhang, Y. Yang, H. Yu, X.T. Dong, Highly sensitive H_2S sensors based on metal-organic framework driven gamma-Fe_2O_3 on reduced graphene oxide composites at room temperature, Sens. Actuators B Chem. 325 (2020), 128804.
[3] Z.J. Song, H.M. Chen, S.S. Bao, Z.X. Xie, Q. Kuang, L.S. Zheng, Nanosheet-assembled, hollowed-out hierarchical gamma-Fe_2O_3 microrods for high-performance gas sensing, J. Mater. Chem. A 8 (2020) 3754–3762.
[4] H.V. Hai, N.D. Cuong, H.D. Mai, H.T. Long, T.Q. Phuong, T.K. Dang, L.V. Thong, N. N. Viet, N. Van Hieu, Superior detection and classification of ethanol and acetone using 3D ultra-porous gamma-Fe_2O_3 nanocubes-based sensor, Sens. Actuators B Chem. 362 (2022), 131737.
[5] T. Yang, L. Du, C. Zhai, Z. Li, Q. Zhao, Y. Luo, D.J. Xing, M.Z. Zhang, Ultrafast response and recovery trimethylamine sensor based on alpha-Fe_2O_3 snowflake-like hierarchical architectures, J. Alloys Compd. 718 (2017) 396–404.
[6] V.X. Hien, L.H. Phuoc, C.T. Khoa, D.D. Vuong, N.D. Chien, High acetone-sensing performance of bi-phase alpha-/gamma-Fe_2O_3 submicron flowers grown using an iron plate, J. Sci. Adv. Mater. Dev. 6 (2021) 27–32.
[7] Q. Qin, X. Zhu, X. Zhang, Synthesis of alpha-Fe_2O_3 hollow spheres with rapid response and excellent selectivity towards acetone, Mater. Sci. Eng. B Adv. Funct. Solid State Mater. 275 (2022), 115482.
[8] H.J. Song, S.W. Yan, Y.L. Yao, L.X. Xia, X.H. Jia, J.S. Xu, 3D alpha-Fe_2O_3 nanorods arrays@graphene oxide nanosheets as sensing materials for improved gas sensitivity, Chem. Eng. J. 370 (2019) 1331–1340.
[9] S.J. Young, Y.H. Liu, Z.D. Lin, K. Ahmed, M.N.I. Shiblee, S. Romanuik, P.K. Sekhar, T. Thundat, L. Nagahara, S. Arya, R. Ahmed, H. Furukawa, A. Khosla, Multi-walled carbon nanotubes decorated with silver nanoparticles for acetone gas sensing at room temperature, J. Electrochem. Soc. 167 (2020), 167519.
[10] Y.Z. Fan, W. Wang, J.F. Zhang, Y. Lu, C.X. Liu, S. Adimi, J.R. Zhou, S.P. Ruan, Y. Chen, Construction of p-n heterojunctions by modifying MOF-derived alpha-Fe_2O_3 with partially covered cobalt tungstate for high-performance ethyl acetate detection, Sens. Actuators B Chem. 344 (2021), 130129.