Room-temperature H$_2$S Gas Sensor Based on Au-doped ZnFe$_2$O$_4$

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Room-temperature type H$_2$S sensing devices that use Au-doped ZnFe$_2$O$_4$ yolk-shell microspheres as the active material have been fabricated using a solvothermal method as well as subsequent annealing and a chemical etching process. The samples are characterized using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS), field-emission scanning electron microscopy (FESEM), and X-ray photoelectron spectroscopy (XPS). The results demonstrate that the doping of Au does not change the spinel structure of the products, which were yolk-shell microspheres, while the particle size varied with the Au doping concentration. Also, the as-fabricated sensor device exhibited excellent selectivity toward H$_2$S gas at the room temperature; the gas-sensing property of 2 wt% Au-doped ZnFe$_2$O$_4$ microspheres was the best. The Au-doped ZnFe$_2$O$_4$ yolk-shell microspheres can be promising as a sensing material for H$_2$S gas detecting at room temperature.

**Keywords** Yolk-shell structure, Au-doped ZnFe$_2$O$_4$ microspheres, H$_2$S, gas sensitivity, room-temperature

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**Introduction**

With the development of industry, the demands for fast-response, cost-effective and portable sensors for toxic/hazardous gases detection are growing, due to their exploitation in protecting human lives as well as in environment monitoring. Among chemoresistive sensing materials, metal oxides semiconductors are the most-used nanostructures in gas sensor manufacturing, because of their simplicity of synthesis and usage, detectable for numerous gases, small dimension and also high compatibility with microelectronic processing. Zinc ferrite (ZnFe$_2$O$_4$), an n-type spinel oxide semiconductor, has attained much more attention, since it can be used widely in photocatalysis, information storage, electronic devices, magnetic materials and gas sensing. Recently, many papers have been published on the synthesis of ZnFe$_2$O$_4$ nanomaterials and applications in the field of gas-sensitive detection. Guo et al.\cite{15} Zhou et al., Bangale et al.\cite{15} and our group\cite{16} prepared sensitive components with ZnFe$_2$O$_4$ to detect harmful gases. There have been some reports showing that ZnFe$_2$O$_4$ is an excellent selective adsorbent and oxidation catalyst for H$_2$S.\cite{17,18} While processing at high temperature is still a problem to be solved. In order to decrease the operating temperature, suitable catalysts, such as noble metals, are incorporated with these sensing materials.\cite{19,20} In addition, effort has also been made to change the microstructure of the material. Noble metals can form the activation center in the semiconductor surface, the empty d orbital can accept electrons, help to improve adsorption, redox capacity, promote charge separation, thereby enhancing the gas-sensitive components of the gas-sensing performance. Besides the effect of the composition of materials, the morphology also has a significant influence on their properties. Many investigations have found in which the micro-morphology of materials is an important factor that affects its gas-sensing properties. At present, numerous distinct structures have been prepared, among these advanced architectures; yolk-shell structured materials have stimulated a great deal of research interest due to their appealing structures, and controllable chemical composition. The yolk-shell structure is advantageous concerning the surface area, density, shell permeability, structural stability, yolk/void/shell configuration and interior voids. Such a structure is even more conducive for gas-molecule-diffusion, and can be used to construct high-performance sensor equipment.\cite{22,23}

In the present work, we successfully synthesized Au-doped ZnFe$_2$O$_4$ microspheres with the yolk-shell structure via a simple one-step solvothermal reaction and a subsequent heat treatment. Various characterizations were carried out to obtain the crystal structural and morphological information of the as-prepared products. Furthermore, in order to demonstrate the potential applications, the resulting yolk-shell structure of Au-doped ZnFe$_2$O$_4$ microspheres was used to fabricate gas-sensor devices, which were then tested for their response to a variety of gases at room temperature.

**Experimental**

**Reagents and chemicals**

Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O), iron(III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O), sodium sulfite (Na$_2$SO$_3$), urea and ferrous sulfide (FeS) were purchased from Tianjin Zhiyuan Chemical Reagent Co. Ltd. (Tianjin, China). Glycerol,
isopropanol, benzene, xylene and ethanol were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Chloroauric acid was purchased from Sinopharm Chemical Reagent Co. Ltd of China. All reagents used were of analytical grade.

**Apparatus**

The compositions and crystallographic phases of the samples were examined by X-ray powder diffraction (XRD) (MAC Science MXP18AHF X-ray diffractometer) using high-intensity Cu-Kα radiation (λ = 1.54056 Å); also, the energy-disperse X-ray spectrum (EDS) was examined on an Oxford 2000 energy disperse X-ray spectrometer. The morphologies and structures of the products were directly observed using field-emission scanning electron microscopy (FESEM, JEOL JSM-7500F, operated at an accelerating voltage of 15 kV). X-ray photoelectron spectroscopy (XPS) measurements were obtained on an ESCALAB 250Xi spectrometer equipped with an Al-Kα radiation source (1486.6 eV). The gas sensing characteristics were measured in a glass test chamber using the gas-sensing measuring system of HW-30A (Hanwei Electronics Co. Ltd., China) under laboratory conditions (20°C, 23% relative humidity).

**Synthesis of materials**

Yole-shell structure Au-doped ZnFe$_2$O$_4$ microspheres were synthesized according to literature. A schematic process for the synthesis of yolk-shell structure Au-doped ZnFe$_2$O$_4$ microspheres is given in Fig. 1. Zn(NO$_3$)$_2$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and urea were completely dissolved in the glycerol-isopropanol solvent. After stirring for several minutes, the chloroauric acid solution was added. Then, a homogeneous solution via a solvothermal strategy and subsequent annealing and chemical etching process was conducted to obtain the final Au-doped ZnFe$_2$O$_4$ products.

**Measurement of the sensing characteristics**

A certain amount of the Au-doped ZnFe$_2$O$_4$ products was thoroughly mixed with deionized water to form a homogeneous slurry. This slurry was uniformly coated on alumina ceramic tube and dried in air at room temperature. Subsequently, four platinum wires of the treated ceramic tube were welded on the basement. Finally, the gas sensors were kept at room temperature for one day in air. By monitoring the output voltage across the sensor, the resistances of the sensor in air or in the test gas could be measured. The gas response (response magnitude) of the sensors was determined to be the $R_{\text{air}}/R_{\text{gas}}$ ratio, where $R_{\text{air}}$ is the resistance of the thick-film sensors in air, and $R_{\text{gas}}$ is that in the mixture of the testing gases and air. In addition, the response time is defined as the time required for the resistance to reach 90% of the equilibrium value after the test gas is injected. The recovery time is the time necessary for the sensor to attain a resistance 10% above the original value in air.

**Results and Discussion**

**Structural and morphological characteristics**

Figure 2 shows the XRD patterns of Au-doped ZnFe$_2$O$_4$ products. The XRD pattern corresponds to the cubic spinel ZnFe$_2$O$_4$ phase given by the standard data file (JCPDS card No. 22-1012), respectively. This means that all of the products have a single spinel phase. The peaks appearing at about 38.2°, 44.3°, 35.1°, 64.6°, and 77.5° correspond to the (110), (200), (
The (211) and (311) planes of cubic Au (JCPDS card No. 01-1172). With increasing Au doping amount, the peaks of Au emerge in the patterns and the intensities also increase. In addition, no peaks of impurities or other crystalline phase are observed, indicating that the purity of the products is high, and there is no other heterogeneous phase, while the microstructure of zinc ferrite nanopowders did not change by Au doping at small amounts.

The EDS spectra of Au-doped ZnFe$_2$O$_4$ products are shown in Fig. 3, which indicate the element distribution of Zn, Fe, O and Au (Table 1). The presence of the Au peaks in the EDS spectrum is used as support of the products in XRD. The results concerning the EDS and XRD patterns show that the Au-doped ZnFe$_2$O$_4$ powders can be synthesized by the solvothermal method without any other unrelated elements.

The morphology of as-prepared samples was examined by FESEM; the FESEM images are shown in Figs. 4(a) - 4(e). From the FESEM images it can be clearly observed that the synthesized Au-doped ZnFe$_2$O$_4$ products were spherical particles, and the sphere size changed irregularly with the increase of Au doping amount. A drastic change in the diameter was observed at a doping concentration of 2 wt%. The particle diameters with 2.15, 2.27, 2.32, 3.71 and 3.22 μm correspond to the 0.5 – 5 wt% Au-doped ZnFe$_2$O$_4$ microspheres, respectively. As can be seen from Figs. 4(a) and 4(b), the spherical architecture was hierarchically constructed of a number of nanosheet-like sub-units, but drastic changes in the surfaces were obtained at doping amounts of 1.5, 2 and 5 wt%. Here, the microspheres have a smooth surface, and are composed of a large number of nanoparticles. Figures 4(g) - 4(i) show a cracked microsphere in the FESEM image corresponding to 2, 0.5 and 5 wt% Au-doped ZnFe$_2$O$_4$ microspheres, respectively, which vividly manifests another unique feature: the yolk-shell structure. The shell thickness of 2 wt% Au-doped ZnFe$_2$O$_4$ is about 630 nm. The FESEM images demonstrated a porous rough surface structure of the microspheres. This unique surface can effectively adsorb gas and promote gas transmission, thereby improving the gas sensor gas-sensing properties.

XPS analysis was performed to examine the surface chemical composition and valence state of the elements of 2 wt% Au-doped ZnFe$_2$O$_4$ microspheres; the XPS patterns are shown in Fig. 5. All of the binding energies in the XPS analysis were corrected for specimen charging by reflecting them to the C 1s peak at 284.6 eV. Figure 5(a) shows the wide spectrum of 2 wt% Au-doped ZnFe$_2$O$_4$ microspheres; it indicates that the composition of as-prepared materials should be Zn, Fe, O and Au. Two fitting peaks with binding energy values of ~1044.9 and ~1021.9 eV exhibited in the Zn 2p spectrum of Fig. 5(b) could be attributed to Zn 2p$_{1/2}$ and Zn 2p$_{3/2}$, respectively. The energy difference of 23.0 eV between the two peaks in the Zn 2p spectrum indicates the normal oxidation valence state of Zn(II) in 2 wt% Au-doped ZnFe$_2$O$_4$.25,26 As Fe 2p spectrum exhibited in Fig. 5(c), two peaks at ~725.4 and ~711.9 eV correspond to Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$, respectively. Additionally, those two peaks occur at binding energies of ~720.1 and ~733.6 eV, in accordance with the shake-up satellite structure, suggesting the Fe(III) state in the cubic spinel ZnFe$_2$O$_4$ phase.27,28

The high-resolution spectrum of O 1s in Fig. 5(d) indicates the existence of two different oxygen species with a broad peak, which is fitted by two peaks at binding energies of ~531.6 eV. The peak at ~530.0 eV is characteristic for surface lattice oxygen; ~531.6 eV is for the surface adsorbed oxygen species.29,30 Since the absorbed oxygen species are able to react with detected gases, they are absolutely instrumental in enhancing the gas performance.31 Au 4f XPS spectra (Fig. 5e) can be differentiated into four peaks as ~84.4, ~87.2, ~88.6 and ~91.3 eV binding energies, corresponding respectively to Au$^+$ 4f$_{7/2}$, Au$^+$ 4f$_{5/2}$, Zn$^{2+}$ 3p$_{3/2}$ and Zn$^{2+}$ 3p$_{1/2}$. However, the XPS spectra of Zn 3p and Au 4f overlaps at the region of 80 – 96 eV binding energies32,33 suggesting that the Au exist in the univalence state in 2 wt% Au-doped ZnFe$_2$O$_4$.34–36

| Table 1 EDS results of Au-doped ZnFe$_2$O$_4$ products (wt%) |
|-----------------|-----|-----|-----|
|                 | Fe  | Zn  | Au  | O   |
| 0.5 wt% Au-doped ZnFe$_2$O$_4$ | 49.83 | 28.42 | 0.48 | 21.28 |
| 1 wt% Au-doped ZnFe$_2$O$_4$  | 52.95 | 24.77 | 0.83 | 21.45 |
| 1.5 wt% Au-doped ZnFe$_2$O$_4$ | 46.29 | 31.3 | 1.33 | 21.08 |
| 2 wt% Au-doped ZnFe$_2$O$_4$  | 48.66 | 28.14 | 2.07 | 21.14 |
| 5 wt% Au-doped ZnFe$_2$O$_4$  | 52.17 | 21.73 | 5.2 | 20.9 |
Gas sensing performances

Regarding gas-sensing performance, the selectivity is an vital factor, since good selectivity determines whether a target species is detectable in a multi-component gas environment. Therefore, the sensor responses of the Au-doped ZnFe₂O₄ yolk-shell microspheres to 100 ppm formaldehyde, benzene, xylene, ethanol, SO₂, NO₂ and H₂S gas were measured at room temperature. As shown in Fig. 6, all of the Au-doped ZnFe₂O₄ yolk-shell microspheres showed a higher response to H₂S gas than that of others. This reveals that the Au-doped ZnFe₂O₄ yolk-shell microspheres have good selectivity to H₂S gas. Among the five different doping amounts of Au-ZnFe₂O₄ microspheres, the 2 wt% of the Au-doped ZnFe₂O₄ gas sensor was very sensitive to H₂S gas. The typical response of this sensor to H₂S gas was 3-times greater than the responses for formaldehyde, benzene, xylene, ethanol, SO₂ and NO₂.

The responses of Au-doped ZnFe₂O₄ yolk-shell microspheres-based sensors toward the range of 1 - 1000 ppm H₂S gas were calculated, and the results are shown in Fig. 7. It can be seen that, with the increase of the H₂S gas concentration, the corresponding sensitivity of the sensor increased, and 2 wt% Au-doped ZnFe₂O₄ shows the best results. It can also be observed that the low detection limit of Au-doped ZnFe₂O₄ yolk-shell microspheres was indicated by the response for H₂S, even at concentrations as low as 1 ppm. We also compared the sensing performances of ZnFe₂O₄ with literature reports for H₂S detection, as summarized in Table 2. From the table, it can be seen that the gas sensor based on 2 wt% Au-doped ZnFe₂O₄ yolk-shell microspheres exhibited a good response for H₂S gas and a lower working temperature than others reported in the literature.

Another two important factors, the response and recovery times used to judge the gas sensing performances, were calculated. In this case, we chose the 2 wt% of Au-doped ZnFe₂O₄ based sensor; the results are given in Fig. 8. As can be seen from Fig. 8(a), the gas sensor showed a constant and stable baseline at the beginning, when the H₂S gas was introduced into the chamber; the resistance of the gas sensor decreased. However, when the chamber was refilled with pure air, it recovered to its original baseline. The response and recovery times were 46 and 629 s, respectively. The reproducibility of the sensor was demonstrated by successively exposing it to H₂S gas at a concentration of 100 ppm for 3 cycles at room temperature; the results are given in Fig. 8(b), which indicate good reversibility of the gas sensor at room temperature.
Fig. 5 XPS spectra of 2 wt% Au-doped ZnFe₂O₄ yolk-shell microspheres.

Fig. 6 Selective responses of the sensor to different test gases with a concentration of 100 ppm.

Fig. 7 Responses of Au-doped ZnFe₂O₄ yolk-shell microspheres as a function of the H₂S concentration at room temperature.
Gas sensing mechanism

The ZnFe₂O₄ is an n-type composite metal oxide semiconductor, and its sensitivity was determined by the resistance change during reactions between the target gas and the oxygen species absorbed on the sensor surface.⁴⁰,⁴¹ When ZnFe₂O₄-based sensors are exposed to air, the oxygen molecules are absorbed on the surface, and chemisorbed species are formed through obtaining electrons from the conduction band of ZnFe₂O₄, providing an electron-depletion layer along with the decreasing conductivity of the sensor.⁴²,⁴³ Temperature determines the species observed on the surface of ZnFe₂O₄; for instance, at room temperature O₂⁻ is chemisorbed.⁴⁴ While it exposed to H₂S gas, the H₂S molecules react with the previously absorbed oxygen species. The reaction between the H₂S gas and the absorbed oxygen species can be expressed using the following equation: ⁴⁴,⁴⁵

\[ 2\text{H}_2\text{S} + 3\text{O}_2\overset{(ad)}{\longrightarrow} 2\text{H}_2\text{O}(g) + 2\text{SO}_2(g) + 3e^- \]

During this process, as a result of the release of electrons into the conduction band of ZnFe₂O₄, the electron-depletion layer becomes thinner, and ZnFe₂O₄ becomes less resistive.

Compared with previous work,⁴⁶ low temperature improves the gas sensing performance of the Au-doped ZnFe₂O₄-based sensor for H₂S gas. A possible explanation should be that the doping of Au creates more active centers on the surface, which promotes the absorption and dissolution of oxygen molecules.⁴⁷,⁴⁸

Furthermore, reducing gas molecules can be broken into more active radicals by noble metal catalysts; as a result, they can diffuse on the sensing material surface and enhance the reaction between the tested gas and the absorbed oxygen.⁴⁷,⁴⁸ When the surface catalytic activity of the sensor strengthen overly, with fewer gas molecules diffused into the sensor, the response will decreases due to a smaller utilization ratio of the sensing body.⁴⁸

Conclusions

In conclusion, Au-doped ZnFe₂O₄ yolk-shell microspheres have been prepared using a solvothermal method, and a subsequent annealing and chemical etching process. Based on the FESEM results, the size of the Au-doped ZnFe₂O₄ yolk-shell microspheres changed with the Au doping amount. This was later supported with Auger spectroscopy and X-ray photoelectron spectroscopy results. In these studies, the presence of Au was confirmed through the detection of specific Au signals. The sensing behaviors of the products were evaluated, and all of the Au-doped ZnFe₂O₄-based sensors showed selectivity for H₂S gas over other gases at room temperature. The 2 wt% of Au-doped ZnFe₂O₄ gas sensor had the best performance for H₂S gas at room temperature. The results certify that doping of the Au properly improves the gas sensing performance at room temperature.

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Table 2 Comparison of the H₂S-sensing performances of gas sensors based on various ZnFe₂O₄ microstructures

| Sensing element                              | Operating temperature/ °C | H₂S response | Concentration, ppm | Ref. |
|-----------------------------------------------|---------------------------|--------------|--------------------|------|
| ZnFe₂O₄ NPs                                  | 80                        | 64.4         | 300                | 38   |
| ZnFe₂O₄ (partially inverse spinel)            | 260                       | 64           | 100                | 17   |
| ZnFe₂O₄ nanocrystalline                       | 150                       | 82           | 200                | 39   |
| 2 wt% Au-doped ZnFe₂O₄ microspheres           | Room temperature          | 65.9         | 200                | This work |

Fig. 8 The 2 wt% Au-doped ZnFe₂O₄ based sensor (a) response/recovery time and (b) response-recovery curve for 3 cycles to 100 ppm H₂S gas.
