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Review

# Highly sensitive $H_2S$ sensor based on solvothermally prepared spinel $ZnFe_2O_4$ nanoparticles

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ABSTRACT

$ZnFe_2O_4$ nanostructures were synthesized through a one-step solvothermal approach using zinc acetylacetonate and iron acetylacetonate as a precursor. The $ZnFe_2O_4$ nanoparticles were obtained at the temperatures 150 °C. Structure features of $ZnFe_2O_4$ nanoparticles were characterized using various methods such as powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy etc. Application of $ZnFe_2O_4$ nanoparticles as gas sensor materials displayed the higher sensitivity, good stability, and repeatability to low concentration $H_2S$ at low temperature. The sensor response can be up to 15.1 to 5 ppm $H_2S$ gas at a low operating temperature of 135 °C. Thus, the $ZnFe_2O_4$ nanoparticles are very promising for chemical gas sensors with good sensing characteristics for environmental and healthcare fields.



**Contents**



## 1. Introduction

The zinc ferrite, $ZnFe_2O_4$, one of n-type semiconductor materials with a direct bulk band gap of 1.86 eV, shows spinel structure, belonging to the cubic crystal system. Spinel structure $ZnFe_2O_4$ with unique physical and chemical properties, which has excellent absorbing performance, is an important soft magnetic material [1–8]. It is also very representative oxidative dehydrogenation catalyst to alkenes organic compounds and sensitive semiconductor catalyst to visible light [9–12]. In addition, nano-sized $ZnFe_2O_4$ has strong antibacterial effect and good gas sensitive characteristic [13–21].

Conventionally, $ZnFe_2O_4$ nanoparticles can be prepared by solid phase, sol-gel, coprecipitation, hydrothermal, microwave hydrothermal, sonochemical reactions, pyrolysis and electrostatic spinning method, etc [12,22–30]. Ranajit Sai et al. prepared $ZnFe_2O_4$ nanoparticles via microwave radiation method with acetylacetone metal oxide as the precursor [6]. By mild hydrothermal and

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calcined methods, Peng research team synthesized porous flower-like nanostructure $ZnFe_2O_4$ [12]. Octahedral $ZnFe_2O_4$ nanocrystals had been successfully synthesized via one-spet hydrothermal method using polyvinylpyrrolidone shape control agent by Wu and Wen et al. [29]. $ZnFe_2O_4$ nanofiber could be prepared via electro-spinning technique by Madhavi Srinivasan [30]. Till date, Gas-sensing properties of $ZnFe_2O_4$ nanostructures have been widely attention and research of gas sensor has been widely carried out, including $ZnFe_2O_4$ nanoparticles to detect $H_2S$ gas [16], $ZnFe_2O_4$ nanoparticles to detect CO gas [17], $ZnFe_2O_4$ nanotube to detect organic gas [18], $ZnFe_2O_4$ hollow nanospheres to detect ethanol gas [19], $ZnFe_2O_4$ nanorods to detect formaldehyde gas [20], and so on. Among them, the research content of $ZnFe_2O_4$ nanostructures used to detect $H_2S$ gas is very few and the recognition of gas ability should be improved. Herein, we report on the synthesis of $ZnFe_2O_4$ nanoparticles via one-step solvothermal method. The $H_2S$ sensing properties of $ZnFe_2O_4$ nanoparticles were investigated. The measurement results showed that they exhibited good sensing properties to $H_2S$ gas at a low working temperature, including high response, fast response and recovery times, good repeatability and long-term stability. Based on the excellent sensitivity of $H_2S$ gas, the relationships between the sensing properties and structure and phase composition of sensitive materials at the nanoscale were studied, and thereby the enhanced mechanism was given.

## 2. Experiment section

$ZnFe_2O_4$ nanoparticles were synthesized via a simple one-step solvothermal route. In a typical reaction process, 1.76 g of iron acetylacetonate ($Fe(C_5H_7O_2)_3 \cdot H_2O$, >95%) dissolved in 35 ml of ethanol mixed with 0.65 g of zinc acetylacetonate ($Zn(C_5H_7O_2)_2 \cdot H_2O$, >95%) under continuous stirring for 10.0 min at room temperature. After stirring, the mixture was then put into a Teflon-lined stainless steel autoclave with a capacity of 50 ml and transferred in the oven for 12 h. The temperature of oven was controlled manually throughout the reaction process at 150 °C. After heating the reactant mixtures, the autoclave cooled to room temperature naturally, the dark brown precipitates were separated by centrifugation, washed with distilled water and absolute ethanol several times. After desiccation in a vacuum oven at 60 °C for 4 h, $ZnFe_2O_4$ nanoparticles were obtained.

The morphology and microstructure of the products were characterized by scanning electron microscopy (SEM, JEOL–JSM–6700F), and transmission electron microscopy (TEM, JEOL 2010) with a Gatan Ultrascan 100 TEM camera for selective area electron diffraction patterns (SAED) and high-resolution TEM (HRTEM) images. The crystal structures were measured by X–ray diffraction (XRD, D/max2550 V, Cu Kα radiation with the wavelength λ = 0.1546 nm). Surface properties of the sub-microspheres were investigated by the Brunauer–Emmett–Teller (BET) method via nitrogen adsorption and desorption measurements, and the pore diameter and the pore size distributions were calculated by the Barret–Joyner–Halenda (BJH) method. The fabrication process of the sensors based on the products has been described elsewhere [31]. The sensor response was defined as S = Ra/Rg, where Ra is the sensor resistance in air and Rg is the resistance in target-air mixed gas, respectively.

## 3. Results and discussion

### 3.1. Structure characterization of $ZnFe_2O_4$ nanoparticles

XRD pattern of $ZnFe_2O_4$ nanoparticles which synthesized at 150 °C for 12 h, is represented in Fig. 1. All the reflection peaks in this prototype were initiated to correspond with the spinel $ZnFe_2O_4$

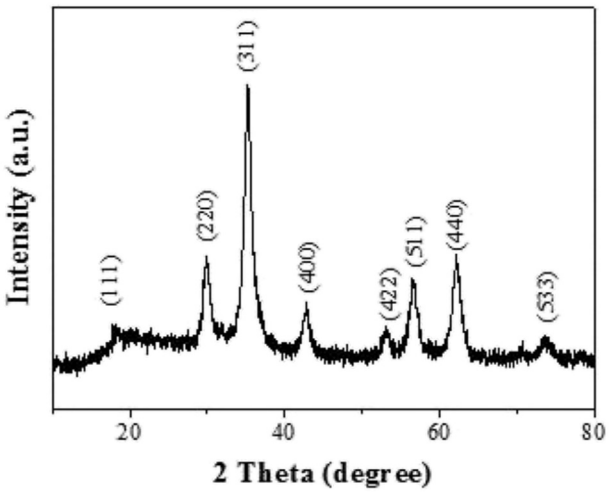


**Fig. 1.** XRD patter of $ZnFe_2O_4$ nanoparticles synthesized by the solvothermal method at 150 °C for 12 h.

which lattice constant for *a* is 8.44 Å (JCPDs No. 22–1022). The phases demonstrated the key features with indices for crystalline $ZnFe_2O_4$ at various 2θ values of (111), (220), (311), (400), (422), (511), (440) and (533). No other impurity peaks such as ZnO and $Fe_2O_3$ were observed, indicating the product purity of $ZnFe_2O_4$ nanoparticles synthesized via solvothermal method is very high. In addition, the sharp diffraction peaks show that small particle size of synthetic products. The highest intensity diffraction peak of the crystal plane (311) and the crystallite sizes of samples can be estimated by using the Scherrer equation,

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where d is the crystallite size, β is the full width at half maximum, θ is diffraction angle and λ is the wavelength of X-ray. The crystallite size corresponding to (311) crystal plane is also calculated and the estimated value of the diameter is 21.5 nm.

Fig. 2 is typical SEM images of the products. Low magnification SEM (Fig. 2(a)) revealed that the size is very small and the sphere is the main shape of $ZnFe_2O_4$ nanoparticles. It can be clearly seen that they are uniform spherical particles with the diameter about 20–30 nm which is in good agreement with the XRD measurement, and there is agglomeration phenomenon exists via high magnification SEM image (Fig. 2(b)). The morphology and size of $ZnFe_2O_4$ nanoparticles were also characterized by TEM. Fig. 3(a) can reveal that they are gathering small particles for the magnetism of $ZnFe_2O_4$ and consist with SEM images. It can be further find that particle size is consist with the calculation result with the scherrer formula in Fig. 3(b).

HRTEM and SAED were employed to obtain the detailed structure information of the single nanoparticle. The typical HRTEM image (Fig. 4(b)) clearly displays that the spacing between two adjacent lattice fringes is 0.26 nm, corresponding to (3 1 1) plane of the cubic $ZnFe_2O_4$. It also can seen $ZnFe_2O_4$ nanoparticles prepared with a high degree of crystallinity through the equally and clear lattice planes. The corresponding SAED pattern shows a series of seven concentric diffraction rings from the inside to the outside in Fig. 4(a). The lattice plane spacing corresponding diffraction rings can been calculated according to electron diffraction formula, r • d = L • λ (where r is the radius of the diffraction rings; d is the lattice plane spacing; L is the distance between the sample to the film; λ is the wavelength of the electron beam). The diffraction