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# Electrical conductivity and gas sensitivity to VOCs of V-doped $ZnFe_2O_4$ nanoparticles

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**Abstract**

$ZnFe_2O_4$ and V-doped $ZnFe_2O_4$ nanoparticles were successfully fabricated by citrate pyrolysis method. The structural and morphological characteristics of the as-sintered powders were investigated by means of XRD and FE-SEM. The results showed all the as-received powders have a spinel-type structure, irrespective of the added V content, and the average size of the spherical particles is below 50 nm with good dispersity. The resistance of $ZnFe_2O_4$-based thick films decreases with increasing the added V content. It is found that the added V has different effects on the sensitivities to different VOCs. Due to the added V, the sensitivities to ethanol and acetone decline greatly and the highest sensitivity temperatures increase, whereas the added V enhances remarkably the sensitivities to benzene, toluene and xylene at high operating temperature. The V-doped $ZnFe_2O_4$ can be promising as a sensing material for gas sensor detecting benzene and its derivatives.


*Keywords:* V-doped $ZnFe_2O_4$ nanoparticles; Electrical properties; Gas sensitivity; Volatile organic compounds (VOCs)

## 1. Introduction

Volatile organic compounds (VOCs) are a kind of important environmental pollutants in the atmosphere. Among the VOCs, benzene and its derivatives, such as benzene, toluene and xylene, were confirmed as a human carcinogen, and could cause diversiform cancers, for example lymphatic and hematopoietic cancers [1]. So it is very necessary and urgent to detect and control VOCs around human beings, especially in the indoor environment, because an average person spends more than 80% of the daytime in the indoor environment either in the home or in the work place [2].

Zinc ferrite ($ZnFe_2O_4$) is a kind of well-known electronic material with the spinel structure. In the past, researchers mainly studied its magnetic properties [3–6]. It is also believed that $ZnFe_2O_4$ is a sort of good catalyst and photocatalyst for various processes [7,8]. In the recent studies, it was observed that $ZnFe_2O_4$ exhibited excellent gas-sensing properties to $C_2H_5OH$, $CH_3SH$, $Cl_2$ and $NO_x$ [9–12]. However gas sensitivities of $ZnFe_2O_4$ to VOCs have not been investigated, to the best of our knowledge. In this work, pure and V-doped $ZnFe_2O_4$ powders were prepared by the citrate pyrolysis method and used for the fabrication of thick films. The electrical and gas-sensing characteristics of thick films to five VOCs, namely benzene, toluene, xylene, ethanol and acetone, were studied.

## 2. Experimental

Citrate pyrolysis method was employed for the preparation of $ZnFe_2O_4$-based powders. A schematic of the synthesis route was given in Fig. 1. The main starting materials were ferric nitrate, zinc nitrate, vanadium nitrate and citric acid, which were of 99.9% purity or better and used with our further purification. Aqueous solutions of iron, zinc and vanadium salts were prepared separately (concentration of 0.5 mol/L each) by dissolving the corresponding salts in water and under constant stirring to facilitate dissolution and then mixed together in stoichiometric proportions. Citric acid solution (concentration of 1 mol/L) was prepared separately and added to the aqueous salt solution with cations to citric acid ratio of 1 : 1. After stirring

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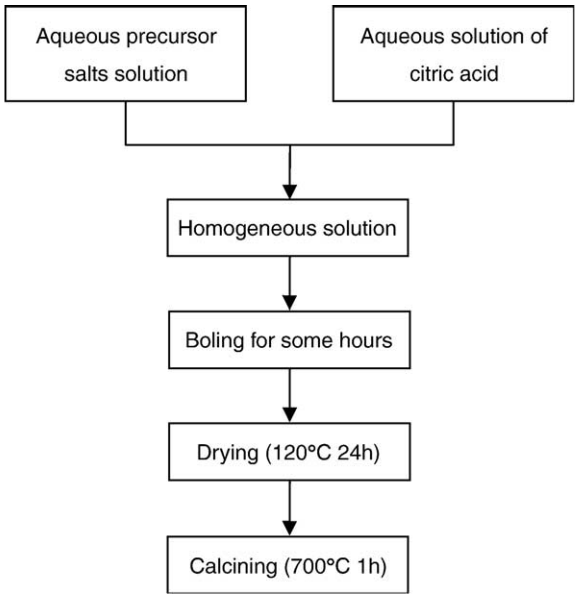


Fig. 1. Schematic of the synthesis process for the preparation of $ZnFe_2O_4$-based powders.

uniformly a brown clear solution was formed. Subsequently, 25% aqueous ammonia was added carefully to the above solution until the neutral solution (pH = 7) was obtained. The solution was then slowly heated under electromagnetic stirring on an electro-thermo plate. As the water evaporated slowly, the solution became more and more viscous. As soon as the viscous matter started to expand quickly, the mixture was dried at 120 °C for 24 h to form a brown fluffy mass, which was crumbled into the precursor powder. The precursor powders were calcined at 700 °C for 1 h in air to get the powders.

The crystalline structures of the as-sintered powders were analyzed with X-ray diffraction (XRD) (PANalytical B.V. x'Pert PRO) using Cu $K_\alpha$ radiation at 40 kV and 40 mA. The microstructure of the as-sintered powders was investigated using a field emission scanning electron microscope (FE-SEM) (FEI sirion 200).

The method for preparation of thick films as gas sensors was described as follows: at first, a paste formed by adding proper amount of distilled water into obtained powders was painted on a small $Al_2O_3$ tube (4 mm in length, 1.2 mm in external diameter and 0.8 mm in internal diameter) on which Au electrode and Pt wires have been fixed at each end. Then the films were sintered at 700 °C for 2 h after drying under air to remove water. Finally, a small Ni–Cr alloy coil with resistance of about 33 Ω was placed through the tube as a heater, which controlled the temperature of films by adjusting the heating power. Before the measurement of electrical and gas-sensing properties, the films were aged at 320 °C in air for one week. Electrical and gas-sensing properties were carried out on a static system in room condition (room temperature was 23 °C, relative humidity 78%). The gas sensitivity, $S$, is given by $S = R_a / R_g$, where $R_a$ and $R_g$ express the resistances of the sensor in air and in detecting gas, respectively. Benzene, toluene, xylene, ethanol and acetone gases were chosen as five probing gases

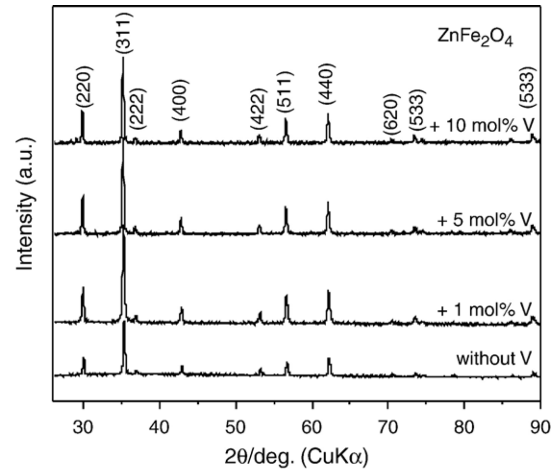


Fig. 2. X-ray diffraction patterns of V-doped $ZnFe_2O_4$ prepared calcining at 700 °C for 1 h.

to characterize gas-sensing properties of $ZnFe_2O_4$-based gas sensors.

## 3. Results and discussion

### 3.1. Characteristics of sensor materials

In order to identify the phases and compositions of the powders calcined at 700 °C for 1 h, these samples were analyzed by XRD and the diffraction patterns obtained were shown in Fig. 2. It is found that all these samples have a spinel structure (JCPDS card no. 22-1012), no $Fe_2O_3$ and ZnO detected. The sharp diffraction peaks of these samples indicate the as-received samples have a high degree of crystallization. With an increase of the content of V dopant, the peaks shifted towards lower angles gradually compared with pure $ZnFe_2O_4$, which can be observed clearly in Fig. 3. It suggests that the added V is present on interstitial or substitutional sites in the $ZnFe_2O_4$ lattice to form solid solutions. The ionic radii of $Fe^{3+}$ and $Zn^{2+}$ are 0.55 and 0.74 Å, respectively, whereas the ionic radius of $V^{5+}$ is 0.59 Å. The ionic radius of $V^{5+}$ is smaller than that of $Zn^{2+}$ and is lightly bigger than $Fe^{3+}$. On the other hand, the spinel structure of $ZnFe_2O_4$ has abundant tetrahedral and octahedral cavities which can be occupied by other

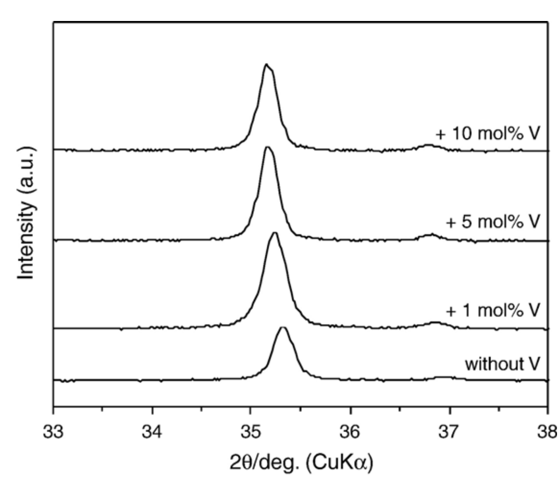


Fig. 3. X-ray diffraction patterns of (311) peaks of the samples with different V contents.