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Simple solid-state chemical synthesis and gas-sensing properties of spinel ferrite materials with different morphologies

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ABSTRACT

Spinel ferrite materials with different morphologies were synthesized by simple solid-state chemical reactions under mild reaction conditions and their gas-sensing properties were investigated in detail. It was found that all sensors based on the as-prepared materials had high responses, low working temperatures, rapid response/recovery characteristics, good selectivity and long-term stability to methanal and ethanol. Among them, $ZnFe_2O_4$ exhibited the best response, which was attributed to its intrinsic semiconductor nature and suitable microstructure. The response value reached 37.3 for 100 ppm of methanal at 260 °C and 29.1 for 100 ppm of ethanol at 300 °C. The response and recovery times were not longer than 5 s and 26 s. This study has yielded helpful insights to explore gas-sensing materials with good comprehensive performance.

1. Introduction

The discovery of new gas-sensing materials is crucial for the development of gas sensors with comprehensive performance because the gas-sensing materials directly influence the characteristics of sensor, such as sensitivity, selectivity and reliability [1–4]. At present, SnO_2, ZnO and Fe_2O_3 are three commonly used gas-sensing materials in the research of gas sensor and have been put into practical use [5–9]. However, practical gas-sensing applications for these materials have enhanced requirements for comprehensive property, and the currently used gas-sensing materials are still unable to meet the actual demand. Thus, some strategies have been attempted to improve the comprehensive gas-sensing property of these materials. While the sensitivity, selectivity and reliability of gas-sensing materials can be improved by doping the metal element or reducing the microsize of the materials [6,10–14], it is still urgent need to constantly explore new gas-sensing materials to meet the increased requirements for gas sensor with excellent comprehensive performances.

Composite metal oxides are an important category in the development field of gas-sensing material. Containing two or more different metals in their structure, they have great developmental potential for gas sensors because of their variable composition and property [15–17]. The crystal structure of spinel ferrite (MFe_2O_4, M = metal) is very stable, the M metal ion can be replaced by other metal ions, but the crystal structure does not fundamentally change, and the structural stability makes them strong prospects for potential application in chemical sensor. Spinel ferrites with specific structures have gained increasing attention because of their higher gas response value and better selectivity than single oxides [18–20].

The present methods for the synthesis of ferrites, such as the high temperature solid state method, the traditional hot decomposition method, the combustion method, the hydrothermal method and the coprecipitation method have advantages [21–23] but also shortcomings, such as high energy consumption, low yield and time-consuming or complicated procedures. Recently, low-temperature solid-state chemical reactions have been used to synthesize inorganic nanomaterials with zero-dimensional, one-dimensional, two-dimensional and hollow nanomaterials [24–31] and have the advantages of simple operation, low cost, mild conditions, short times and high productivity for obtaining nanomaterials with different morphologies.

In this paper, the synthesis of spinel ferrites with different morphologies was achieved by simple solid-state chemical reactions using inexpensive reactants. The determinate composition of M (metal) and Fe and the desired spinel ferrite structures have been obtained via control of the reagent ratios and simple manipulation under mild conditions. This method for fabricating spinel ferrites offered not only simple synthetic steps and low cost but also low energy consumption and less pollution. The gas-sensing performance of these spinel ferrites has been investigated to generate new materials for gas sensor that have excellent comprehensive performance.

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2. Experimental

2.1. Preparation of ferrite materials

The ferrites MFe_2O_4 (M=Fe, Co, Ni, Mg, Cd and Zn) were synthesized by solid-state chemical reaction. All of the reagents were analytically pure from commercial sources and used without further purification. Distilled water was used throughout the experiment. A typical synthesis for $CoFe_2O_4$ was as follows. 3 m mol of solid cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$) and 6 m mol of solid ferrous chloride ($FeCl_2 \cdot 4H_2O$) were separately weighed and mixed after grinding for 5 min in different mortar agates. After being completely mixed, 10 m mol of uniformly ground oxalate ($H_2C_2O_4 \cdot 2H_2O$) was introduced into the reaction system. The reaction started immediately upon the addition of oxalate, accompanied by the release of heat and evaporation of acetic acid, and it finished basically in less than 15 min. To ensure the completion of the reaction, the mixture was ground for another 30 min. Subsequently, the mixture was dried in air and calcined at 600 °C for 30 min. The synthetic procedures for Fe_3O_4 ($FeFe_2O_4$), $NiFe_2O_4$, $MgFe_2O_4$, $CdFe_2O_4$ and $ZnFe_2O_4$ were the same as the above process, using the corresponding metal acetate and ferrous chloride as the starting materials, respectively. All yields were greater than 92%.

2.2. Characterization of ferrite materials

X-ray diffraction spectra were measured on a Bruker D8 ADVANCE diffractometer (Germany) equipped with graphite monochromatized Cu K_α radiation at 40 kV and 40 mA (λ=1.54056 Å) from 20° to 80° with a scan rate of 6°/min at room temperature to identify the composition and crystalline phases of the materials. Scanning electron microscope (SEM) images were obtained on a LEO 1430 VP scanning electron microscope (Germany) with an accelerating voltage of 15 kV for the observation of the size and morphology of the materials. The gas-sensing tests of ferrites were carried out in a glass test chamber using a computer-controlled gas-sensing measuring HW-30A system (Hanwei Electronics Co. Ltd., China) to investigate the gas-sensing properties.

2.3. Fabrication of gas sensors

First, a portion of the as-synthesized material was crushed into uniform powder in a mortar and mixed with an appropriate amount of water to form a homogeneous slurry. Second, the paste was uniformly coated onto an Al_2O_3 tube, each end of which had two gold leads that were installed as electrical contacts. Water was used as the adhesive to form the slurry, so the binder was removed by placing the Al_2O_3 tube in air for several hours without heating in a muffle stove. Finally, a Ni–Cr heater capable of controlling the temperature in the range of 100 to 500 °C was inserted into the Al_2O_3 tube to control the operating temperature. Then, the Al_2O_3 tube was welded onto a bakelite substrate, completing the gas-sensing elements. Subsequently, the as-fabricated sensors were aged at 300 °C for 240 h until the resistance of the sensors in air was stable to ensure their stability and repeatability.

The response value, which is defined as the ratio of the electrical resistance in air (R_a) to that in a target gas (R_g) at different operating temperatures, was obtained by adjusting the heating power to determine the optimal operating temperatures. Following that, the response to different gases with concentrations from 10 ppm to 1000 ppm was measured at the optimum working temperature by injecting different gas volumes into the sealed test chamber.

3. Results and discussion

3.1. Structure and morphology of ferrite materials

Fig. 1 showed the XRD patterns of the as-prepared ferrites. The diffraction peaks of the six samples agreed well with the standard cards (JCPDS-653107, JCPDS-030864, JCPDS-540964, JCPDS-170464, JCPDS-221063 and JCPDF-221012) which indicated that the spinel types Fe_3O_4, $CoFe_2O_4$, $NiFe_2O_4$, $MgFe_2O_4$, $CdFe_2O_4$ and $ZnFe_2O_4$ had been obtained. No diffraction peaks of the reactants and other impurities were observed, which indicated that the purity of the as-obtained ferrites was relatively high.

Fig. 2 provided the SEM images of the as-prepared ferrites, indicating that the products varied in size and morphology. Among them, $NiFe_2O_4$ was composed of the largest particles, with particle sizes reaching several micrometers. From Fig. 2(d), we can see that the $MgFe_2O_4$ materials have a spherical shape and uniform size, with particle sizes distributed between 30 and 40 nm, as well as a certain degree of agglomeration. The Fe_3O_4 and $CdFe_2O_4$ particles have mostly sphere-like shapes, and obvious aggregation existed in $CdFe_2O_4$. The $CoFe_2O_4$ and $ZnFe_2O_4$ presented rod-like morphologies, unlike the others. It is notable that a hole was clearly observed in the rod structure of $ZnFe_2O_4$. Agglomeration occurred in all of the ferrites because their primary particle sizes are small and they have high surface activity, such that particles agglomerate to reduce the surface energy and achieve a more stable structure. The morphology of these ferrite materials differs because their different crystal growth habits lead to unequal growth directions for their respective metal ions during the solid-state reaction process. The different nucleation and growth rates of the ferrite crystals also contributed to the different morphologies.

The specific surface areas of the as-prepared ferrites are shown in Table 1, as calculated by the BET method. The six ferrites have different specific surface areas, of which the specific surface area of $NiFe_2O_4$ is the smallest, at only 10.52 $m^2 g^{-1}$, while $ZnFe_2O_4$ has the highest specific surface area, reaching 67.14 $m^2 g^{-1}$. The different specific surface areas will provide different numbers of active sites that are responsible for the responses to target gases, which may lead to differences in the gas responses of these materials.

3.2. Gas-sensing properties of ferrite materials

The gas response of gas-sensing materials is affected by not only their particle size but also their surface states, adsorbed oxygen and crystal lattice defects. To improve the comprehensive properties of gas-sensing materials, they were doped with noble metals, rare earth elements and oxides. However, undoped materials with excellent comprehensive performance are undoubtedly attractive. To this end, we investigated the comprehensive gas-sensing characteristics of as-prepared ferrite materials with different microstructures.

Ferrite, as a composite oxide semiconductor material, undergoes interface distortion of its lattice structure to reduce the free energy of the system. This causes many dangling bonds on the surfaces of these materials, so surface adsorption often occurs, thus offsetting the distortion. When the ferrite is exposed in air, oxygen (with high electronegativity in air) easily adsorbs on the ferrite surface and obtains electrons from the surface, forming negative oxygen ions. The n-type semiconductor material resistance increases because of the lack of electrons (the resistance for p-type decreases). This adsorption is divided into two types—one is physical adsorption of O_2 molecule when the temperature is low. Another is chemical adsorption of O^- and O^{2-} ions at higher temperatures. When a reducing gas appears in the surrounding environment, the reducing gas reacts with the adsorbed oxygen