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Ethanol-sensing characteristics of $CdFe_2O_4$ sensor prepared by sol–gel method

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Abstract

$CdFe_2O_4$ powder with the structure of spinel-type was fabricated by sol–gel method in the citric acid system. The structure and the crystal phase of the powder were characterized on an X-ray diffractometer (XRD). The shape and the size were analyzed by transmission electron microscope (TEM). Several items were investigated, including effects of calcining temperature on gas-sensing properties, gas response vs. working temperature, selectivity and long-term stability. The results demonstrated that the $CdFe_2O_4$ sensor prepared with the powder calcined at 700 °C has a high response, an excellent selectivity, a quick response behavior, and a good stability to ethanol comparing with the $CdFe_2O_4$ sensors which dealt with at other temperatures. Its response to 100 ppm ethanol is 55 working at 250 °C.

Keywords: $CdFe_2O_4$; Ethanol sensor; Response characteristics

1. Introduction

Ethanol-sensing material has been widely and deeply studied. Conventional ethanol sensors, mostly based on SnO_2 [1], ZnO [2], TiO_2 [3], and Fe_2O_3 [4], and usually suffering from cross-response to other gases, need a high working temperature, or have low long-term stability, although they have rather high response to ethanol. So the research for new ethanol-sensing materials and developing the properties of conventional ethanol-sensing materials has become an active research field. New ethanol sensors are based on In_2O_3 [5], V_2O_5 [6], and complex oxide [7,8]. Their properties still need further investigation.

Spinel-type oxide with a formula of AB_2O_4 is important complex oxide in gas-sensing materials. The literature has reported $CdFe_2O_4$ sensor to show a high response to dilute CH_3SH [9] and ethanol. The response of $CdFe_2O_4$ sensor prepared by chemical precipitation method was more than 20 to 100 ppm ethanol at 300 °C [10]. And the Ag doped $CdFe_2O_4$ sensor prepared by sol–gel response was 39.18 to 45 μmol L^{-1} (about 1000 ppm) ethanol at 330 °C [11]. In this study, $CdFe_2O_4$ powder was prepared by sol–gel method, and its response to 100 ppm ethanol was 55 at 250 °C. The material prepared by the present method shows high response and low working temperature when compared with the materials mentioned previously.

2. Experimental

2.1. Preparation of $CdFe_2O_4$ powders

$CdFe_2O_4$ nanopowder was prepared by sol–gel method. $Cd(NO_3)_2{\cdot}4H_2O$, $Fe(NO_3)_2{\cdot}9H_2O$, and citric acid were used as raw materials. $Cd(NO_3)_2{\cdot}4H_2O$ and $Fe(NO_3)_2{\cdot}9H_2O$ (molar ratio = 1:2) were mixed in de-ionized water. 0.2 M citric acid was introduced into the mixed solution (molar ratio Cd + Fe/citric acid = 1:2). The mixture was stirred and sol formed. The sol was evaporated on a water bath at 80 °C then dried at 102 °C in baking oven until xerogel formed. The xerogel was ground in agate mortar and turned into powder. The powder was slowly heated to 400 °C and pre-calcined for 4 h to make the organic matter decompose completely then calcined between 700 and 900 °C for 4 h.

X-ray diffraction (XRD) patterns of the nanopowder were obtained with an X-ray diffractometer (Bluker D8-Advance) using Cu Kα radiation (λ = 1.5406 Å) with operating voltage of 40 kV and current of 20 mA. The shape and the size of powder were analyzed by transmission electron microscopy (JEM-100SX).

2.2. Fabrication of element and measurement of gas-sensing properties

Appropriate quantity of α-terpineol was added to the powder. The mixture was then ground to form paste. The paste obtained was coated onto ceramic

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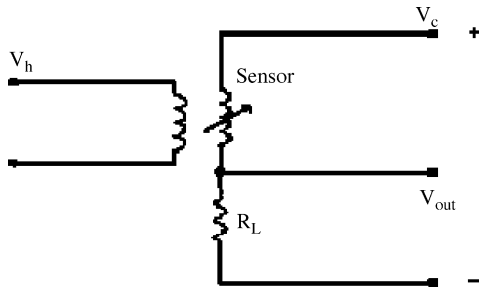

Fig. 1. Graphic of testing principle.

tubes. The two platinum wires had been installed at each end of the tube. The paste on the ceramic tubes was calcined at 600 °C for 1 h in air and aged at 320 °C for 240 h. A small Ni–Cr alloy coil was placed through the tube as a microheater. Electrical contacts were made with two platinum wires attached to the electrodes. The sensors were set up in a glass chamber and kept under a continuous flow of fresh air for 10 min before measurement. When sensors were tested, a measured quantity of gases was injected into the tested chamber and mixed by a fan for 30 s (liquid reagents were firstly evaporated then mixed by a fan for 30 s). The measuring principle of gas-sensing properties was shown in Fig. 1. The heating voltage (V_h) was supplied to the coils for heating the sensors and the circuit voltage (V_c) was supplied across the sensors and the load resistor (R_L) connected in series. The signal voltage (V_{out}) across the load, which changed with species and concentration of gas, was measured. The sensitivity for gases, S, is defined as $S = R_a/R_g$, where R_a and R_g are the resistance of the sensors in the air and in the testing gases/air mixture, respectively.

3. Results and discussion

3.1. Structural characteristics of $CdFe_2O_4$ powder

Fig. 2 shows the X-ray diffraction patterns of $CdFe_2O_4$ powder calcined at 700–900 °C for 4 h. Spinel-type $CdFe_2O_4$ formed when the gel was calcined at 700 and 800 °C, but the weak diffraction peaks of Fe_2O_3 phase were observed in the pattern. When the calcining temperature was elevated to 900 °C, the Fe_2O_3 phase disappeared primarily. And the sharp and intense peaks appeared in the XRD profiles, indicating a high degree of crystallinity and increased grain sizes of the nanoparticles. The crystallite sizes calculated according to Scherrer's equation were about 21, 48, and 55 nm for $CdFe_2O_4$ powder calcined at 700, 800, and 900 °C, respectively. Fig. 3 shows the micrographs and the size of $CdFe_2O_4$ particles. It seemed that the particle sizes were about 20–60 nm. Some big particles were aggregates of small crystallites of $CdFe_2O_4$.

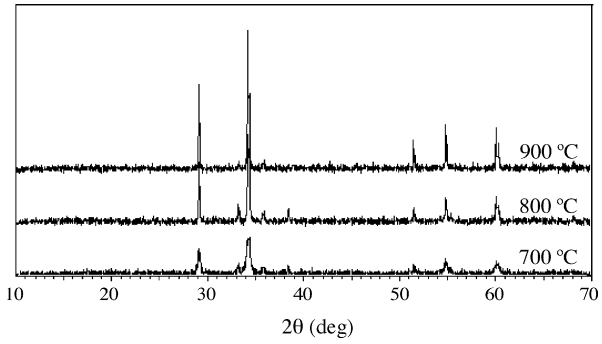

Fig. 2. XRD pattern of $CdFe_2O_4$.

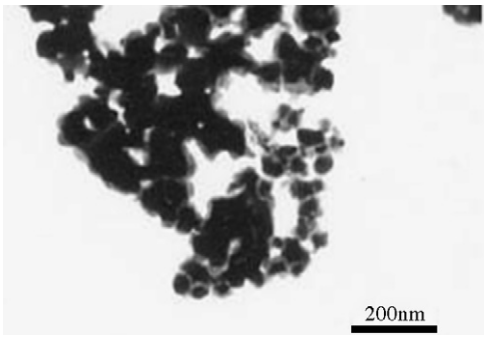

Fig. 3. The TEM micrograph of the $CdFe_2O_4$ calcined at 700 °C.

3.2. Gas-sensing properties

To determine the optimum working temperature of these sensors, the responses are examined as a function of working temperature in 100 ppm ethanol concentration, as shown in Fig. 4. When the working temperature varies from 175 to 400 °C, responses increase rapidly at first, and then decrease slowly.

When sensors exposed to the air, O_2 was adsorbed on their surface. And the adsorbed oxygen would be translated into chemisorbed oxygen at a definite temperature.

C_2H_5OH gases and the chemisorbed oxygen can take place the following reaction [12]:

$$C_2H_5OH_{gas} + O_{ad}{}^{2-} \rightarrow C_2H_5O_{ad}{}^{-} + OH_{ad}{}^{-}$$

$$C_2H_5O_{ad}{}^{-} \rightarrow (C_2H_5)_2O_{ad} + O_{ad}{}^{-} + e^{-}$$

$$C_2H_5OH_{gas} + O_{ad}{}^{2-} + \text{hole} \rightarrow CO_2 + H_2O + V_O{}^{-}$$

where $V_O{}^{-}$ is a doubly charged oxygen vacancy. These reactions infuse electrons into the $CdFe_2O_4$ material, leading to an increase in electron concentration, and a decrease in resistance of the $CdFe_2O_4$-based sensor.

The chemisorbed oxygen concentration augmented and achieved maximum value with the increasing working temperature. When the chemisorbed oxygen's absorption–desorption attained a dynamic equilibrium, the responses of sensors to ethanol gas reached the maximum at 250 °C. The maximum

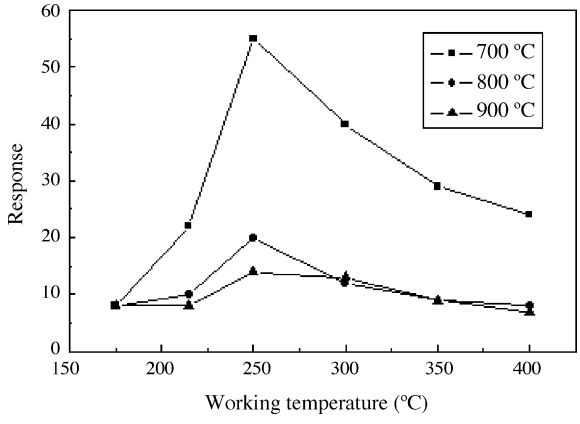

Fig. 4. Gas response of sensors as a function of working temperature to 100 ppm ethanol.