



# Facile synthesis of hollow MnFe<sub>2</sub>O<sub>4</sub> nanoboxes based on galvanic replacement reaction for fast and sensitive VOCs sensor



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## ABSTRACT

Hollow MnFe<sub>2</sub>O<sub>4</sub> nanoparticles were successfully synthesized based on simple galvanic replacement reaction with Mn<sub>3</sub>O<sub>4</sub> as a precursor. The chemical composition and nanostructure of the as-prepared samples were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. MnFe<sub>2</sub>O<sub>4</sub> was applied to decorate interdigital electrodes and the obtained sensors were used to detect fourteen kinds of volatile organic compounds at different operation temperature from 160 °C to 280 °C.

Results show that the sensor has good sensitivity, repeatability and long-term stability for ethanol gas determination at 210 °C. The detection linear range for ethanol is 2 ~ 400 ppm, and the response and the recovery time was 7.5 s and 8.0 s, respectively. Besides, the fabricated sensor also displayed decent performance in measuring *n*-decane in the concentration range of 2 ~ 400 ppm at 260 °C. Finally, gas-sensing mechanism of the prepared sensor was clearly studied.

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## 1. Introduction

Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room-temperature conditions [1]. VOCs can be naturally occurring compounds or human-made, and some of them are harmful to human health as well as ecological environment [2]. Recently it was found some VOCs in human breath can be used as potential biomarkers to reflect health state and help disease diagnosis [3,4]. Therefore, it is necessary to develop an effective method to detect VOCs for atmosphere monitoring and human health assessment. Although common analytical techniques such as high-performance liquid chromatography (HPLC) [5], spectrophotometry [6] and gas chromatography (GC) [7] can determine VOCs accurately and precisely, these large-equipment based methods are generally expensive, complex and time-consuming as collected samples can only be assayed in a laboratory. Therefore, cost-effective and user-friendly gas sensing apparatus, which also allows for real-time and on-the-spot detection, is highly required [8,9].

Metal-oxide gas sensor is one of the most promising devices for measuring VOCs. The extensive use of such sensors is mainly owing to their outstanding merits including strong response, high sensitivity, real-time detection, low cost and stable repeatability [10–14]. Spinel ferrites, a member of metal oxides, have been widely utilized as functional material, of which the general chemical composition is MFe<sub>2</sub>O<sub>4</sub> (M = Mn, Mg, Zn, Ni, Co, Cd, etc.) [15–17]. In recent years, a few spinel ferrites like ZnFe<sub>2</sub>O<sub>4</sub>, NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> have been reported to fabricate gas sensors for detection of VOCs including toluene, acetone and ethanol [18–20], due to their outstanding gas-sensing ability.

Detection sensitivity of spinel ferrites largely hinges on their structural and chemical characteristics, which are very much related to the employed synthesis strategy. Several approaches have been reported for preparing spinel ferrite, such as hydrothermal method [21,22], co-precipitation [23,24], sol-gel [25,26], thermal decomposition [27], solid-state reaction [28], solvothermal method [29]. However, these methods usually hold disadvantages like expensive surfactants and tedious synthetic procedures [16]. Hence, it is vitally important to develop a simple and cost-effective synthetic tactic. Galvanic replacement reaction is one of the most versatile approaches in synthesizing hollow bimetallic nanostructures with controllable compositions and pore structures [30]. It possesses a corrosion process that is driven by the difference in

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electrochemical potential of two metallic species. The hollow interior is generated from oxidatively dissolving nanocrystals of one of the bimetals, which are used as reactive template and precursor. This tactic has also been utilized for producing hollow metal-oxide nanostructures [31]. Compared with other common methods, galvanic replacement method features shorter reaction time and milder reaction temperature. In addition, highly coherent atom reaction of this method can render spinel ferrites small and uniform dimension [32], which is a great advantage to gas-sensing performance.

In this work, we prepared hollow  $\text{MnFe}_2\text{O}_4$  via galvanic replacement reaction with  $\text{Mn}_3\text{O}_4$  used as reactive template. Morphology and composition of  $\text{MnFe}_2\text{O}_4$  were characterized. The resulting sample was used to fabricate gas sensor which was then applied to fourteen kinds of VOCs by using a self-made sensor testing system. In addition, gas-sensing mechanism of the  $\text{MnFe}_2\text{O}_4$  gas sensor was discussed.

## 2. Experimental

### 2.1. Reagents and instruments

Oleylamine, oleic acid, anhydrous manganese acetate, xylene and  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  were obtained by Adamas Reagent Co. Ltd. (Shanghai, China). Methanol, ethanol, acetone, benzene, toluene, styrene, anisole, hexanal, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane, were purchased from Titan Scientific Co. Ltd. (Shanghai, China). *N,N*-dimethyl formamide (DMF) was purchased from Sigma–Aldrich (Shanghai, China). All chemicals were of analytical grade and used without further purification.

Interdigital electrodes (IE) were obtained from Changchun Mega Borui Tech. Co. Ltd. (Changchun, China). It has  $\text{Al}_2\text{O}_3$  substrate with dimension of  $13.4 \times 7 \times 0.635$  mm and 8 pairs of comb-type Au strips on the surface and 3 pieces of  $5 \Omega$  heating resistors on the other side. Both the width of Au strip and the strip space are 0.15 mm. WK 6500B Precision impedance analyzer was supplied by Wayne Kerr Electronics Co. Ltd. (West Sussex, UK). Mass flow controller (MFC) was purchased from Laifeng Technology Co. Ltd. (Chengdu, China). Surface morphology of prepared materials was characterized with a Zeiss Supra55VP scanning electron microscope (SEM) operating at 20 kV and an FEI Tecnai G2 transmission electron microscope (TEM). Structure of the prepared materials was characterized by X-ray powder diffraction (XRD) on a Bruker D8 advance X-ray diffractometer ( $\text{Cu-K}\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) from  $10^\circ$  to  $90^\circ$ . X-ray photoelectron spectroscopy (XPS) was performed on a PHI1600 ESCA system (120 W, 100 eV). The specific surface area was measured by using a Quantachrome NOVA 1000 based on the Brunauer–Emmett–Teller (BET) experiment.

### 2.2. Synthesis of $\text{Mn}_3\text{O}_4$ and hollow $\text{MnFe}_2\text{O}_4$

The procedure for getting  $\text{MnFe}_2\text{O}_4$  was as follows: 0.17 g anhydrous manganese acetate, 0.67 g oleylamine and 0.14 g oleic acid were dissolved in 15 mL xylene by ultrasonication for 15 min. The solution was put into a flask attached with a condenser pipe, a thermometer and a dasher, and then heated from room temperature to  $90^\circ\text{C}$  with continuously stirring at 200 rpm. Subsequently, 1 mL deionized water was injected into the reaction mixture and stirring was continued for 1.5 h at  $90^\circ\text{C}$ . After that, 1 mL 1 M  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  was added into the system and the reaction lasted under stirring for 1.5 h at  $90^\circ\text{C}$ . Afterwards, the mixture was cooled down to room temperature and 100 mL ethanol was added, followed by centrifugation at 5000 rpm for 15 min. Finally, the obtained sediment was washed with ethanol repeatedly and vacuum dried in an oven at  $60^\circ\text{C}$  for 12 h to get dried  $\text{MnFe}_2\text{O}_4$ .

For comparison,  $\text{Mn}_3\text{O}_4$  was synthesized by using the same strategy but in the absence of adding  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ . All the samples were calcined at  $500^\circ\text{C}$  for 4 h in a muffle furnace.

### 2.3. Preparation of IE gas sensors

Before use, Au surface of IE was soaked in piranha solution (98%  $\text{H}_2\text{SO}_4$  + 30%  $\text{H}_2\text{O}_2 = 3:1, v/v$ ) for 10 min to remove organic residues. Then the electrode was rinsed with acetone, *n*-butyl alcohol and deionized water successively, and dried under a gentle stream of  $\text{N}_2$ .  $\text{MnFe}_2\text{O}_4$  ( $\text{Mn}_3\text{O}_4$ ) was dispersed in DMF to make homogeneous suspension of 0.04 g/mL. Gas sensing platforms were fabricated by dripping the suspensions on IE. The prepared sensors were then dried at  $60^\circ\text{C}$  for 2 h in air.

### 2.4. Gas sensing measurements

Performance of modified IE was studied in a self-made sensor testing system which was shown in Fig. 1. This system delivered target organic vapours at controlled concentration to gas cell using synthetic air as supporting and diluting gas. Air flow through mass flow controller<sub>1</sub> (MFC<sub>1</sub>) at a rate of  $f_1$  (sccm) brought evaporated vapour from liquid source, which was subsequently diluted by MFC<sub>2</sub> at a rate of  $f_2$  (sccm). The total flow rate of MFC<sub>1</sub> and MFC<sub>2</sub> was invariable at 1000 sccm. Concentration of target organic vapour was carefully adjusted via MFC<sub>1</sub> and MFC<sub>2</sub>, and calculated through equation:

$$C(\text{ppm}) = \left( \frac{P_i}{P} \times \frac{f_1}{f_1 + f_2} \right) \times 10^6 \quad (1)$$

where  $P$  is input air pressure (atmospheric pressure in our experiment), and  $P_i$  is saturated partial pressure of target VOCs obtained by the following Antoine equation [33]:

$$\log p_i = A - \frac{B}{C + T} \quad (2)$$

where  $A$ ,  $B$ , and  $C$  are Antoine constants, and  $T$  is the temperature in Celsius ( $T$  is  $25^\circ\text{C}$  in our experiment). During measurements, electrode was placed in a gas cell with electrical feed through. When organic vapor was brought in the cell, electrical resistance of sensor was monitored. Afterwards, the chamber was purged with pure air. Typical test included alternating the exposure of the sensor between vapor/air mixture and purging air. Sensing response was defined as  $R_a/R_g$ , where  $R_a$  and  $R_g$  are resistance in air and target gas, respectively. Response or recovery time was defined as the time to reach 90% response or recovery equilibrium upon exposure to target organic vapor or air.

## 3. Results and discussion

### 3.1. Characterization of the samples

The surface morphology of  $\text{MnFe}_2\text{O}_4$  was characterized by using electromicroscopy. As displayed in Fig. 2A,  $\text{MnFe}_2\text{O}_4$  is nanoparticles with narrowly-distributed size. TEM image in Fig. 2B further shows that  $\text{MnFe}_2\text{O}_4$  is hollow nanoboxes with side length about 20 nm. The specific surface area of  $\text{MnFe}_2\text{O}_4$ , measured by the BET adsorption, was found to be  $67.70 \text{ m}^2 \text{ g}^{-1}$ . The crystal structure and compositions of the prepared materials were identified by XRD, XPS and EDS. As shown in Fig. 2C, XRD patterns of  $\text{Mn}_3\text{O}_4$  and  $\text{MnFe}_2\text{O}_4$  agree well with the patterns of JCPDS cards (No. 24-0734 and 38-0430). Such results suggest that a portion of manganese ion of  $\text{Mn}_3\text{O}_4$  is replaced by ferric ion during reaction and the final product structure is iwakiite. Fig. 2D shows XPS spectra of both samples, wherein the peaks of Mn, Fe and O can be observed. Moreover, high-resolution XPS graphs of Mn 2p and Fe 2p are exhibited

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