Sensors and Actuators B 195 (2014) 509–514

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Improvement of response to formaldehyde at Ag–$LaFeO_3$ based gas sensors through incorporation of SWCNTs

Y.M. Zhang[a], J. Zhang[a], J.L. Chen[b], Z.Q. Zhu[a], Q.J. Liu[a,*]

[a] Yunnan Key Laboratory of Nanomaterials & Technology, Yunnan University, 650091 Kunming, China
[b] The State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, 650106 Kunming, China

ARTICLE INFO

Article history:
Received 18 June 2013
Received in revised form 8 January 2014
Accepted 10 January 2014
Available online 23 January 2014

Keywords:
Gas sensor
$LaFeO_3$
Single-walled carbon nanotubes
Formaldehyde

ABSTRACT

The $LaFeO_3$ modified by silver (Ag–$LaFeO_3$) further modified by single-walled carbon nanotubes (SWCNTs–Ag–$LaFeO_3$) with different weight ratio were prepared using a sol–gel method combined with the microwave chemical synthesis. The phase structures and micro-morphology of SWCNTs–Ag–$LaFeO_3$ were characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM), respectively. Indirect-heating sensors using SWCNTs–Ag–$LaFeO_3$ sensitive materials were fabricated on an alumina tube with Au electrodes and platinum wires. Gas-sensing characteristic of SWCNTs–Ag–$LaFeO_3$ to formaldehyde was investigated. It is found that the structure of SWCNTs–Ag–$LaFeO_3$ is of orthogonal perovskite. The gas-sensing properties of the Ag–$LaFeO_3$ sample modified by SWCNTs with 0.75% weight ratio (0.75%SWCNTs–Ag–$LaFeO_3$) are the best. The response of 0.75%SWCNTs–Ag–$LaFeO_3$ powder to 0.5 ppm formaldehyde is 23 at 86 °C. The detect limit to formaldehyde is 0.2 ppm. The response and recovery times are 6 s and 20 s, respectively. Those good properties make them the promising candidates for practical detectors to formaldehyde.

1. Introduction

Formaldehyde is considered to be one of the most important industrial and commercial chemicals due to its chemical activity, high purity and relative cheapness [1–3]. It is well known that formaldehyde has been classified as a mutagen and possible human carcinogen by both the US Environmental Protection Agency (EPA) and the World Health Organization (WHO) for its toxin, anaphylaxis and accumulation [4,5]. So it is very necessary to monitor the concentration of formaldehyde in atmospheric environmental quickly and accurately. Gas sensors based on semiconducting oxides are thought to be an effective means to monitor the gases because they are small, low cost and easy to use [6]. Single-walled carbon nanotubes are also the ideal candidates as active elements for fabricating gas sensors because SWCNTs are composed almost entirely of surface atoms, possess ultrahigh ratio of surface to volume and are expected to exhibit excellent sensitivity toward gas absorbates [7–10] and also possess excellent electronic properties, and good environmental stability [9].

Since SWCNTs were First used as sensors to detect NO_2 and NH_3 [11], the SWCNTs-based gas sensors have been successfully used to detect variety of gas or chemical vapors, such as NO_2 [12], O_2 [13] and H_2 [14]. And then, gas sensors based on SWCNTs to detect formaldehyde have been reported. A theoretical study suggested that SWCNTs doped with boron and nitrogen might be a potential candidate for detecting pollutants in indoor air [15]. 30 ppb formaldehyde has been detected when SnO_2 Film was doped by OH-functionalized multi-walled carbon nanotube, but it needs to be performed at high temperature (250 °C) [16]. An antimony–carbon nanotube–SnO_2 Film has been used to detect 500 ppm formaldehyde [17]. However, the utilization of SWCNTs sensors to detect formaldehyde is limited, mainly because of a weak physical adsorption between SWCNTs and formaldehyde [15]. Herein we report a highly sensitive and selective detection of formaldehyde using SWCNTs to modify Ag–$LaFeO_3$ which, based on our previous work, has good formaldehyde adsorption capability [18]. In our previous work, the SWCNTs were added before the calcination, which may cause the damage of the SWCNTs after calcination. For this motive, we add SWCNTs after the calcination in order to make sure that the SWCNTs exist and work as expected. The response to 1 ppm formaldehyde of Ag–$LaFeO_3$ based sensor is about 25 at the optimal operating temperature of 90 °C. To improve the response to better detection, Ag–$LaFeO_3$ was incorporated with SWCNTs. The result shows that Ag–$LaFeO_3$ incorporated with SWCNTs could easily and recoverably detect formaldehyde at a few hundred ppb level (the units are used as 0.2 or 0.5 ppm in the text for the sake of comparison) at a very low temperature (86 °C). This sensor also exhibited excellent selectivity to formaldehyde over

* Corresponding author. Tel.: +86 871 65035376; fax: +86 871 65035376.
E-mail addresses: qjliu@ynu.edu.cn, liu_qingju@hotmail.com (Q.J. Liu).

0925-4005/$ – see front matter
http://dx.doi.org/10.1016/j.snb.2014.01.031

those interfering organic gas, such as methanol, toluene, acetone, gasoline and water.

2. Experimental

2.1. Preparation of SWCNTs–Ag–LaFeO$_3$

Based on our previous experiments [18], the sample Ag–LaFeO$_3$ with Ag:La = 1:99 mol ratio (1/99Ag–LaFeO$_3$) was found to be the most promising for the selectivity to formaldehyde gas. In order to improve the gas-sensing response and decrease the operating temperature, 1/99Ag–LaFeO$_3$ was further modified with SWCNTs (x = SWCNTs:1/99Ag–LaFeO$_3$ = 0.25%, 0.50%, 0.75% and 1.00%, weight ratio). 1/99Ag–LaFeO$_3$ was prepared using a sol–gel method combining with microwave chemical synthesis. All the chemicals used are analytic grade reagents without further purifications from Tianjin Kermel Chemical Reagents Development Center. 0.99 mmol $La(NO_3)_3 \cdot 6H_2O$, 1.00 mmol $Fe(NO_3)_3 \cdot 9H_2O$ and 1.00 mmol citrate were dissolved in 100 mL distilled water as solution A. 0.01 mmol $AgNO_3$ were dissolved in 10 mL distilled water and added to the solution A, and then polyethylene glycol (PEG) was added. The final mixed solution was kept stirring at 80 °C for 8 h, and then was put in the microwave chemical device to synthesize for 2 h. The sol was dried at 150 °C and ground, and then heat treated at 800 °C for 2 h. Thus 1/99Ag-LaFeO$_3$ was prepared.

After 1/99Ag–LaFeO$_3$ was mixed with SWCNTs according different weight ratio, the mixtures was added into 50 mL deionized water, respectively, and decentralized under ultrasonic concussion for 15 min. After, they were treated in the microwave chemical synthesizer for 2 h and then dried. The SWCNTs–Ag–LaFeO$_3$ samples were prepared.

2.2. Fabrication of gas sensor

The prepared powders were further mixed with ethanol and ground to form a paste, which was subsequently printed onto an alumina tube. There are two Au electrodes placed at the both end sides of the tube. The length of the alumina tube is 4 mm and the diameter is 1.2 mm. We controlled the thickness of the sensing element layer by measuring with a vernier caliper in our experiment, and the quantity is calculated according to the density and volume. The thickness of the SWCNTs–Ag–LaFeO$_3$ compounds layer is 0.6 mm after calcination. In order to improve their stability and repeatability, the gas sensors were aged at 150 °C for 170 h in air. The gas response β was defined as the ratio of the electrical resistance in gas (R_g) to that in air (R_a) [18].

2.3. Characterization

The X-ray Diffraction (XRD) patterns were obtained for the phase identification with a D/max23 diffractometer using Cu $K\alpha_1$ radiation (λ = 1.54056 Å), where the diffracted X-ray intensities were recorded as a function of 2θ. The accelerating voltage was 35 kV and the applied current was 25 mA, and the sample was scanned from 10° to 90° (2θ) in steps of 0.02°. The particle morphology of the sample was tested by transmission electron microscope (TEM, JEM-2100).

3. Results and discussion

Gas-sensing response of SWCNTs–Ag–LaFeO$_3$ material with x = 0.75% is better than those with x = 0.25%, 0.50% and 1.00%. In this paper, we mainly discuss the material with x = 0.75%.

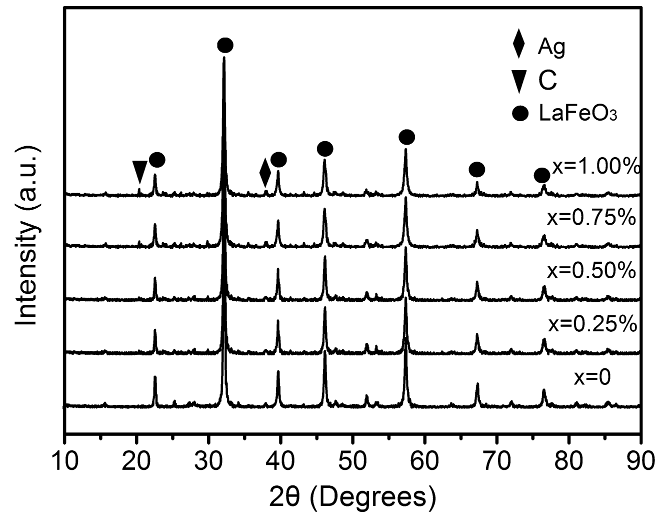

Fig. 1. XRD patterns of SWCNTs–Ag–LaFeO$_3$ ($0 \le x \le 1.00\%$) powders.

3.1. Structure and micro-morphology characterization

X-ray powder diffraction patterns of 1/99Ag–LaFeO$_3$ and SWCNTs–Ag–LaFeO$_3$ samples are showed in Fig. 1. The patterns indicate that the structure of 1/99Ag–LaFeO$_3$ and the SWCNTs–Ag–LaFeO$_3$ is orthogonal perovskite. The half-peak widths increase with the increase of the doping amount of SWCNTs. This is because in the range of x = 0.25% to x = 0.75%, the SWCNTs as impurity phase exists between grains and thus inhibit the growth of crystalline grain [19]. And according to Scherrer formula ($D = k\lambda/\beta \mathrm{Cos}\,\theta$, k = 1, where λ is the wavelength of X-ray, θ is the diffraction angle, and β is the true half-peak width.) the crystallite size is smaller, the half-peak width is bigger. The average crystallite size was estimated by means of Scherrer formula through measuring the half-peak widths of the lines in the pattern, The average crystallite size for 1/99Ag–LaFeO$_3$ and SWCNTs–Ag–LaFeO$_3$ with x = 0.25%, 0.50%, 0.75% and 1.00% are about 45 nm, 37 nm, 33 nm, 28 nm and 36 nm, respectively.

Transmission electron micrographs for 1/99Ag–LaFeO$_3$ and 0.75%SWCNTs–Ag–LaFeO$_3$ are shown in Fig. 2. The morphological features reveal that the grain size decreases with adding the SWCNTs. For 1/99Ag–LaFeO$_3$ (Fig. 2(a)), the particles are generally irregular and agglomerated, and the particle size was in the range of 30–90 nm. While on the surface of 0.75%SWCNTs–Ag–LaFeO$_3$ (Fig. 2(b)), there are many spherically shaped particles which are uniform in size and well dispersed on the surface of SWCNTs, the particle size was in the range of 10–40 nm. Thus the specific surface area of 0.75%SWCNTs–Ag–LaFeO$_3$ is increased, which can adsorb formaldehyde more easily and enhance the response. Comparing with the XRD results, TEM images reveal that there were various sizes of particles in 1/99Ag–LaFeO$_3$ and 0.75%SWCNTs–Ag–LaFeO$_3$. The big particles are composed of small crystallites.

3.2. The effect of SWCNTs on resistance

The relationship between resistances of SWCNTs-Ag-LaFeO$_3$ samples and operating temperature are shown in Fig. 3, and also the effect of the SWCNTs amount on the resistance is in Fig. 3. It is found that the resistances of all samples significantly decrease with the temperature increasing, which is the typical property of the semiconductor resistance and temperature. When the temperature is low, the electron on valence band did not possess enough energy to jump to the conduction band, the conductivity is low; as the temperature rises, the electron