Sensors and Actuators B 171–172 (2012) 679–685

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Synthesis and H_2S gas sensing properties of cage-like α-MoO_3/ZnO composite

Hai-Long Yu[a], Li Li[a], Xin-Ming Gao[a], Yue Zhang[a], Fanna Meng[a], Tie-Shi Wang[a], Gao Xiao[b], Yu-Jin Chen[a,*], Chun-Ling Zhu[b,*]

[a] College of Science, Harbin Engineering University, Harbin 150001, China
[b] College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

ARTICLE INFO

Article history:
Received 3 January 2012
Received in revised form 14 May 2012
Accepted 16 May 2012
Available online 15 June 2012

Keywords:
Sensor
α-MoO_3
ZnO
H_2S sensing characteristics
Cage-like composite

ABSTRACT

α-MoO_3/ZnO composite with a novel cage-like morphology, composed of nanosheets with a thickness of about 25 nm, was synthesized via a hydrothermal method. The cage-like composite was of porous characteristics with a pore size distribution from 4 to 174 nm. The Brunauer–Emmett–Teller (BET) surface area of the cage-like composite was 58.22 m^2/g, which was great higher than that of α-MoO_3 nanorods (8.94 m^2/g). The special structural characteristic of the composite resulted in its excellent H_2S sensing properties including very high sensor response, low working temperature and good selectivity.

1. Introduction

With the development of industry, various types of gases are increasingly released into the air, resulting in a serious environmental pollution. As a colorless and acidic gas with a "rotten egg smell", hydrogen sulfide (H_2S) has very harm to the health of human beings. Therefore, it is very important and essential to develop H_2S gas sensors with good sensing performances.

In the last decades chemical sensors based on semiconducting oxide materials, such as SnO_2, CuO, WO_3 and In_2O_3 [1–4], have been extensively investigated owing to their low cost, good stability and simplicity in fabricating sensors. Among them, ZnO semiconductor has wide applications in gas sensors for detecting H_2S gas [5–13]. For example, Wang et al. have synthesized ZnO nanorods and found that the sensors based on the nanorods could detect 0.05 ppm H_2S gas with the response value of 1.7 at room temperature [11]. However, its response time is very long (about 25 min). Liao et al. have reported the ZnO nanorods array sensor, which could be used for detecting 300 ppm H_2S with the response value of about 2.5 at 100 °C [12]. But the tested H_2S concentration is relatively high. Recently, Ramgir et al. have grown ZnO nanowires on substrates with seed particles, and found that the sensor response of the nanowires is about 4–30 ppm H_2S at 350 °C [13]. However, high working temperature may limit their practical application. Therefore, the H_2S sensing properties of ZnO nanostructures still need to be improved.

Recently, hetero-nanostructured materials for chemical sensor have attracted much attention because the sensitivity and selectivity can be manipulated by the component phases [14–23]. The enhanced gas sensing properties of those composites resulted from a variation of heterojunction barrier under the different gas atmospheres [20] and/or a synergetic effect of different sensing materials in the hetero-nanostructures [17–19]. Therefore, hetero-nanostructured materials containing ZnO such as ZnO/SnO_2, ZnO/CuO, and ZnO/Fe_2O_3 have been used as sensing materials [23,16,24]. However, most of them are mainly used to detect CO, ethanol, acetone, and gasoline gas. Herein we report the synthesis of porous α-MoO_3/ZnO composite with a novel cage-like morphology via a hydrothermal method. The porous composite is composed of nanosheets with a thickness of 25 nm. Especially, it can detect H_2S gas down to 500 ppb at 270 °C. Even at 100 °C it also has very strong response to 100 ppm H_2S gas.

2. Experiment

2.1. Synthesis of samples

2.1.1. Synthesis of α-MoO_3 nanorods

All chemicals used were analytical grade without further purification and purchased from Tianjin Kermel Chemical Reagent Co., Ltd. α-MoO_3 nanorods were synthesized by a hydrothermal

* Corresponding authors. Tel.: +86 451 82519754.
E-mail addresses: chenyujin@hrbeu.edu.cn (Y.-J. Chen), zhuchunling@hrbeu.edu.cn (C.-L. Zhu).

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http://dx.doi.org/10.1016/j.snb.2012.05.054

method [25,26]. Simply, 7.2 g of α-MoO_3 powder was reacted with 55 ml of 30% aqueous H_2O_2 and dissolved completely under stirring for more than 6 h. 27 ml of concentrated nitric acid and 170 ml of distilled water were added to the solution above, respectively. The mixture was allowed to stand for 4 days at room temperature. 35 ml of the mixture was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 ml for hydrothermal treatment at 170 °C for 45 h. As the autoclave cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with deionized water and absolute ethanol, and dried in air.

2.1.2. Synthesis of α-MoO_3/ZnO cage-like composite

0.035 g of α-MoO_3 nanorods obtained above was dispersed in 15 ml of 0.2 M ethylenediamine (EDA) solution under stirring severely for 10 min. 15 ml of 0.1 M zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was dropped to the suspension above. The mixture was then transferred into a Teflon-lined stainless steel autoclave with a capacity of 50 ml for hydrothermal treatment at 120 °C for 12 h. As the autoclave cooled to room temperature naturally, the precipitates were separated by centrifugation, then washed with deionized water and absolute ethanol, and dried at 80 °C for 12 h in air.

2.1.3. Synthesis of ZnO microrods

ZnO microrods were synthesized if the α-MoO_3 nanorods were not added in the reaction system under the same conditions as those for the preparation of the cage-like composite.

2.2. Analysis techniques

The morphology and microstructure of the products were characterized by scanning electron microscopy (SEM, JEOL-JSM-6700F), and transmission electron microscope (TEM, JEOL 2010). The crystal structures were measured by X-ray diffraction (XRD, D/max2550 V, Cu Kα radiation). The atomic ratio of Zn to Mo were determined by energy dispersive spectrometer (EDS) equipped in SEM (the operation voltage is 20 kV). Surface properties of the porous composite were investigated by BET method via nitrogen adsorption and desorption measurements, and the pore diameter and the pore size distributions were calculated by the Barret–Joyner–Halenda (BJH) method. The gas sensing properties were tested by ZWS1-WS-30A system (Zhongxi yuanda Science and Technology Co., Ltd., China) with a test chamber of 18 l, a gas-intake window, and 30 testing channels. The standard tested gases were purchased from Beijing Kshergas Co., Ltd., China. Generally, in order to improve the stability, the sensors were aged at 300 °C for 2 days before the measurements. A stationary state gas distribution method was used for testing the gas sensing properties. Detected gases such as H_2S were injected into the test chamber and mixed with air. The sensor response was measured repeatedly by five times.

2.3. Fabrication of gas sensor

The fabrication and testing principle of the gas sensor are similar to those described in our previous reports [27–31]. Simply, the sample was dissolved in absolute ethanol, and a drop was spun on a ceramic tube between metal electrodes to form a thin film with a thickness of about 0.1 mm. A metal alloy coil through the ceramic tube was used to supply the working temperature of the gas sensor. The sensing properties of the H_2S gas sensors were measured under atmosphere conditions with a relative humidity of 18% and ambient temperature of 22 °C. The sensor response (S) is defined as $S = R_a/R_g$, where R_a is the sensor resistance in air and R_g is the resistance in target-air mixed gas, respectively. The response and recovery times were defined as the time needed for 90% of total resistance change after the sensor was exposed to the tested gas and air, respectively.

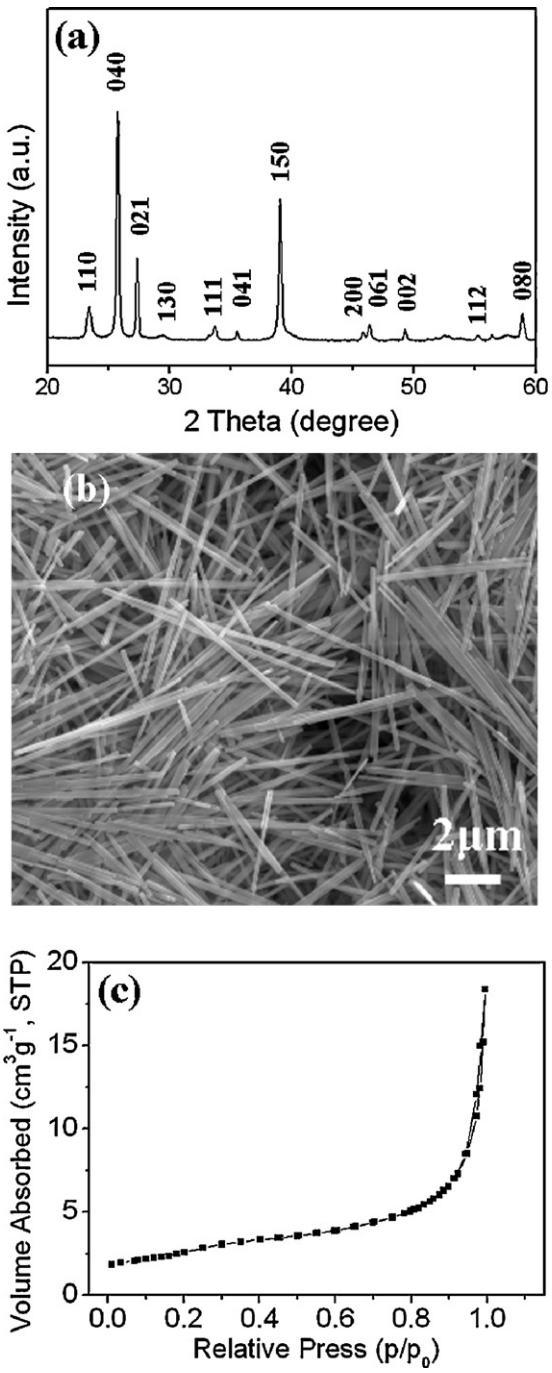

Fig. 1. (a) XRD pattern, (b) SEM image and (c) nitrogen adsorption–desorption isotherms of α-MoO_3 nanorods.

3. Results and discussion

3.1. Structure characterization of α-MoO_3 nanorods

Fig. 1(a) shows XRD pattern of the as-synthesized α-MoO_3 nanorods. Compared with the data in JCPDs No. 35-0609, all diffraction peaks in the pattern can be indexed to orthorhombic α-MoO_3. The SEM image shown in Fig. 1(b) reveals that uniform α-MoO_3 nanorods can be obtained. The average length and the diameter of the nanorods are about 12 μm and 170 nm, respectively. The