



Full Length Article

Outstanding gas sensing performance of CuO-CNTs nanocomposite based on asymmetrical schottky junctions



Yiming Zhao^a, Muhammad Ikram^a, Jiawei Zhang^{b,*}, Kan Kan^a, Hongyuan Wu^a,
Wanzhen Song^a, Li Li^a, Keying Shi^{a,*}

^a Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education, Key Laboratory of Physical Chemistry, School of Chemistry and Material Science, Heilongjiang University, Harbin, 150080, PR China

^b Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, School of Chemistry and Material Science, Heilongjiang University, Harbin 150080, PR China

ARTICLE INFO

Article history:

Received 1 July 2017

Received in revised form

13 September 2017

Accepted 20 September 2017

Keywords:

1D CuO-CNTs composite

Carbon nanotubes (CNTs)

Nitrogen dioxide (NO₂)

Gas sensor

ABSTRACT

To fabricate a high-performance material for sensor devices at room temperature and further improve the synthetic approach of sensing materials, one dimensional (1D) CuO-CNTs nanocomposites were prepared with CNTs and CuO nanorods (NRs) via a facile reflux method. The 1D composite with the molar ratio of CuO and CNTs at 2.4:1 displays excellent gas sensing performance, i.e. the lowest detectable limit of 970 ppb and the short response time of 6 s–97.0 ppm NO₂ at room temperature. In the 1D composite, the CNTs part provides a channel to enable effective and fast carrier transport, while the CuO NRs fabricates an asymmetrical schottky contact at the interface between the composites and the Au electrode. The advantage of the synergy of CNTs and CuO which possesses superior conductivity benefits the sensing of our 1D CuO-CNTs composite by providing affluent electrons.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Industrial development in the past decades has enormously increased the amount of toxic gases in the atmosphere, which results in dramatic consequences for both the environment and public health [1,2]. Among various air pollutants, the noxious gases such as NO and NO₂ (formulated as NO_x) are highly toxic. When the levels of NO_x are above 1 ppm, it causes serious diseases in humans body such as damaging respiratory system, lung tissues and heart disease [3]. The NO₂ gas also plays a major role in photochemical smog, ozone depletion and acid rain, causing pollution and damaging water sources [4–6]. Consequently, developing sensor devices that detect NO_x gas at room temperature is a popular research direction in the field of gas sensing [7].

Generally, good sensing performance can be achieved while materials have merits including uniform distribution, excellent morphology and nanostructures with large surface area to volume ratio. The manipulatable carrier in charge transport channel is also one of the greatest promises for gas sensing device (GSD). Most of GSDs reported are consisting of only single one dimensional

(1D) functional material mounted at each two fingers of an electrode. The two contact ends are usually designed to have ohmic characteristic to enhance conductance and minimize the resistance of carriers that flow across the contacts; however, it is not good enough for commercial applications due to the low response of gas sensors. Wang et al. reported a non-symmetrical schottky contact of GSD with one end in ohmic contact and the other end in schottky contact. This featured structure can greatly enhance the GSD response through adjusting the electrical conductivity [8].

CNTs possess a large surface area to volume ratio, which would benefit to improve the gas response. Moreover, the proportion of 1D structure radii and Debye length offers greater potential in sensing performance [9–12]. It, however, is difficult for a single CNTs-based gas sensor to form a non-symmetrical schottky contact of GSD. To overcome this drawback, CNTs composite sensors have been explored for 1D well-designed nanostructures.

In recent years, many efforts have been devoted to modifying functional CNTs with semiconductor metal oxides (SMOs) such as ZnO, In₂O₃, SnO₂ and CuO [13–16]. These composites have been successfully used for NO_x detection [17–20]. Among SMOs, CuO is increasingly attractive for gas-sensing application because of its p-type semiconductivity, high catalytic activity, narrow band gap (1.2 eV in bulk), fast redox ability [21], high-rate capability [22], abundant availability, non-toxic nature and low production cost

* Corresponding authors.

E-mail addresses: jiaweizhang1@163.com (J. Zhang), shikeying2008@163.com (K. Shi).

[23–26]. The 1D CuO nanostructures can serve as significant building blocks for nanodevices and integrated nanosystems [17]. The electroconductive limitation of the nanostructure may attribute to intrinsic defects/vacancies [27]. Therefore, it is desirable to use 1D CuO nanostructures as an additive for appropriate electrical conductivity to improve gas sensing properties. So far, the CuO NRs/nanowires have been investigated for sensing performance in the range of 200–400 °C as a working temperature [28–32]. A CuO-CNTs thin film has been synthesized to sense ethanol, showing high working temperature (400 °C) and low response time [33]. Given above difficulties, it may be more convenient by introducing a conductive material or an electronic channel network, which would fasten response time and lower working temperature.

Herein, the 1D CuO-CNTs composites have been synthesized by a facile reflux technique. The small CuO NRs were modified on the exterior surface of CNTs. And then, electronic channel network was fabricated by the connection of the high conductive channel of CNTs with the low conductive channel of CuO NRs. The Ohmic/Schottky contacts between the 1D CuO-CNT composites and the Au electrode were adjusted by thermal treatment (based on the device current-voltage characterization (I_{ds} - V_{ds})). The 1D CuO-CNTs in gas sensing may show some interesting characteristics: (i) the highly conductive CNTs part may improve the conductivity of whole composite; (ii) the diameters of CuO NRs which fall within Debye length L_d (3.74 nm) and $2L_d$ may facilitating the defects/vacancies creation; (iii) the CuO NRs may modify the microstructures of the 1D CuO-CNTs composite and alter the electrical conductivity, which together might benefit for the formation of asymmetrical schottky contacts with Au electrode. Therefore, the 1D CuO-CNTs sensor to NO₂ gas displays excellent sensing properties with a high response and a short response time at room temperature.

2. Experimental section

2.1. Hydroxylation of CNTs

All the chemicals were of analytical grade and used as-received without further purification. (Multi-walled) CNTs were purchased from Shenzhen Nanotech Port Co. Ltd, with purity of >97.0%. Specific amount of CNTs was functionalized by 100.0 mL of mixed acids (HNO₃:H₂SO₄ in 1:3 (v/v) ratio) under constant stirring for 30 min and then ultrasonication for 4 h and finally filtered and washed with deionized water until the pH reached 7. The washed sample were dried at 60 °C for 12 h and the final product of hydroxylated CNTs were obtained.

2.2. Synthesis of 1D CuO-CNTs composites

The hydroxylated CNTs of different concentrations i.e. (0.005 g, 0.010 g, 0.015 g) were dispersed in 49.0 mL *N,N*-Dimethyl Formamide (DMF) and 21.0 mL deionized water. The solution was ultrasonic for 20 min, and heated up to 60 °C, and then 0.40 g Cu(CH₃COO)₂·H₂O and 1.46 g Cetyltrimethylammonium Bromide (CTAB) were added and stirred vigorously. Later, 0.40 g NaOH was added to the solution, being retained at 60 °C and refluxed for 15 min. Finally, the solution was cooled down to RT for filtration. After washing with ethanol and deionized water, the samples were dried at 50 °C in a vacuum oven. The as-prepared 1D CuO-CNTs composites with (theoretical) CuO:CNTs molar ratio of 4.8:1, 2.4:1 and 1.6:1 were named as CuO-CNT-1, CuO-CNT-2 and CuO-CNT-3, respectively. The components of the samples were listed in Table S1.

2.3. Apparatus

Thermo gravimetric-differential scanning calorimetry (TG-DSC) analysis of the samples was performed by TA-SDTQ600. The crystal phase of the samples was characterized by X-ray powder diffraction (XRD, D/MAX-III-B-40 KV, Japan, Cu-K α radiation, λ = 1.5406 Å). The Brunauer-Emmett-Teller (BET) surface area of the products were measured by N₂ adsorption-desorption (TriStar II 3020). The surface morphology of the composites was characterized by scanning electron microscopy (SEM, HITACHI S-4800). Transmission electron microscopy (TEM, JEOL-2100) was performed to inspect the structures of the composites. X-ray photoelectron spectroscopy (XPS) was carried out using AXIS ULTRA DLD (Shimadzu Corporation) system to analyze the adsorbed oxygen species in the samples. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) plot measurements were carried out by using an electrochemical working station (CHI660C, Shanghai, China) in a half-cell setup configuration at RT. In the EIS measurement, the range of frequency was 0.01 Hz–100 kHz, and the excitation amplitude was 4 mV. Current-voltage characteristics (I_{ds} - V_{ds}) was performed on 1D CuO-CNT device using a Keithley 2602 source meter. I_{ds} - V_{ds} curves of the 1D CuO-CNT device was measured (the gate voltage V_g = 0.1 eV).

2.4. Gas sensing tests

1.0 mg for each set of 1D CuO-CNT composite was evenly dispersed in 1.0 mL of deionized water to prepare a suspension. A 0.05 mL suspension was dropped onto the interdigitated Au electrode (the width of Au fingers was about 2 μ m). The sensor was treated at 250 °C (or 300 °C and 400 °C) in Ar for 1 h and a CNT based gas sensor was obtained.

The sensor was mounted into a test chamber with an inlet and an outlet. The chamber was flushed with air for 2 min to remove any contaminants from the flask and also to stabilize the film before testing. Syringe was used to inject the required volume of NO₂ gas (99.8%, NO < 0.2%) into the test chamber. Then, NO₂ as the detected gas would come into contact with the surface of the samples. The changes in the electrical resistance of the samples were recorded by a home-made automatic resistance apparatus over time. Finally, the sensor resistance was recovered by purging the chamber with air. The electrical resistance measurements of the sensor were carried out at RT with a relative humidity of (RH) around 26.0%.

The sensor response was defined as the ratio $(R_0 - R_N)/R_0$, where R_0 and R_N were the resistances of the sensor in air and NO₂ gas, respectively. The response time was defined as the time required for the variation in resistance to reach 90% of the equilibrium value after a test gas was injected. The material was tested to respond to various detecting gases such as NO₂, H₂S, NH₃, CO or H₂, and the highest response (to a kind of gas) signified a good sensing selectivity of the material.

3. Results and discussion

3.1. Composition and morphology

TG-DSC analysis was displayed in Fig. 1. As seen from the TG-DSC curves of CNTs (Fig. 1a), the mass ratio of CNTs begins to decrease at about 460 °C and sharply decreases in going from 570 °C to 685 °C. For CuO-CNT-1, CuO-CNT-2, and CuO-CNT-3 (the calculated molar ratios of CuO:CNTs are 4.8:1, 2.4:1 and 1.6:1, respectively), the decreased mass was attributed to consumption of CNTs in the range of temperatures from 240 °C to 550 °C (Fig. 1b). The change indicated that the interaction between CNT and CuO was stronger.

Download English Version:

<https://daneshyari.com/en/article/5347199>

Download Persian Version:

<https://daneshyari.com/article/5347199>

[Daneshyari.com](https://daneshyari.com)