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Graphene-zinc oxide based nanomaterials for gas sensing devices

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Abstract

Herein, we report the preparation of a hybrid material by combination of modified graphene and ZnO. The morphological and compositional analyses of the obtained material have been performed by means of scanning electron microscopy and energy dispersive X-ray analysis. The functional properties of the prepared structures have been investigated for their application in gas sensor devices. The gas sensing performance of the hybrid material show that the structure can be used for fabrication of chemical sensors, as well as in electronic nose technology.

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Keywords: Graphene; graphene oxide; ZnO; gas sensor

1. Introduction

Over the last decades, semiconductor materials were considered as very attractive materials for application in sensing devices, solar cells, as well as in energy storage and conversion [1–4]. Especially metal oxides are promising materials for fabrication of chemical sensors due to their advantages, such as low cost, easy production, simple measuring electronics, etc. [5–8].

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With the development of chemical industries, the improvement of the sensing performance of metal oxide materials for the detection of toxic, explosive and hazardous gases is becoming more important. Among the metal oxide materials, ZnO is one of the widely investigated structures for the chemical sensing due to its high thermal/chemical stability and good oxidation resistance [6,9]. Gas sensors based on ZnO usually operate at temperatures of about 200-450 °C [6,10]. The high temperature promotes the red-ox reactions underlying the sensing mechanism of chemiresitors [11]. Therefore, the capability to decrease the material working temperature is an important issue for fabrication of low power consumption and small size chemical sensors.

NO_2 is a toxic and colorful gas. It is generated during different combustion processes [12]. Due to this reason, the detection and the control of NO_2 in power plants, factories and combustion engines is very important. Nanostructured ZnO has attracted interest for the sensing applications because it provides large surface area, which is advantageous for the enhancement of the material sensing performance. Different strategies, such as surface modification, doping, functionalization and use of multi-compositional structures have been applied to improve the sensing properties of ZnO [10]. Recently graphene oxide has been studied for applications in gas sensing devices. Investigations have shown that graphene oxide is a promising material for the sensing applications [13].

In this work, we report the fabrication of a composite material based on graphene oxide and ZnO nanostructures with subsequent thermal reduction of graphene oxide at 250 °C. The sensing properties of the obtained material have been tested towards NO_2 and H_2. The presence of graphene oxide improved the response of the composite to NO_2 compared to pristine ZnO nanostructures indicating that the prepared nanocomposite material is promising for fabrication of NO_2 sensors.

2. Experimental

ZnO nanostructures were synthesized according to the procedure reported in our previous work [14]. For the fabrication of ZnO nanostructures we deposited thin films of metallic Zn on alumina substrates by means of radio frequency (RF) magnetron sputtering. The average thickness of the obtained Zn thin films was 500 nm. Then, we anodized thin films of Zn in Teflon electrochemical cell using two-electrode system. The samples were anodized in 2 M oxalic acid dihydrate ($C_2H_2O_4{\cdot}2H_2O$) containing ethanol at room temperature. We used a platinum foil as a counter electrode. As-prepared structures were zinc oxalate dihydrate ($ZnC_2O_4{\cdot}2H_2O$). We performed $ZnC_2O_4{\cdot}2H_2O$-to-ZnO transformation of the samples by thermal annealing in the furnace at 400 °C under the atmosphere of 50% O_2 + 50% Ar for 4 h.

We produced the graphite oxide from natural graphite (SP-1, Bay Carbon) using a modified Hummers method, as described elsewhere [15]. Then, we prepared aqueous dispersions of graphene oxide at various concentrations by stirring graphite oxide solids in pure water (18.0 MΩ·cm resistivity, purchased from Barnstead) for 3 hours and sonicating the resulting mixture (VWR B2500A-MT bath sonicator) for 45 minutes. For the fabrication of the composite structure, we drop casted 5 µl homogeneous dispersion of the graphene oxide with concentration of 0.05 mg/ml onto ZnO nanostructures prepared on square alumina substrates. Afterwards, we annealed the prepared composite material in the furnace at 250 °C in the atmosphere made of 20% O_2 and 80% Ar for 1 h that results in partial reduction of graphene oxide in the composite structure.

The morphological analyses of the prepared materials were carried out using a LEO 1525 scanning electron microscope (SEM) equipped with field emission gun. Elemental composition of the obtained samples was studied by means of energy dispersive X-ray analysis (EDX). For the functional measurements, we deposited platinum electrodes on the surface of the obtained samples using RF magnetron sputtering. Then, we deposited a platinum heater on the backside of the alumina substrates.

Gas sensing properties were tested by means of the flow-through technique at atmospheric pressure, using a constant synthetic airflow (0.3 l/min) as carrier gas for the analyte dispersion. The desired gas mixtures were obtained by means of a computer controlled gas flow system and 50% relative humidity at 20 °C by mixing dry air with saturated humid air (produced by bubbling synthetic air through a column of water kept at 25 °C and then condensed at 20 °C) in the desired proportions. Sensor conductance was monitored by means of the volt-amperometric technique at constant bias voltage.

3. Results and discussions

Fig. 1 shows SEM images of the obtained composite materials with the different magnifications. As can be seen in the images ZnO nanoparticles with the average diameter of 20 nm agglomerated into the chain-like shaped structures forming ZnO nanowires. The images clearly show that the graphene oxide decorated the ZnO nanoparticles. Compositional analysis showed that the graphene oxide in the composites after annealing at 250 °C was partially reduced resulting in C:O ratio of 82:18. Thus, the annealed nanocomposite structure was denoted as RGO–ZnO Fig. 2 (a) reports the conductometric sensing performance of the obtained nanocomposite material towards NO_2 and H_2. In Fig. 2 (a) shows the calibration curve of the RGO-ZnO and ZnO structures for NO_2. RGO–ZnO has a higher response to NO_2 and a lower response to H_2 compared to pure ZnO at the relatively low working temperature (150 °C). The sensing results show that by the coupling of ZnO with the graphene oxide it is possible to improve the material selectivity.

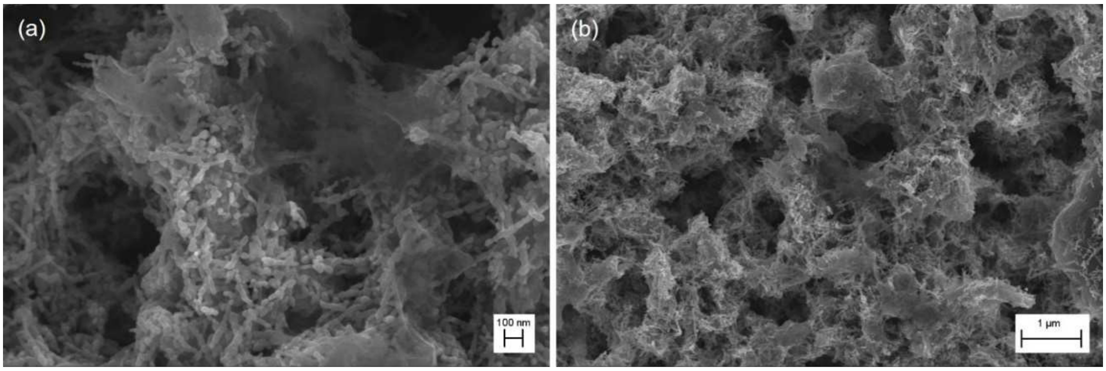

Fig. 1. SEM micrographs of the prepared structures based on graphene oxide and ZnO with different magnifications.

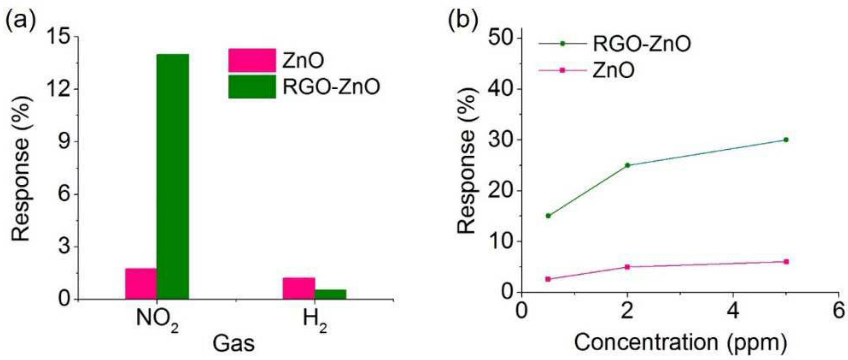

Fig. 2. (a) Response of the RGO-ZnO and pristine ZnO samples towards 0.5 ppm NO_2 and 100 ppm of H_2 at the working temperature of 150 °C and in humid air (relative humidity RH=50% @ 20°C); (b) Calibration curve of the RGO-ZnO and ZnO structures for NO_2 at an operating temperature of 150 °C and in a humid air background (RH=50% @ 20°C)

4. Conclusion

In summary, we fabricated a composite material based on reduced graphene oxide and ZnO nanostructure. The gas sensing properties of the obtained nanocomposites were investigated by exposing them to NO_2 and H_2. The composite material showed better gas sensing performance compared to the pure ZnO nanostructures for NO_2 at the relatively low working temperature. The preliminary results show that RGO–ZnO is promising structures for the development of NO_2 gas sensing devices.

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