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Acetylene gas sensing properties of an Ag-loaded hierarchical ZnO nanostructure-decorated reduced graphene oxide hybrid

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ABSTRACT

Acetylene (C_2H_2) gas sensors were developed by synthesizing an Ag-loaded hierarchical (Hrc) ZnO nanostructure-reduced graphene oxide (Ag/ZnO Hrc-RGO) hybrid using a facile and rapid photochemical method. Morphological characterizations showed the formation of well-dispersed Ag nanoparticles-loaded hierarchical ZnO nanostructures onto the 3- to 5-layer thick RGO sheets. The hierarchical ZnO nanostructures were composed of numerous randomly oriented porous ZnO nanosheets with an average sheet thickness of 6 nm. It was also observed that Ag nanoparticles with an average diameter of 40 nm were closely affixed onto the ZnO nanosheets. Structural analysis revealed good agreement with the standard crystalline phases of ZnO, Ag and RGO. Gas-sensing characteristics of the synthesized materials were carried out in a temperature range of 25–300 °C at different C_2H_2 gas concentrations. At 200 °C, 5 wt% Ag/ZnO Hrc-RGO hybrid showed a preferable detection of C_2H_2 with high sensor response (12.3 toward 100 ppm), fast response time (57 s), a limit of detection (LOD) of 3 ppm, good linearity, with excellent reproducibility and selectivity. The fabricated sensor also showed less humidity effect in an open air environment.

1. Introduction

Increased concern about adverse impacts from the emission of various toxic and flammable pollutants on the environment and human health, increasingly promotes the development of accurate and low-power consuming gas sensors for reliable detection and monitoring of such pollutants. To meet the demand, during the last few decades, metal-oxide semiconductors (MOS)-based gas sensors have been the subject of extensive research and development [1]. With the continued development of various metal oxides, zinc oxide (ZnO) with different nanostructures (such as nanoparticles, nanowires, nanorods, nanofibers, microdisks, flowers, etc.) have become promising candidates for ultrasensitive sensors owing to their simplicity, low cost of preparation, and excellent chemical and thermal stability [2–6]. It is well established that the performance of such sensors is significantly influenced by the synthesis process and the architecture of the sensing materials. In recent years, great attention has been focused on the fabrication of low-dimensional building blocks into three-dimensional (3D) ordered hierarchical ZnO architectures at the nanoscale level. Such a unique and complex architecture not only provides more opportunities for exploring novel properties, but also promotes sensing behavior with superior performances owing to their ordered crystalline nanostructures, high surface-to-volume ratios, porosity, excellent gas molecule adsorption capabilities, and special physical and chemical properties [7]. However, many suffer from limitations, such as high operating temperature, slow response time, and poor selectivity and reproducibility, making them impractical monitors for area air quality and safety. Therefore, to overcome the sufferings, research attention has been focused on increasing the sensor performance at low temperatures, which is usually realized by the incorporation of noble metals or carbon materials on the surface of the base metal-oxide sensors [8–10].

It has been reported that the introduction of noble metals can produce some kind of synergistic effect, which influences the material's electronic and chemical distribution favorable to the adsorption of oxygen species, and results high performance in metal-oxide based sensors. Besides, two dimensional (2D) carbon material (graphene) as a support catalyst acts as a bridge inside the sensing materials, which greatly enhances the charge transfer among them. It can also act as an electron acceptor to increase the depletion layer of metal-oxide sensor and helps to boost the sensing performance [10].

Acetylene (C_2H_2) is an unsaturated, highly toxic and flammable hydrocarbon, widely used as fuel or raw material in many

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mechanical and chemical industries. In recent years, considerable interest has been focused on the development high-performance C_2H_2 sensors because of safety reasons. Numerous research results in the literature have reported significant improvements, but limitations like complex synthesis processes, high operating temperatures, detection limits, and selectivity are still the subjects of intensive research.

Recently, our group [11] reported a ZnO nanoparticles (NPs)-reduced graphene oxide (ZnO/RGO) based C_2H_2 sensor with a high response magnitude of 18.2 (100 ppm), a limit of detection (LOD) of 30 ppm at 250 °C, and a relatively slow response time (100 s). Wang et al. [12] synthesized a 5 at% Ni-doped ZnO nanofiber, and their device showed a maximum response of 17 (2000 ppm) at 250 °C. Tamaekong et al. [13] reported on Pt/ZnO thick films by using the flame spray pyrolysis method with a response of 43 (1000 ppm) and an LOD of 50 ppm at 300 °C. Zhang et al. [14] reported the most enhanced C_2H_2 sensing properties by synthesizing a hierarchical nanoparticles-decorated ZnO microdisk using a hydrothermal method. Their sensor showed a very high response magnitude of 52 (200 ppm), a large detection range of 1–4000 ppm, and a fast response time (15 s) at high temperature (420 °C). In addition, a few results for SnO_2 NPs [15], Pd–SnO_2 [16], Sm_2O_3–SnO_2 [17], Au/MWCNT [18], Ag/Pd–SiO_2 [19], Ag/ZnO [20], etc., have been reported in the literature with a few improvements. Most recently, our group [21] reported an Ag/ZnO NPs-decorated RGO hybrid synthesized via a chemical method. The fabricated sensor device showed excellent sensing performance, such as a high response of 21.2 (100 ppm), a fast response time (25 s), and excellent selectivity at 150 °C.

In the current work, we presented an Ag-loaded hierarchical (Hrc) ZnO nanostructure-decorated RGO hybrid, synthesized via a facile and rapid photochemical route. In our previous work [21], we investigated the sensing behaviors in a closed chamber, whereas in this work, we studied the sensing behaviors in an open air environment. We hope that our fabricated sensor device will open up additional opportunities to fabricate an efficient and practical C_2H_2 sensor in the near future.

2. Experimental details

2.1. Synthesis of materials and device fabrication

All the chemicals used in the synthesis process were of analytical grade purchased from Sigma–Aldrich Co. Inc., and were used without further purification.

2.1.1. Synthesis of hierarchical ZnO nanostructures

Hierarchical ZnO nanostructures (ZnO Hrc) were synthesized via hydrothermal method. In a typical process, 4 M of $Zn(CH_3COO)_2{\cdot}2H_2O$ and 2 M of sodium hydroxide (NaOH) were dissolved in deionized (DI) water through vigorous stirring for 30 min. Few drops of ammonium hydroxide (NH_4OH) were then added to the solution as a capping agent to maintain a pH level of 9. The mixer was then transferred to a Teflon-lined autoclave, heated at 200 °C for 10 h and naturally cooled to room temperature. A little precipitation of white-colored ZnO suspension was then washed several times using DI water and dried at 60 °C overnight to get the fine ZnO powder.

2.1.2. Synthesis of RGO

Graphene oxide (GO) was prepared from extra pure graphite powder (particle size < 50 μm) by modified Hummer method [22]. The aqueous suspension of GO (10 mg/mL) was diluted with N,N-dimethyl formamide (DMF) through sonication treatment in an ultrasonic bath for 1 h to make a homogenous suspension of GO in DMF/water (80:20 v/v). Then, 1 mL of hydrazine monohydrate was added to the solution as a reducing agent, and stirred for 6 h at an elevated temperature of 80 °C. The resulting RGO suspension was black in color and was preserved for further experimental use.

2.1.3. Synthesis of Ag/ZnO Hrc-RGO hybrid

Ag-loaded ZnO Hrc (Ag/ZnO Hrc) nanostructures were prepared through a photochemical route. In the synthesis process, 0.5 g of pure-hierarchical ZnO powder and 3 wt% of silver nitrate ($AgNO_3$) was dissolved in 20 mL of DI water through sonication treatment for 30 min. Irradiation of the solution was carried out using 230–250 nm light segment of a 300 W mercury lamp for 30 min. Ag contents were varied from 3, 5 and 7 wt% to obtain the optimum ratio of Ag to ZnO. Subsequently, to prepare the hybrid sample, 30 mL of RGO solution was added to Ag/ZnO Hrc solutions containing different amount of Ag with vigorous stirring for 1 h at 80 °C.

For gas sensing measurement, the pure ZnO Hrc, Ag/ZnO Hrc and Ag/ZnO Hrc-RGO hybrid were deposited on an Al_2O_3 substrate. The fundamental steps were as follows: Interdigitated (IDT) electrodes of gold with a line-distance of 100 μm were fabricated on the 6 mm × 12 mm Al_2O_3 substrate via lift-off process and radio frequency (RF) magnetron sputtering. The sensing material was then deposited on the IDT electrodes via air-brush spraying and metal mask (selective area). The substrate was heated to 110 °C on a hot-plate during spraying.

2.2. Characterization and sensor test

Structural properties of the sensing materials were investigated using X-ray diffractometer (XRD) (Rigaku Ultima IV) with Cu Kα (λ = 0.154 nm) radiation with a 2θ scanning range of 10–80°. The surface morphology was examined by field emission scanning electron microscopy (FESEM; JEOL JSM-7600F) and transmission electron microscopy (TEM; JEOL JEM-2010F) with an accelerating voltage of 10 kV. Energy dispersive spectrometer (EDS, JEOL JEM-2010F) was carried out for compositional analysis.

For gas sensing characterization, the fabricated sensor device was attached on a ceramic heater, and fixed on a stand in an open air environment. A narrow tube was placed on the top of the sensor device to flow C_2H_2 gas. A computerized mass flow controller (ATOVAC, GMC 1200) system was used to vary the concentration of C_2H_2 in synthetic air. The gas mixture (synthetic air and C_2H_2) was delivered on top of the sensor device at a constant flow rate of 50 sccm (standard cubic centimeters per minute) with different C_2H_2 concentration. Gas concentration was controlled and measured by the following equation:

$$Gas_{con.}(ppm) = \frac{Flow\ rate_{air} + Flow\ rate_{gas}}{Total\ flow\ rate}$$

The gas flow was stopped between each C_2H_2 pulse to allow the surface of the sensor to return to atmospheric condition. A Keithley probe station (SCS-4200) with a bias voltage of 1 V was used for all measurements and data acquisition. The device was tested at temperatures ranging between 25 °C and 300 °C for various C_2H_2 concentrations. The sensor response (S) was calculated using R_a/R_g, where R_a and R_g are the resistances in the presence of air and carrier gases, respectively. The response time and recovery time of the sensors were defined as the time to reach 90% of the total resistance change.

3. Results and discussion

3.1. Structural and morphological studies

Fig. 1 shows the XRD patterns of pure ZnO Hrc, Ag/ZnO Hrc and Ag/ZnO Hrc-RGO hybrid. The observed characteristic