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Selective hydrogen sulfide (H_2S) sensors based on molybdenum trioxide (MoO_3) nanoparticle decorated reduced graphene oxide

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ABSTRACT

This paper investigates a selective method of sensing hydrogen sulfide using molybdenum trioxide (MoO3) nanoparticle decorated graphene oxide (GO). Reduced graphene oxide was synthesized from natural graphite (NG) by the modified Hummer's method and decorated with the MoO_3 nanoparticles. Sensors were fabricated by the spin coating of MoO_3-decorated rGO between Pt electrodes on alumina substrate (Al_2O_3). In comparison with pristine rGO sensor, the MoO_3–rGO chemiresistors have a clear response to hydrogen sulfide down to 50 ppm at 70 °C. Thermal characterization of the sensor is studied. Results show that the fabricated devices have the maximum gas response at about 160 °C. Selectivity tests indicated that these sensors have poor respond to interfering analytes such as ethanol, carbon monoxide and nitric oxide. Furthermore, the effect of MoO_3 content and graphene oxide suspension concentration on the sensor response is investigated. Hereby it is shown that the sensor content of 3 wt% MoO_3 and of 5 mg/ml of GO suspension concentration has the highest sensitivity. Decorated reduced graphene oxide chemiresistors offer advantages such as remarkable potential for mass production due to their ease of manufacturing, good performance, and significant selectivity.

1. Introduction

Hydrogen sulfide (H_2S) is widely used in various chemical industries and research laboratories. It is emitted in nature from biological processes as well as mines and petroleum fields. H_2S is an extremely toxic gas that produces severe effects on the nerve system even at low concentration of 250 ppm. Therefore, several studies have been reported on H_2S gas sensitive materials [1–5].

Current methods of hydrogen sulfide detection are based on three main technologies, semi-conductive chemiresistive metal oxides, electrochemical and chemical field-effect transistors [6]. Among these techniques, the metal-oxide and electrochemical sensors do not have good selectivity regarding to a range of interferrent gases [7]. The field-effect techniques are far more selective, but have a high cost of fabrication. Thus, there is a demand for a low-cost and selective sensing technology that could be applied to large-scale production. MoO_3 has a strong affinity to H_2S and hence, it is hypothesized that H_2S will form MoS_2 by reacting with the surface of these nanoparticles [8,9]. The MoO_3 particles act as a promoter and this decoration will invariably change the electrical properties of the rGO layers [10,11]. Graphene as a monolayer carbon film with two-dimensional honeycomb sp^2 network has attracted considerable attention, due to its exceptional electronic and mechanical properties [12]. It shows unique physical and chemical properties which makes it promising candidate for high-tech applications such as energy storage, nanocomposites

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and gas sensors. However, mechanically exfoliated graphene is not an appropriate source for mass production [13]. Reduced graphene oxide can be regarded as a low cost alternative material. In recent years, some researchers have reported the use of reduced graphene oxide to fabricate gas sensors, which have been shown to detect gases such as NO_2, NH_3 and H_2 in low concentrations [13,14]. The properties of rGO-based gas sensor have been shown by changing of interface charge layer due to adsorption of reducing or oxidizing gases [15]. It has been discussed that rGO has high affinity for a wide range of gases which when physisorbed or chemisorbed onto its surface would produce a change in the electronic structure of the rGO as the adsorbed molecule would act as electron donors or acceptors on the rGO surface, which leads to changes in the conductance of rGO. However, there are different molecules that can regulate the carrier concentration; hence the selectivity cannot be neglected [16]. In recent years, some researchers reported nanostructured based gas sensors functionalized by chemical groups like carboxyl, amide or metal groups to detect H_2S [17]. It is noted that in regard to nanostructured material such as CNTs, nanofibers and nanorods, the reduced graphene oxide is an appropriate alternative due to its ease of manufacture and low cost raw materials [18]. However, few studies, conducted for doped or decorated rGO in H_2S detection so far. Gutes et al. showed that Au-doped graphene is sensitive to H_2S [19], but the recovery of the sensor was slow due to the formation of strong S–Au bonds.

Therefore in this study, we report the fabrication and characterization of a molybdenum trioxide (MoO_3)-decorated reduced graphene oxide (rGO) chemiresistors, to understand the actual effect of MoO3. It has been observed that the electronic properties of molybdenum trioxide decorated rGO (MoO_3–rGO) have a strong electrical response to H_2S exposure compared with the typical interfering gases like carbon monoxide (CO) and nitric oxide (NO).

2. Material and methods

2.1. Reduced graphene oxide synthesis

GO was synthesized from natural graphite (NG) by the modified Hummer's method [20]. The oxidized graphite in water was ultrasonicated to achieve GO sheets followed by centrifugation for 30 min at 3000 rpm to remove any unexfoliated oxidized graphite. The pH of GO dispersion in water (5 mg/ml) was adjusted to 11 using a 5% ammonia aqueous solution. The suspension of GO was reduced to rGO by exposing to hydrazine vapor for 20 h at 40 °C followed by low temperature annealing for 1 h at 200 °C.

2.2. Decoration of MoO_3 particles

An incipient impregnation process was used for Mo decoration of rGO using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as precursor. A metal precursor $(NH_4)_6Mo_7O_{24}$ with 1 wt% Mo was added to some water depending on the pore size of the support. Then it is impregnated to the rGO supportand dried at 70 °C and finally calcined at 550 °C for 2 h in the nitrogen to convert the Mo to MoO_3 [21].

2.3. Preparing of gas sensor

The sensor fabricated on an alumina (Al_2O_3) substrate with dimensions of (10 mm × 10 mm × 1 mm). Then a pair of Platinum (Pt) interdigitated electrodes with an apparent thickness of 200 nm were deposited and formed with radio-frequency magnetron sputtering at 7.5×10^{-2} Torr and room-temperature. To make a sensitive layer, 1 mg of the MoO_3–rGO was dispersed in 30 ml of ethanol by ultrasonic vibration for 3 h to achieve the well-mixed suspension. Afterward, by employing the spin coating, the suspension was coated on the surfaces of the Pt-electrodes and the Al_2O_3 substrate with the spin and period of 800 rpm and 20 s, respectively. Then, the coated layers were heated in air at 150 °C for 30 min to eliminate the excess solvents in the coating layers.

2.4. Gas detection setup

A schematic view of the fabricated chemiresistor and the gas detection setup used for electrical measurements of the chemiresistors is shown in Fig. 1. A gas detection equipment consists of gas suppliers, mass flow meters, a detector unit, a U-like quartz glass reactor with a diameter of 2.5 cm and a length of about 150 cm, and a jacket heater. An A/D board and GAS4 software were used for a data acquisition. The desired set point of the operating temperature was controlled by a DC power supply system. The temperature was measured by a J-type thermocouple, inserted in to thermal contact with heater-sink. The output DC voltage from thermocouple was monitored by a multimeter and a digital thermometer placed in parallel to the multimeter, to convert the thermocouple output voltage into the corresponding value of the temperature unit. The DC electrical conductance of the sensors during the gas exposures has been measured by the volt-amperometric technique in the two-pole format by an additional multimeter. The fabricated devices inserted in the glass reactor and connected to the measurement unit by wires to record the variation of electrical conductance of the sensitive films versus time. Dry air and H_2S (in mixture with nitrogen) were used as reference and detecting gases, respectively. The gas sensing experiments have been performed at temperature of 70 up to 350 °C, and the total flow rate of H_2S and carrier dry air per exposure were kept constant at 200 ($cm^3\ min^{-1}$). The concentrations of H_2S gas were controlled by a mass flowmeters and regulated by diluting dry air through a mixer. The initial resistance (R_{air}) was measured in dry air at test temperature. The sensitivity of the nanosensors was calculated as the ratio of the change in its electrical resistance with H_2S to its resistance with dry air.

3. Results and discussion

3.1. rGO characterization

The reduction of GO to rGO was verified by X-ray photoelectron spectroscopy (XPS). Fig. 2 shows the XPS data of GO dispersed on Al_2O_3. Fig. 2(a) displays the four components of carbon- based atom in different functional groups of GO; (I) the non-oxygenated C–C bond (284.4 eV, pink curve), (II) C–O bond (286.7 eV, green curve), (III) the C═O bond (287.5 eV, blue curve), (IV) C(O)O (289.2 eV, cyan curve). Fig. 2(b) shows