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ZnO nanosheets/graphene oxide nanocomposites for highly effective acetone vapor detection

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ABSTRACT

ZnO nanosheets/graphene oxide (GO) nanocomposites were synthesized for highly selective, quick response acetone detection. Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to characterize the morphologies, microstructures and compositions of the nanocomposites. The effect of GO on the sensing performances of the nanocomposites was investigated. It was found that 10 wt% GO was the optimized loading and the response value reached 35.8 under the exposure of 100 ppm acetone. The unique sensing properties were attributed to the synergistic effects of rigid ZnO nanosheets and flexible GO, including large specific surface area, rich functional groups of GO etc. This work will contribute to the development of new acetone sensors and broaden the application of GO composite materials.

1. Introduction

Acetone is extensively used to dissolve plastic, purify paraffin and dehydrate tissues, which is easy to evaporate at room temperature [1]. The inhalation of acetone will cause headache, fatigue, narcosis and even harmfulness to nerve system. Hence, it is necessary to monitor the acetone gas of workplace for the sake of personal safety. In addition, the acetone concentration is a very important symbol for detecting diabetes mellitus [2]. Therefore, highly sensitive and selective sensors for acetone detecting are required for the rapid assessment of diabetes and related diseases. The detection of acetone is usually based on expensive analytical instruments such as gas chromatography and infrared spectrometer, which are only available in laboratory [3,4]. Acetone sensors based on semiconductor metal oxides are promising alternatives for rapid detection because they are low cost, highly sensitive and easily carried around [5]. Recently, with advantages of large surface area, high surface to volume ratio and special physicochemical properties, metal-oxide nanomaterials such as SnO_2, WO_3, In_2O_3 and $ZnFe_2O_4$ have attracted wide interest for being used as acetone sensing materials [6–8]. Although lots of progresses on acetone sensors have been obtained, there are still some shortcomings such as low response speed and low selectivity. As a typical n-type semiconductor, ZnO is an important gas sensing material due to its good response to reducing or oxidizing gases, low cost, and being friendly to the environment [9–11]. Various ZnO nanostructures such as nanowires, nanorings, nanocombs and nanosprings have been prepared [12]. Compared with other ZnO nanostructures, two-dimensional (2D) ZnO nanosheets show some merits, such as good response speed and high response to target gas, which are due to the large surface area-to-volume ratio and the selectively exposed crystallographic plane [13]. However, the application of ZnO nanosheets is limited by their rigidity, and they are easily destroyed in the process of sensor preparation [14]. The structure of nanosheets can be maintained if ZnO nanosheets are composited with some flexible materials.

As a representative of flexible material, graphene is a 2D monolayer carbon atomic sheet with remarkable electronic conductivity, superior mechanical property, large surface area and high thermal stability [15–17]. Similar to graphene, graphene oxide (GO) based gas sensors have also raised concerns due to simple fabrication, the abundant surface functional groups and high surface area [18]. GO/semiconductor hybrid nanostructures have attracted great attention in gas sensor due to the synergistic effect of two materials and the additional functionality of the GO [19–22].

In this work, nanocomposites of ZnO nanosheets and GO were fabricated for highly efficient acetone sensing. The nanocomposites sensor can take advantage of the following advantages: firstly, the

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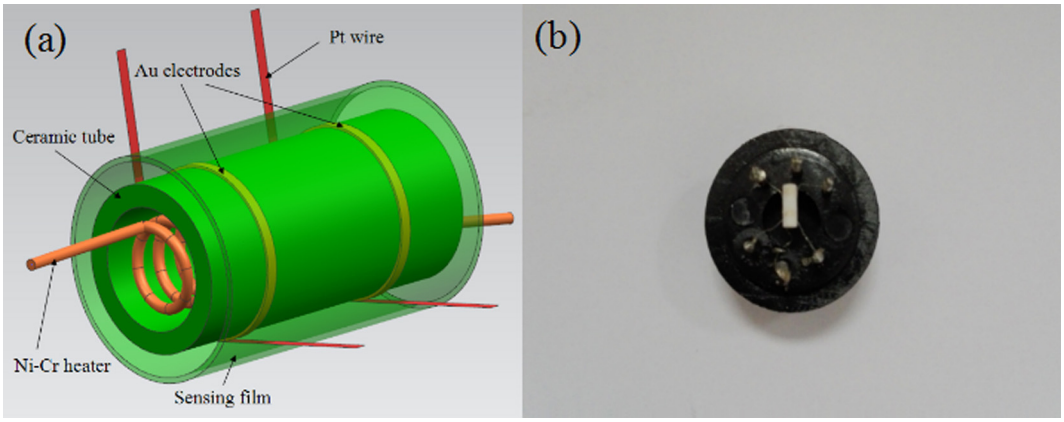

Fig 1. (a) The schematic structure and (b) the photograph of the gas sensor.

structure of ZnO nanosheets can be maintained due to flexibility and lubricity of GO. Secondly, the two-dimensional (2D) morphology of ZnO nanosheets and GO can simultaneously increase the effective surface area. Thirdly, surface functional groups of GO are in favor of gas adsorption, which is important for gas detecting. Lastly, the electron transport properties of composites can be regulated by the synergistic effect of GO and ZnO nanosheets. The microstructures, morphologies and compositions of samples were investigated by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS), respectively. The sensing properties of ZnO nanosheets and ZnO/GO nanocomposites were comparatively studied by using gas sensor evaluating system. The response value, response and recovery time were analyzed through the response-recovery characteristic curves to confirm the sensing performances. The acetone sensing mechanism and the effect of GO were discussed based on the experimental results.

2. Experimental

2.1. Preparation of the ZnO/GO nanocomposites

All the chemicals were analytical grade from Aladdin Reagent (Shanghai) Co. Ltd., and used without further purification.

ZnO nanostructures were prepared via chemical vapor deposition (CVD) method [23]. In a typical procedure, ZnO powder, graphite and phosphor pentoxide (P_2O_5) were grinded to form a uniform precursor with the ratio of 1:1:2.5 wt%. Au with a thickness of 1 nm was evaporated on the Si (100) substrate via electron beam evaporation. The substrate was placed in the centre of tube furnace. A porcelain boat containing 0.8 g precursor was placed in the uptake of tube furnace. The furnace was heated up to 1000 °C within 30 min and kept for 5 min. 70 sccm Ar and 40 sccm O_2 was used as the carrier gas. P doping is one of the key factors to obtain ZnO nanosheets. Without P doping, branched pure ZnO nanostructures can be obtained, which are also used to fabricate sensors in this work.

The preparation of graphite oxide was as follows [24,25]: 10.0 g graphite powder and 5.0 g $NaNO_3$ were mixed in a flask, and then cooled in ice bath. 230 mL concentrated (98 wt%) H_2SO_4 solution was then added to the mixture. After 10 min of stirring, $KMnO_4$ was added gradually and kept stirring in ice bath for another 15 min. The mixture was then kept at 35 °C and stirred for 50 min until a thick paste formed. 460 mL deionized water was then added, and the reaction temperature was increased gradually. The mixture was kept at 100 K and stirred for 30 min. Finally, 1000 mL deionized water and 3 mL 30% aq. H_2O_2 were slowly added to the mixture and stirred for 5 min. The obtained yellow dispersion was repeatedly washed with deionized water to remove remaining salt, and the obtained graphite oxide was then dried under vacuum at 50 °C for 3 days.

The preparation of ZnO/GO nanocomposites: GO was dispersed into 50 mL ethanol and ultrasonic for 2 h to obtain the uniform solution [24,26]. A certain amount of GO solution was impregnated on ZnO nanosheets under ultrasonic. The ZnO/GO nanocomposites were obtained after drying at 60 °C for 8 h.

2.2. Characterization of materials

The crystal structures of the pure ZnO, ZnO nanosheets and ZnO/GO nanocomposites were determined by XRD (Bruker, D8 Advance, Germany) with Cu-Kα (λ = 0.15418 nm) radiation in the range of 10–80 ° at room temperature. The morphology was investigated via FE-SEM (FEI, Quanta FEG 450, USA). The composition was investigated by XPS (TMO, ESCALAB 250 Xi, England), and the position of C1s peak (284.5 eV) was used to correct the XPS binding energies. Raman spectra measurement was carried out by using Raman Microscopy (Horiba, LabRAM HR Evolution, France) with an excitation wavelength of 532 nm.

2.3. Fabrication of sensors

Sensors based on ZnO/GO nanocomposites were fabricated, where the mass ratio of GO was varied to clarify its effect. For comparison, sensors using P-doped ZnO nanosheets and undoped pure ZnO as the starting materials were also fabricated. As shown in Fig. 1, the sensing material (0.1 g) was dispersed in 1 mL ethanol and grinded in an agate mortar to form a homogeneous paste, then the paste was coated on a ceramic tube with a pair of gold electrodes attached with Pt wires. A Ni–Cr heating wire inserted into the tube was used to control the operating temperature of sensor. The ceramic tube and heating wire were welded onto a pedestal with six probes to get the gas sensor.

2.4. Measurement of sensors

The sensing properties of the sensors were studied by using an intelligent gas sensing analysis system. Schematic description of the gas sensor and the gas testing unit is given elsewhere [27,28].The operating temperature of sensor was controlled by the Ni–Cr heating wire with the adjustable and continuous heating current from 0 to 400 mA. A static testing system was used to research the sensing properties, and the different concentrations of vapors