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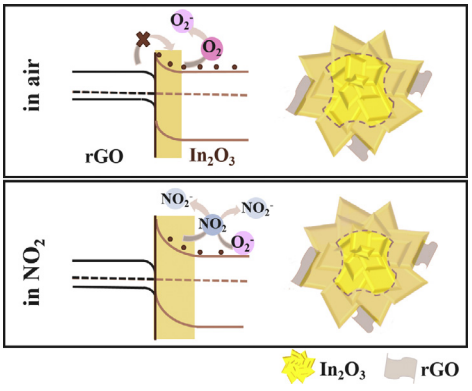
Flower-like In_2O_3 modified by reduced graphene oxide sheets serving as a highly sensitive gas sensor for trace NO_2 detection

Jie Liu [a], Shan Li [a], Bo Zhang [a], Yinglin Wang [a], Yuan Gao [a,*], Xishuang Liang [a], Yue Wang [b], Geyu Lu [a]

[a] State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, 2699 Qianjin Street, Changchun 130012, China
[b] State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Street, Changchun 130012, China

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we described gas sensors based on the materials composed of hierarchical flower-likeIn_2O_3 and reduced graphene oxide (rGO), which were fabricated by a facile one-step hydrothermal method. The rGO-In_2O_3 composites exhibited enhanced sensing performance towards NO_2 through comparison with the pure In_2O_3 sample. The operating temperature can be tuned by the percentage of rGO in the composites. The sensor based on 5 wt% rGO-In_2O_3 could work at room temperature with a high response value to 1 ppm NO_2. 3 wt% rGO-In_2O_3 composite was adopted for the ultra-sensitivity gas sensor owing to its extremely low limit of detection of 10 ppb with rapid response time to NO_2. The sensor also exhibited excellent selectivity and stability. The ultra-sensitivity of rGO-In_2O_3 should be related to synergistic effect of the hierarchical structure of In_2O_3 and the presence of rGO in the composites, which provided enhanced surface area and local p-n heterojunctions in rGO/In_2O_3 composites.

1. Introduction

NO_2 is continually released to the environment from combustion sources and automobiles. It is a dangerous air pollutant to plants and respiratory system of human beings and animals, and it threatens environmental security as a source of photochemical smog and acid rain [1,2]. The development of simple and cost-effective chemical sensors with excellent performance towards trace NO_2 for health and environmental monitoring is greatly imperative.

The resistance-type gas sensors based on semiconducting metal oxides have been widely studied due to the advantages on low cost, practical convenience and ready miniaturization [3–5]. To

* Corresponding author.
E-mail addresses: gaoyuan@jlu.edu.cn (Y. Gao), lugy@jlu.edu.cn (G. Lu).

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fabricate a highly sensitive and stable NO_2 gas sensor, many metal oxide materials, such as SnO_2 [6], ZnO [7] and Zn_2SnO_4 [8], have been evaluated. In_2O_3, as a typical *n*-type semiconductor, also has exhibited promising applications in gas sensors in detecting various hazardous gases, especially for NO_2 [9,10]. With the going deep of the research, In_2O_3 with nanostructures were synthesized in order to improve the performance of devices, such as nanowire [11], nanosheet [12], mesoporous [13], urchin-like [14] and many other hierarchically complex micro/nanostructures [15]. Particularly, hierarchical nanostructures using lower dimension nanocrystals as the building blocks attract more interest due to their less gas diffusion length, higher mobility, and relatively larger specific surface area than the agglomerated nanoparticles [16].

Graphene, a two dimensional monoatomic thick building block of a carbon allotrope, exerts a tremendous fascination, which is expected as a promising material for gas sensing [17]. Researchers combined reduced graphene oxide (rGO) with metal oxides such as the oxides of titanium [18], zinc [19], tungsten [20], copper [21], indium [22,23], stannum [24] to detece NO_2. The formation of the local heterojunctions in metal oxide semiconductor/graphene composites have been proved to play a positive role in the sensing process [25,26]. A few works reported about the gas sensing performance based on rGO-In_2O_3 composites. Liang et al. advocated an additive-free synthesisof In_2O_3 cubes embedded into graphene networks by microwave-assisted hydrothermal method successfully for the first time [22]. Wang et al. fabricated the In_2O_3–rGO nanocomposite based gas sensor for detection of NO_2 at room temperature [23]. Although they can work at room temperature, their sensing performance is need further improvement for practical applications, especially in sensor response. To acquire high accuracy to monitor gas concentration, sensors with ultra-sensitivity and extra-high response are eager to be explored.

Accordingly, hierarchical nanostructures as well as graphene incorporation have been demonstrated to be efficient methods to enhance gas-sensing performances towards NO_2, and their combination should be a quite promising route to improve sensing properties further. In this work, we reported a facile one-pot hydrothermal method without extra additives to synthesize rGO-In_2O_3 composites. The flower-like hierarchical structure of In_2O_3 offered high surface area and more active sites, and the existence of rGO allowed the formation of local p-n heterojunctions. The as-fabricated sensors based on rGO-In_2O_3 composite exhibited an excellent selectivity and a significant response to NO_2 in the wide concentration range from 10 ppb to 1 ppm at relatively low operating temperatures. In addition, the operating temperature could be tuned by the amount of rGO in composites.

2. Experimental

2.1. Material synthesis

All the reagents (analytical-grade purity) were used without any further purification. Graphene oxide (GO) was synthesized from purified graphite powder according to the modified Hummers' method [27]. The purified GO were then dispersed in deionized water to make a 0.07 mg/mL solution by ultrasonication. A series of rGO-In_2O_3 composites (1.0, 3.0, 5.0, 7.0 and 10.0 wt% rGO) were synthesized by one-step hydrothermal reaction. In a typical preparation process, 0.38 g $In(NO_3)_3{\cdot}4.5H_2O$ was dissolved in 20 ml deionized water, then stirred for 30 min. The diverse volume of GO solution was added into the above solution to obtain a series of mixtures with certain rGO/In_2O_3 mass ratio and added distilled water till total volume was 36 ml. Subsequently, 3 g urea was added into above solution. Ultrasonication is necessary when adding reagents into solution. After that, the uniform dispersion was sealed in a 50 mL Teflon-lined stainless-steel autoclave, and transferred into a hydrothermal apparatus to be maintained at 120 °C for 12 h, in which reduction of the GO and formation of nanoparticles occurred simultaneously. After cooling to room temperature naturally, the resultant products were collected by centrifugation. After washing several times, the resultant products were freeze-dried and then calcined at 300 °C for 2 h. For comparison, pristine In_2O_3 and rGO were synthesized individually by the same procedure without any other additives.

2.2. Characterizations

X-ray power diffraction (XRD) analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα1 radiation (λ = 1.54056 Å). Field emission scanning electron microscopy (FESEM) images were recorded on a JEOL JSM-7500F microscope operating at 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were carried out using a JEOL TEM-3010 instrument, operating at an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB250 spectrometer. Raman spectra were recorded on a Raman confocal microspectrometer (LabRAM HR Evolution, Jobin-Yvon, Horiba, France) excited by a He−Ne laser (632.8 nm, 13.6 mW). The Fourier transform of the IR (FTIR) spectrum was obtained by an infrared spectrometer (NICOLET, Is10). Thermogravimetric analysis (TGA) was performed using a Thermogravimetric Analyzer (Netzsch STA 499 F3). N_2 absorption–desorption isotherms were measured using a Micrometrics Gemini VII surface area and porosity system by high purity nitrogen as absorbate at 77 K. The work function of pristine rGO and pristine In_2O_3 were measured by ultraviolet photoelectron spectroscopy (UPS, PREVAC R3000/VUV5 K/MX-650 Poland) with a He I (21.21 eV) gas discharge lamp as the UV source.

2.3. Fabrication and measurement of sensor

Gas sensors were fabricated as follows: the as-prepared powder was mixed with the deionized water in order to make a paste, which was smeared onto the surface of a commercially produced ceramic tube (4 mm in length, 1.2 mm in external diameter, and 0.8 mm in internal diameter, which was previously integrated with gold electrodes) to form a thick film. After drying at room temperature for 30 min, a Ni–Cr heating wire was inserted into the ceramic tube to form an indirect-heated gas sensor [13]. The gas sensing properties of sensors were measured by static test system..

3. Results and discussion

3.1. Structural and morphological characteristics

Fig. 1 shows the XRD patterns of the as-prepared GO, rGO, In_2O_3 and rGO-In_2O_3 composites. As the typical XRD patterns of GO, a strong peak at 2θ of 10.82° corresponding to the (001) plane was evident in Fig. 1a, indicating the successful preparation of GO by oxidation of the graphite powder [28]. After hydrothermal treatment, the sharp peak at 10.82° disappeared and a broad peak appeared at approximately 25°, confirming the conversion from GO to rGO [24]. Fig. 1b illustrates the XRD patterns of In_2O_3 and rGO-In_2O_3 composites. All of the diffraction peaks of In_2O_3 indexed to the cubic phase In_2O_3 according to JCPDS card No. 71-2194. Meanwhile, the diffraction peaks of rGO-In_2O_3 composites with different ratio of rGO were in accordance with that of pure In_2O_3, illustrating that In_2O_3 in the composite was as well as the cubic phase. The absence of typical peaks belonging to rGO was ascribed to the low amount and low diffraction intensity of rGO [29]. As the