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Improvement of NO_2 gas sensing performance based on discoid tin oxide modified by reduced graphene oxide

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ABSTRACT

A facile one-step hydrothermal method for a novel discoid crystal of rutile SnO_2 modified by reduced graphene oxide (rGO) is reported in this work. X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were performed to characterize the structure and morphology of the SnO_2/rGO composites. Uniform discoid rutile SnO_2 monocrystal with a diameter of approximately 100 nm and a center thickness of 40 nm was anchored on both sides of rGO nanosheets. The SnO_2/rGO composite exhibited preferential detection toward NO_2 with high response, good selectivity and reproducibility. The response of the sensor to 1 ppm NO_2 at 75 °C was nearly one order of magnitude higher than that of SnO_2, and the detection limit was improved to 50 ppb. The improved response was discussed and the gas sensing mechanism was established.

1. Introduction

Since air pollution has become an urgent global problem with the development of industry and technology, detecting gases, especially toxic gases as the basis for controlling air pollution, has become increasingly significant. NO_2 is a toxic compound produced by combustion in power plants and combustion engines. This gas is harmful to the environment and is a major cause of acid rain, photochemical smog and pollution haze. EPA recently established a new 1-h standard at 0.1 ppm, which is well below the values fixed by previous safety guidelines, to provide requisite protection of public health [1–3].

Among the different types of gas sensors, metal oxides (MOS) semiconductor sensors are widely used in toxic and flammable gas detection because of their sensitivity, selectivity and stability. SnO_2 is an important n-type semiconductor with a wide band gap (E_g = 3.6 eV), which was first reported in the 1990s. It is one of the most intensively investigated materials because of its widely important applications such as gas sensors [4,5], solar cells [6,7], lithium-ion batteries [8,9] and transparent electronics [10]. Most high-response SnO_2 sensors typically operate at high temperatures of over 200 °C for enhanced adsorption and reactivity. However, high temperatures intensify the aggregation between particles, and high working temperatures lead to power waste. Existing SnO_2 sensors with low operating temperatures usually show poor gas sensing performance, especially in detection limit, response and recovery time. Given the fact that the composition, size and morphology of MOS exhibit a considerable impact on their properties, tremendous efforts have been devoted to improving the performance of MOS semiconductor sensors. The formation of a heterojunction by introducing other promising materials into composites also enhances the sensing performance. Numerous studies have proved that the p–n heterojunction formed by n-type and p-type materials can play a positive role in the sensing process [11–15].

Graphene is a single-layer sp^2 carbon atom lattice. This material, has become a star compound for gas sensors because of its outstanding qualities, such as high charge carrier mobility, mechanical robustness, large surface area (2630 $m^2 g^{-1}$) [16], special optical propertieies, and good thermal stability. Graphene and reduced graphene oxide (rGO)-based nanostructures have been widely studied for gas sensor applications because of their high sensitivity to electrical perturbations from gas molecule adsorption as a result of their ultra-small thickness [17]. rGO has lower conductivity, more dangling bonds and defect than intrinsic graphene, which do good to its adsorption and interaction with target gas.

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Some research groups recently introduced graphene or rGO to MOS-based materials, and obtained unique structure composites to improve sensing performance. MOS/rGO was proved to be effective for constructing high-performance gas sensors [18–20]. Pinna reported a room-temperature hydrogen sensor based on SnO_2/rGO and Pt–SnO_2/rGO [21]. Highly aligned SnO_2 nanorods on graphene sheets were synthesized to enhance the sensitivity to H_2S at the operating temperature of 260 °C [22]. Selective acetone and hydrogen sulfide sensors based on SnO_2 nanofibers functionalized with rGO nanosheets were fabricated at operating temperatures of 200 °C and 350 °C, respectively [23]. The NH_3 sensing performance of flower-like SnO_2/rGO composites was investigated at room temperature [24]. Zhang et al. found that SnO_2 nanoparticles/rGO composites exhibited high response to NO_2 at low operating temperature (50 °C) [25]. And high-performance NO_2 sensing of 3D mesoporous rGO aerogel-supported SnO_2 nanocrystals was studied at low temperature [26]. Although the studies on SnO_2/rGO have improved the NO_2 sensing performance compared to intrinsic graphene at room temperature or relative low operating temperature, their gas sensing response and detection limit should still be developed further.

In this work, SnO_2/rGO with a novel structure was synthesized through a facile one-step hydrothermal method. The SnO_2 in the composites was discoid rutile monocrystalline with rough surface. The sensors based on the SnO_2/rGO composites were fabricated, and their NO_2 sensing performance was investigated. The SnO_2/rGO exhibited n-type semiconductor behavior in the gas sensing process because of the small amount of rGO. Investigations on gas sensors showed that sensors based on SnO_2/rGO composites exhibited more than one order of magnitude improvement in the response and a shorter response time compared with that of individual SnO_2.

2. Experimental

2.1. Materials

All chemicals were the analytical-grade reagents and used without any other further purification. Graphite powder, potassium peroxydisulfate, phosphorus pentoxide, potassium permanganate, sulfuric acid, sodium citrate ($Na_3C_6H_5O_7{\bullet}2H_2O$), stannous sulfate were purchased from Sinopharm Chemical Reagent Co. Ltd. (China).

2.2. Instrumentation

X-ray diffraction (XRD) patterns of the as-prepared products were conducted on a Rigaku D/max-2500 X-ray diffractometer using Cu-Ka radiation, at a scanning speed of 12°/min. Field emission scanning electron microscope (SEM) was taken on a JEOL JSM-7500F microscope operating at 15 kV. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and selected-area electron diffraction (SAED) were conducted on a JEOL JEM-3010 microscope with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB MKII X-ray photoelectron spectrometer.

2.3. Synthesis and characterization of the SnO_2/rGO composite

Graphene oxide (GO) was prepared by a modified Hummer's method as described in reference [27]. The SnO_2/rGO material was synthesized via a hydrothermal method with $SnSO_4$ and GO as precursors. In a typical process, 0.1 g $SnSO_4$ and 1.37 g $Na_3C_6H_5O_7{\bullet}2H_2O$ were dissolved in 32 mL mixture of deionized water and glycerol (5:3, v:v) under continuous stirring. Then 1.37 mL HCl (38%) was added into the above solution and following with aliquot GO solution (0.5 mg, 1 mg, 2 mg). After 30 min vigorous stirring, the mixture which had formed a homogeneous solution was transferred into a Teflon-lined stainless-steel autoclave and maintained at 180 °C for 24 h. After the hydrothermal procedure, the autoclave cooled down naturally to room temperature. Afterward, the product was collected by centrifugation and washed several times with deionized water, and dried at −50 °C. Finally, a series of SnO_2/rGO composites with 0.7, 1.4 and 2.8 wt.% rGO was obtained. For control experiments, rGO and pure SnO_2 were prepared under the same condition with only GO and without adding GO respectively. All samples were freeze-dried without any treatment before characterization.

2.4. Fabrication and measurement of gas sensors

The gas sensors were fabricated as follows: the as-prepared materials were mixed with deionized water to form slurry, and made a uniform thick coating layer using a small brush with the slurry onto an alumina tube (4 mm in length, 1.2 mm in external diameter, 0.8 mm in internal diameter) which was attached with a pair of gold electrodes. After the coating layer drying in air at room temperature, the alumina tube was heat treated at 350 °C for 2 h. In order to control the operating temperature of sensors, a Ni–Cr alloy coil was inserted to the alumina tube as a heater. The gas-sensing properties were investigated using a RQ-2 series Intelligent Test Meter (China) by testing the changing of resistances of the coating layer when the tube was exposed in air and tested gases atmosphere under laboratory conditions (30 RH%, 22 °C). The gas-sensing properties of the sensors were measured with a static gas-sensing characterization system, environmental air was used as both a reference gas and a diluting gas to obtain desired concentrations of target gases. A typical testing procedure was as follows. Firstly, the sensor was put into the chamber of air to get a steady state, then the sensor was took to another chamber filled with the uniform tested gas, which was injected with calculated amount. When the response reached a constant value, the sensor was transferred back to chamber containing air and kept there until complete recovery. The response of the gas sensor is defined as the ratio of the resistance of the sensor in the tested gases (R_g) to that in air (R_a). For oxidizing tested gases, that is Response = R_g/R_a, while for the reducing tested gases, Response = R_a/R_g. The response and recovery time is defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption respectively.

3. Results and discussion

3.1. Morphological and structural characteristics

The XRD patterns of the crystallographic structure of GO, rGO, SnO_2 and SnO_2/rGO composites are shown in Fig. 1. The diffraction peak at around $2\theta = 11.2°$ in Fig. 1a belongs to the (0 0 1) reflection of GO. The rGO sample showed two characteristic diffraction peaks at 24.4° and 42.8°, which corresponded to the (0 0 2) and (1 0 0) planes of graphene, indicating that GO was reduced to rGO via the hydrothermal treatment [28]. All diffraction peaks in the SnO_2 patterns could be clearly indexed to rutile SnO_2 according to JCPDS card No. 41-1445. The mean spherical crystallite size of the SnO_2 calculated by the Scherrer equation was 53 nm. The pattern of SnO_2/rGO was similar to that of SnO_2, and no obvious diffraction peaks of rGO were observed owing to small amount of rGO in the composites and its intrinsic weak diffraction intensity.

The morphology and microstructure of the samples were characterized using field-emission scanning electron microscopy (FESEM). As shown in Fig. 2a, b, the GO exhibited the wrinkled flaky structure, and the obtained rGO after hydrothermal treatment showed a more curly structure and aggregation. SEM images of the SnO_2 and SnO_2/rGO are shown in Fig. 2c, d. The SnO_2 particles with