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High-performance sulfur dioxide sensing properties of layer-by-layer self-assembled titania-modified graphene hybrid nanocomposite

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ABSTRACT

This paper demonstrates layer-by-layer (LbL) self-assembled titania (TiO_2)/graphene film device towards ultralow sulfur dioxide (SO_2) gas sensing at room temperature. The as-prepared film was realized through the layer-by-layer alternative deposition of TiO_2 nanospheres and graphene oxide (GO) to form a nanostructure, and followed by thermally reducing GO into reduced graphene oxide (rGO). The nanostructural, morphological and compositional properties of TiO_2/rGO sample was examined by SEM, TEM, XRD, EDS and Raman spectroscopy. The gas-sensing properties of TiO_2/rGO hybrid were investigated at room temperature against low concentration SO_2 gas. The sensor in our work exhibited ppb-level detection, rapid response and recovery, good reversibility, selectivity and repeatability for SO_2 gas sensing. The possible sensing mechanism for the presented sensor was attributed to the synergistic effect of TiO_2 and rGO, as well as special interaction at TiO_2/rGO interfaces. This work shows that the fabricated TiO_2/rGO film sensor possesses potential applications for SO_2 detection with advantages of cost-effective, low power consumption and distinguished sensing abilities.

1. Introduction

Sulfur dioxide (SO_2) is one of major compounds of vehicle exhaust, as well as the main emissions of the thermal power plants and chemical production process [1,2]. Moreover, SO_2 gas is not only an environmental atmospheric pollutant, but it is also a hazardous gas having a human tolerance of about 5 ppm, which can bring to some serious diseases of human beings, such as respiratory, cardiovascular diseases and lung cancer [3–5]. Because of its toxicity to human health and environmental contamination, trace detection of SO_2 gas has attracted considerable attention. Up to now, many methods and instruments such as spectroscopy and solid-state electrochemistry techniques have been developed for SO_2 detection, but they are expensive and cumbersome [6–8]. Recently, metal-oxide semiconducting (MOS) materials such as SnO_2 [9], ZnO [10], TiO_2 [3,6,11] and WO_3 [12], were extensively employed for constructing SO_2 gas sensor. Among them, TiO_2 has been widely investigated for gas sensing due to its unique physicochemical properties, it suffers from high operating temperature (200–400 °C), resulting in high power consumption and difficulty in integration [13,14]. Therefore, exploring a novel sensing material and method toward SO_2 detection at room temperature is highly desired.

Graphene, a two-dimensional monolayer of graphite sheet consisting of sp^2 hybridized carbon atoms, has attracted the attention of gas sensing community owing to its unique nanostructure, excellent physical and chemical properties [15–17]. Graphene-based nanostructures have been extensively used to detect several gas species at extremely low concentrations, even down to the single molecule level at room temperature, which can be ascribed to the unprecedented electronic conductivity, high specific surface area, ultra-small thickness, extremely low-noise characteristics and high thermal stability [18,19]. Among graphene derivatives, graphene oxide (GO) and reduced graphene oxide (rGO) have triggered recently tremendous attention due to their facile preparation and novel applications [20]. Although great potentials have reported on graphene, its sensitivity to gas species detection is limited. Shao et al. has revealed that intrinsic graphene is not an efficient material towards SO_2 by using first-principles approach based on the spin-polarized density functional theory [21]. Notably, metal oxide-decorated graphene is emerging as a class of candidate materials to construct high-performance gas sensors towards various gas species, such as ethanol, acetone, NO_2, NH_3 and H_2S [22–26].

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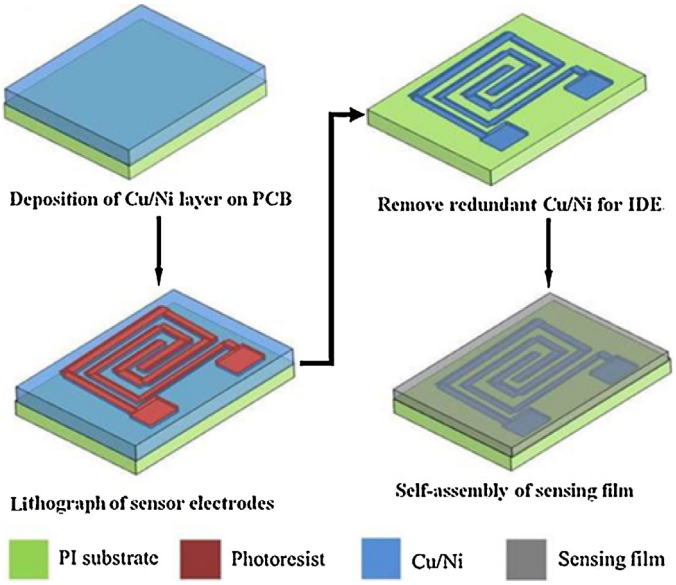

Fig. 1. Illustration for the sensor fabrication.

Ren et al. fabricated a SO_2 gas sensor with CVD grown graphene configured in a field effect transistor (FET) device, and its sensing properties at a SO_2 concentration of 50 ppm was exhibited [27]. Furthermore, at least to our knowledge, the SO_2 gas sensor based on metal oxide-decorated graphene hybrid film has not been reported till now.

In this work, we presented a novel ppb-level SO_2 gas sensor based on TiO_2/rGO composite film, which was fabricated by using layer-by-layer (LbL) self-assembly technique and facile thermal reduction. The hierarchical nanostructure of TiO_2/rGO thin film was fabricated on the substrate with interdigital microelectrodes. The resulting TiO_2/rGO hybrid film was characterized by using SEM, TEM, XRD, EDS and Raman spectroscopy. The sensing properties of the presented SO_2 sensor were investigated by exposing to ultralow-concentration of SO_2 ranging from 1 ppb to 5 ppm at room temperature. As a result, the sensor achieved ppb-level detection, fast response-recovery characteristics, good selectivity and long-term stability towards SO_2 at room temperature.

2. Experiment

2.1. Materials

Urea (≥99%) and $Ti(SO_4)_2$ (≥96%) were offered by Sinopharm Chemical Reagent Co. Ltd. The high-purity graphene oxide (GO) suspension was supplied by Chengdu Organic Chemicals Co. Ltd (Chengdu, China). Polycation and polyanion used for LbL assembly were 1.5 wt% PDDA (Sigma-Aldrich) and 0.3 wt% PSS (Sigma-Aldrich) with 0.5 M NaCl in both for ionic strength.

2.2. Sensor fabrication

The typical process for manufacturing the sensor device is shown in Fig. 1. A Cu/Ni layer with thickness of 20 μm was first deposited on PCB substrate using sputtering system. Subsequently, positive photoresist (PR) was coated on the substrate to make interdigital electrodes (IDEs) pattern using lithography, and then the redundant Cu/Ni layer was etched out to form micro-IDEs via exposure and development. The width and gap spacing of 200 μm for the IDE fingers is designed. Lastly, the sensing film was self-assembled onto the sensor substrate.

The fabrication process was constituted by hydrothermal synthesis of TiO_2 and LbL self-assembly of TiO_2/graphene film. During the hydrothermal preparation of TiO_2 crystals, $Ti(SO_4)_2$ and urea were firstly dissolved into DI water with the concentration of 0.5 mol/L and 1 mol/L, respectively, followed by thermally heating the resulting solution in a stainless-steel autoclave for 3 h at 180 °C. Afterward, TiO_2 suspension was obtained by centrifugation at 3000 rpm for 10 min, and subsequently washed several times to remove excess sulfate ions. Hydrothermally synthesized TiO_2 were employed as a partner of GO to form a hierarchical nanostructure using LbL self-assembly technique, as shown in Fig. 2. First, two bi-layers of PDDA/PSS were self-assembled as precursor for substrate modification. Subsequently, multilayer TiO_2/GO and a monolayer of TiO_2 on-top were coated. Intermediate rinsing and drying were performed after each monolayer assembly, which can prevent the aggregation during the LbL deposition [28,29]. Finally, the presented TiO_2/GO film device was heated at 220 °C for 2–3 h in order to reduce GO into rGO [30]. The film resistance is greatly decreased via thermally reduction of GO. And thus, layer-by-layer self-assembled TiO_2/rGO nanostructure was obtained as sensing film.

2.3. Instrument and analysis

The surface morphologies of TiO_2, rGO, and TiO_2/rGO nanostructures were measured with field emission scanning electron microscopy (FESEM, Hitachi S-4800). The XRD spectrum for TiO_2, GO, rGO and self-assembled TiO_2/rGO nanostructure was characterized with X-ray diffractometer (Rigaku D/Max 2500PC, Japan). Raman spectra were measured using a confocal microprobe Raman instrument (RamLab-010, Horiba JobinYvon, France), and 632.8 nm He-Ne laser was used to excite the spectra. The nanostructure of the as-prepared samples was observed by a transmission electron microscope (TEM; JEOL JEM-2100, Japan). The elemental composition was examined by Hitachi S-4800 equipped with an energy dispersive spectrometer (EDS).

The gas sensing properties of the presented sensor were investigated at room temperature of 25 °C by measuring the electrical resistance when exposed to target gases, as reported in our previous work [31]. Experiments were performed in a closed testing chamber equipped with appropriate inlet and outlet for gas flow. Air used as background gas and a known volume of analyte SO_2 gas was injected inside the testing chamber to achieve the desired concentration for test. Air was allowed to pass into the testing chamber after every target gas exposure cycle. Normalized response is defined by $S = |R_{air} - R_{gas}|/R_{air} \times 100\%$, where R_{gas} and R_{air} are the electrical resistance of the sensor in the given concentration of SO_2 gas and air, respectively.

3. Results and discussion

3.1. Sample characterization

The SEM surface images of TiO_2, rGO, self-assembled TiO_2/rGO samples and cross-sectional image of multi-layer TiO_2/rGO film are shown in Fig. 3. Fig. 3(a) shows as-synthesized TiO_2 sample has nanosphere shape with a diameter around 10 nm, and Fig. 3(b) shows that the rGO film has wrinkles which overlap at the edges, and also exhibits randomly aggregated morphology as typical feature for rGO. Fig. 3(c) shows the SEM image of TiO_2/rGO nanostructure, rGO flakes are wrapped on the TiO_2 nanosphere surface or bridge-connected between neighboring TiO_2 balls, indicating good contacts between TiO_2 and rGO closely. Fig. 3(d) illustrates the cross-sectional image of layered TiO_2/rGO sample, which confirms the sensing film has clearly laminated nanostructure and the thick-