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Fabrication and characterization of an ultrasensitive humidity sensor based on metal oxide/graphene hybrid nanocomposite

Dongzhi Zhang[a,*], Hongyan Chang[a], Peng Li[b,*], Runhua Liu[a], Qingzhong Xue[c,d]

[a] College of Information and Control Engineering, China University of Petroleum (East China), Qingdao 266580, China
[b] State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instruments, Tsinghua University, Beijing 100084, China
[c] State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), Qingdao 266580, China
[d] College of Science, China University of Petroleum (East China), Qingdao 266580, China

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ABSTRACT

This paper demonstrated a flexible humidity sensor based on tin dioxide/reduced graphene oxide (RGO) nanocomposite film. The humidity sensor was fabricated on a polyimide substrate with microelectrodes by using a facile one-step hydrothermal route. The hydrothermal synthesized SnO_2 nanoparticles and SnO_2/RGO hybrid nanostructures were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The humidity sensing properties of the presented SnO_2/RGO nano-hybrid sensor were investigated by exposing it to a broad humidity range of 11–97%RH at room temperature. Compared with traditional humidity sensors, the SnO_2 modified graphene sensor demonstrated an ultrahigh sensitivity and a rapid response/recovery characteristic over a full humidity range measurement, highlighting the unique advantages of hydrothermal synthesis for sensors fabrication. Finally, the possible humidity sensing mechanism of the proposed sensor was discussed by using complex impedance spectra and bode diagrams. These observed results demonstrate that RGO modified with metal oxide is promising nanomaterials for constructing high performance humidity sensors in widespread applications.

1. Introduction

As a common type of sensor, humidity sensor is of vital importance in various applications for many aspects, such as industrial, medical, ecological and environmental monitoring [1,2]. So far, various transduction techniques such as capacitive [3,4], resistive [5,6], optical fiber [7,8], field effect transistor (FET) [9], surface acoustic wave (SAW) [10,11], and quartz crystal microbalance (QCM) [12,13] have been used to fabricate humidity sensors. Moreover, several kinds of sensing materials including polymers [14], ceramics [15], metal oxide semiconductors (MOs) [16], carbon nanotubes and their composites [17] have been employed in humidity sensors. MOs-based humidity sensors exhibited certain advantages of low cost, simple construction, small size and compatibility with modern electronic devices, compared with other types of humidity sensors. Among them, tin dioxide (SnO_2) as a stable n-type semiconducting material with bandgap of 3.6 eV, is one of popular candidates for making low-cost gas sensing devices, due to its unique physicochemical properties depend upon the humidity surrounding them. However, SnO_2-based sensors commonly have the shortcoming of poor selectivity between gas species [18,19]. Parthibavarman et al. have synthesized SnO_2 nanoparticles by microwave irradiation method and investigated their humidity sensing properties in environment monitoring [18]. Yadav et al. have fabricated nanocrystalline SnO_2 thick film-based humidity sensor on alumina substrate using screen printing technique [19]. The pristine SnO_2 sensors exhibited certain advantages when compared to other types of humidity sensors, but do not have abruptly change the resistance values at higher RH due to its high resistivity, limiting their commercialization and practical applications. Researchers have reported in improving the humidity sensitivity of SnO_2 by element doping, such as La^{3+}, Ce^{3+}, K^{+} and Sb^{3+} [20–22]. However, either the high cost or the less availability of many of these dopants is a disadvantage to use them.

Currently, graphene has attracted significant interest for a wide range of applications as an excellent nanomaterial, which is mainly attributed to its large specific surface area of 2600 $m^2 g^{-1}$, high chemical stability, and exceptional electrical properties such as low noise level and high carrier mobility [23]. Many efficient sensors based on graphene and its derivatives have been constructed for the detection of environmental gases, such as H_2,

* Corresponding authors.
E-mail addresses: dzzhang@upc.edu.cn (D. Zhang), pengli@mail.tsinghua.edu.cn (P. Li).

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NO_2, NH_3, acetone and acetylene [24–28]. Among graphene derivatives, graphene or reduced graphene oxide (RGO) has aroused tremendous attentions currently due to its facile preparation and novel applications [29,30]. Notably, recent advances demonstrated that the decoration of graphene with metal oxide nanoparticles was an effective method for constructing high-performance sensors [31]. RGO as highly conductive sp^2 carbon atom film, serving as an anchor to promote the electrons transfer in the metal oxide nanoparticles, thus lead to a better sensing performance. Liu et al. constructed NO_2 gas sensor using RGO-ZnO hybrid composite as sensing material [32]. Wang et al. fabricated an efficient gas sensor based on CuO–ZnO/RGO ternary composite, exhibiting more outstanding sensing properties to acetone than that of CuO–ZnO and ZnO/RGO, respectively [33]. Esfandiar et al. successfully synthesized ribbon-like Pd–WO_3 incorporated RGO nanostructure as efficient hydrogen gas sensor [34]. These investigations demonstrated that the graphene-based metal oxide nanocomposite exhibited a large enhancement in gas sensing properties in comparison with pure metal oxide or graphene counterpart.

The aim of this work is to investigate a flexible capacitive humidity sensor based on SnO_2 decorated RGO nano-hybrid film for realizing high-performance at room temperature, which was successfully prepared by using a facile method of one-step hydrothermal treatment. The structure of RGO/SnO_2 hybrid composite was characterized by SEM and XRD. The humidity sensing behavior of the as-prepared RGO/SnO_2 hybrid composite was investigated under various relative humidity (RH) levels. This humidity sensor exhibited an ultrahigh sensitivity and a short response/recovery time over a wide range of RH levels. Furthermore, the possible humidity sensing mechanism of the proposed sensor was discussed by using complex impedance spectra and bode diagrams.

2. Experiment

2.1. Materials

Tin tetrachloride pentahydrate ($SnCl_4{\cdot}5H_2O$) (≥99%) was offered by Shanghai Hansi Chemical Industry Co. Ltd (Shanghai, China). The graphene oxide (GO) nanosheets (>99%) were supplied by Chengdu Organic Chemicals Co. Ltd. All the above chemicals were used as received without further treatment.

2.2. Sensor fabrication

The sensor was fabricated on a flexible polyimide (PI) substrate through microfabrication technology. The polyimide here is only used as substrate, and the electrodes are fabricated by metal sputtering. Fig. 1(a) shows the illustration of microfabrication process for the sensor. A 20 μm thick Cu/Ni layer was firstly deposited on PI substrate (75 μm thick) with a sputtering system. Subsequently, photoresist (PR) was applied to make a pair of interdigital electrodes (IDEs) pattern by using lithography technique, and then the redundant Cu/Ni was etched out to form micro-IDEs by using exposure and development. A sensing film was finally coated on the sensor surface. The IDEs pattern window on the PI substrate provided an outline dimension of 5 mm × 5 mm, the IDE finger thickness was 20 μm, and the width and gap both was 75 μm. Fig. 1(b) shows the optical image of 4 × 6 sensors array on a flexible PI substrate.

The sensing film of SnO_2/RGO hybrid composite was prepared by using a facile route of hydrothermal treatment of $SnCl_4$ solution in the presence of graphene oxide. Firstly, 2 mL of GO (0.5 mg/mL) and 24 mg of $SnCl_4{\cdot}5H_2O$ were added into 20 mL of DI water by sonication for 10 min (40 kHz) and stirring for 1 h. Followed by transferring the above resulting solution into a 40 mL Teflon-lined, stainless-steel autoclave and heated at 180 °C for 12 h. GO was converted into conductive RGO under hydrothermal reduction. After the autoclave was cooled down to room temperature, the as-prepared products were obtained via centrifugation at 3000*r*/min for 10 min, subsequent washing with DI water for several times to remove excess chloride ion. Finally, the resulting SnO_2/RGO dispersion was drop-casted onto the substrate, and followed by vacuum-drying in an oven at 50 °C for 2 h. Moreover, RGO film was prepared for purpose of subsequent characterization by the above method but without addition of $SnCl_4{\cdot}5H_2O$.

2.3. Instrument and analysis

The surface morphologies of RGO and SnO_2/RGO hybrid composite were inspected with field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan). The XRD pattern for RGO and SnO_2/RGO were characterized with an X-ray diffractometer (Rigaku D/Max 2500PC, Japan) using Cu Kα (λ = 1.5418 Å) radiation, a scanning range of diffraction angle (2θ) was 10–80°, and a scanning rate was 2°/min.

The experimental setup used for humidity sensing measurement is described in our previous work [6]. The experiments were performed at an ambient temperature of 25 °C. The humidity sensing properties were investigated by exposing the SnO_2/RGO hybrid composite sensor to various relative humidity (RH) levels, which were achieved by several saturated aqueous solutions. Saturated solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $CuCl_2$, NaCl, KCl and K_2SO_4 in a closed vessel were employed to obtain 11%, 23%, 33%, 43%, 52%, 67%, 75%, 85% and 97%RH levels, respectively. The electrical properties of the proposed sensor prototype under various RH levels were measured by using a precision LCR meter (TH2828, China). The response of the sensor as a function of RH was achieved by exposing it inside the closed vessels with different RH levels (11–97%) for the adsorption of water molecules, and the sensor could be recovered upon exposure to dry air conditioned by phosphorus pentoxide (P_2O_5) powder (RH 0%) for the release of water molecules. Sensitivity (S) used to characterize the sensor performance was defined as $S = \Delta C/\Delta RH$ (unit: pF/%RH), where ΔC is the sensor response change in capacitance, and ΔRH is the RH change. The hysteresis error was defined as a deviation due to hysteresis between upscale-going and downscale-going indications in terms of the full measured quantity. The time taken by a sensor to achieve 90% of the total resistance change is defined as the response or recovery time.

3. Results and discussion

3.1. SEM and XRD characterization

Fig. 2 shows the observed SEM images of as-prepared RGO film and SnO_2/RGO hybrid composite. The SEM image of RGO in Fig. 2(a) indicates that the RGO film has wrinkles which overlap at the edges, and exhibit randomly aggregated RGO sheets. Fig. 2(b) exhibits the nanosphere-shaped SnO_2 nanocrystals, and Fig. 2(c) shows that SnO_2 nanocrystals are attached on the surface of RGO sheets, in which the presence of SnO_2 nanocrystals reveals that hydrothermal treatment of GO and $SnCl_4$ solution is an effective method for synthesizing SnO_2/RGO hybrid composite.

The XRD characterization for RGO, SnO_2 and SnO_2/RGO hybrid composite is illustrated in Fig. 3. The XRD pattern of RGO in Fig. 3(a) shows a prominent peak at 2θ angle of 24.7°, which is attributed to RGO, in contrast with the data in the diffraction standard for RGO (PDF#74-2330 RIR 10.41). According to the Bragg formula, $\lambda = 2d$