Materials Chemistry and Physics 207 (2018) 135–140

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

High-sensitive humidity sensor based on graphene oxide with evenly dispersed multiwalled carbon nanotubes

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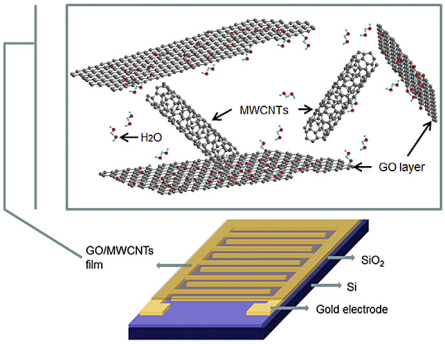
HIGHLIGHTS

- GO with evenly dispersed MWCNTs on Au interdigitated electrodes (IDEs) was obtained.
- The fabrication process was simple and low-cost.
- The sensor showed superior sensitivity to humidity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Keywords:
Graphene oxide
Multiwalled carbon nanotubes
Humidity
Capacitive sensor

ABSTRACT

Using graphene oxide (GO) as a dispersant for multiwalled carbon nanotubes (MWCNTs), a high-sensitive humidity sensor based on GO film with evenly dispersed MWCNTs on Au interdigitated electrodes (IDEs) is presented in this paper. The sensitivity of the sensor with GO/MWCNT film is thirteen times more than that of the sensor with GO film. Scanning electron microscopic characterizations confirm the presence of GO/MWCNT with the less stacking layers compared with GO. This may be attributed to the addition of MWCNTs which plays a supporting role in the GO/MWCNT composite material. This structure would lead to bigger accessible surface area of the composite material and accelerate the diffusion of the water molecules. This study demonstrates that the GO/MWCNT composite could be used for high-sensitive humidity detection.

1. Introduction

Humidity is a common factor in most of the experiments and industries, and it has significant effect on both comfort and health. The widely used sensing materials are polymers [1], semiconducting materials [2], porous silicon [3], porous ceramics [4] and carbon materials [5,6,7]. During these materials, carbon materials have attracted much attention because of its good advantages such as low-cost, large-scale synthesis, good electronic [8,9] and mechanical properties.

Graphene oxide (GO) is the oxidized product of graphene and is formed when a range of reactive oxygen functional groups (carboxyl, hydroxyl and epoxy group) are chemically bonded to the sp^2 hybridized network of graphene sheets [10]. In addition to some features of graphene, the existence of these oxygen groups makes GO hydrophilic [11] and renders it a good candidate for use

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https://doi.org/10.1016/j.matchemphys.2017.12.033
0254-0584/

as sensing material in humidity detection. S. Borini et al. demonstrated a touchless interfaces utilizing GO humidity sensor to recognize different whistled tunes [12]. H. Bi et al. developed a capacitive humidity sensor using GO as a sensing material [13]. In those humidity sensing devices, the interaction of GO with water molecules produces some change in the electrical impedance of GO film and is responsible for the response of the GO based sensors. However, the stacking of the overlapping graphene oxide sheets [14,15] would only produce a surface area much lower compared to the theoretical surface area. So the desired sensing effect cannot be achieved.

As another form of carbon, carbon nanotubes (CNTs) have a lot of applications in sensing field. H. Beitollahi et al. used the modified carbon paste electrode for determination of certain chemical substances and found the modified electrode display high selectivity in the measurement of sulfite or useful for the determination of captopril [16,17]. C.L.Chao et al. studied the humidity sensitive properties of MWCNTs systematically and proposed that the sensitivity of CNTs to humidity can be enhanced with chemical treatment [18]. But because of the intertubular Van der Waals interactions and high chemical inertness [19], while dispersed in common solvents, CNTs usually generate inhomogeneous dispersions and large aggregates. This problem greatly hinders their practical use in sensing field of applications [20]. To circumvent this difficulty, several routes have been proposed. Some researchers used wet chemical oxidation with inorganic acids to make CNTs functional [21]. Another technique for producing functionalized CNTs is plasma treatments. M.G. Trulli et al. [22] evaluated the physical-chemical properties and the colloidal stability of the plasma treated MWCNTs. They found that the resulting dispersions of PT-CNT powders in water remained stable for at least one month (i.e. about 70% of suspended particles). However, these methods mentioned above are complicated and often result in structural damage and properties degradation of CNTs [23].

Recently, GO has been used as a surfactant to disperse CNTs. The GO/MWCNT composite material prepared through simple sonication and centrifugation have good solubility in water [24]. Through strong pi-pi stacking interaction, GO offers adhesion of CNTs onto its flat layers, so GO can function as exceptional dispersants for CNTs in aqueous solution without any additional organic solvents involved [25]. Thus we expect that the composite of one-dimensional MWCNTs and two-dimensional GO could solve the common shortage of these two materials and offer higher surface area, so as to have better properties in humidity sensing.

In this paper, we built a high-sensitive humidity sensor based on graphene oxide with evenly dispersed multiwalled carbon nanotubes. The morphology of this GO/MWCNT composite material was studied. The essential characteristics of this sensor, such as sensitivity and response time were evaluated. The mechanism of the capacitive sensor with GO/MWCNT composite film was also analyzed.

2. Experimental

2.1. Materials

All chemicals in this article were purchased from XFNANO Technology Co., Ltd. unless otherwise indicated. Graphite oxide was synthesized by the oxidative treatment of natural graphite using a modified Hummers method [26]. Subsequently, GO sheets were achieved by ultrasonication of graphite oxide dispersion (2 mg/mL) for 1 h. Then the aqueous suspensions of GO was obtained.

MWCNTs (length, 5–30 μm; outer diameter (OD)<8 nm) produced by the CVD method, were supplied by Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, China. MWCNTs were dispersed in water (2 mg/mL) to prepare the raw MWCNTs solution.

2.2. Fabrication of the IDE sensors

Interdigitated electrodes (IDEs) were prepared to fabricate these humidity sensors. IDEs were fabricated with different inter-finger spacing. These electrodes were fabricated on a Si wafer with a top layer of thermally-formed SiO_2 (400 nm) Ti/Au layers with a thickness of 100 nm/300 nm were deposited on an n-type silicon wafer with a top layer of SiO_2 using magnetron sputtering. The above electrode processing was aiding by YAGUANG electronics Co., Ltd. Before the deposition of sensing film, the IDEs were cleaned with deionized water and ethanol in an ultrasonic washing unit for 30 min and then vacuum dried for 1 h. MWCNTs powder was added into GO solution followed by ultrasonication to obtain stable GO/MWCNT (2.5:1) aqueous dispersion. A few drops of the GO/MWCNT suspension were cast onto Au IDEs through a pipette, followed by drying under a temperature of 45 °C for 1 h to form the GO/MWCNT sensing film on IDEs. For comparison, the IDEs sensor with GO film was produced in the same way.

2.3. Apparatus

The morphology and structure of the GO film and GO/MWCNT film were characterized by scanning electron microscope (SEM, JSM-7500F, JEOL Ltd., Japan). Fourier transform infrared (FTIR) spectrum of GO and GO/MWCNT (KBr dispersed pellets) in the range of 400–4000 cm^{-1} were recorded on a fully computerized Nicolet iS10 spectrometer (Thermo Fisher Scientific Inc., USA). Raman spectra of GO and GO/MWCNT samples were characterized by Raman spectroscopy (inVia, Renishaw, UK) with a 633 nm pump laser. The capacity shifts of the IDEs sensors were monitored by a LCR analyzer (4100, Wayne Kerr Electronics., UK).

2.4. Humidity sensing experiments

The sensing properties of the humidity sensors were measured using saturated salt solutions. The solutions were prepared by dissolving LiCl (RH 11.3%), CH_3COOK (RH 22.5%), $MgCl_2$ (RH 32.8%), K_2CO_3 (RH 43.2%), $Mg(NO_3)_2$ (RH 54.3%), NH_4NO_3 (RH 62.1%), KCl (RH 62.1%), KNO_3(RH 84.3%) and K_2SO_4 (RH 97.3%) in deionized water. A commercial hygrometer (Rotronic, Hydroclip HC2-S3, Switzerland, with a measure accuracy ± 0.8%RH at 25 °C) was applied in this system to calibrate the RH and temperature in the test bottle. The sensors were exposed in those different relative humidity environments respectively.

3. Results and discussion

3.1. Solubility and morphology

It can be seen in Fig. 1 that the pristine MWCNTs cannot form stable suspensions in water, thus leads to serious precipitation and aggregation. The mixture of GO/MWCNT is dark brown and without precipitation, suggesting that MWCNTs are dispersed in aqueous media.

3.2. Characterization

As shown in Fig. 2a, GO Shows a typical fold layered structure. In Fig. 2b, it is hard to find the MWCNTs alone. Most of them are wrapped uniformly into the GO sheets and play a supporting role in the GO/MWCNT composite material. So the stacking of GO is suppressed to a certain extent.