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Detection of very low humidity using polyelectrolyte/graphene bilayer humidity sensors

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ABSTRACT

An impedance-type humidity sensor was prepared by sequentially depositing the thin films of crosslinked and quaternized poly(4-vinylpyridine) (QC-P4VP) and reduced graphene oxide (RGO) onto interdigitated gold electrodes. The QC-P4VP/RGO bilayer sensor reveals much lower impedance than QC-P4VP based sensor in the environments with low relative humidity (RH) levels, and could detect ultra-low humidity (0.18%RH) with very high response magnitude (impedance increase of 500% between 2.1%RH and 0.18%RH) at room temperature. Moreover, the bilayer sensor shows small hysteresis (~4.5%RH) and fast response ($t_{90\%}$ of 21 s and 78 s for adsorption and desorption processes, respectively). The effect of the concentration of RGO precursor, the deposition order and thickness of the sensing films, temperature, and the structure of the electrodes on the humidity sensing behaviors of the bilayer-structured sensors has been thoroughly examined, and the humidity sensing mechanism was explored.

1. Introduction

In recent years, graphene (GN), which is a two dimensional nanomaterial with unique electrical, electronic, and mechanical properties, has become the focus of researches in material science. There have been numerous papers on the application of GN and its composites in a wide variety of fields ranging from reinforced structural materials, conductive materials, supercapacitors, secondary batteries, separation films to solar cells [1–8]. Meanwhile, inspired by the report that single or few layer GNs could detect individual gas molecules [9], great efforts have been devoted to the chemical and biosensors based on GN for highly sensitive and fast detection of a broad spectrum of species, such as NO_2, NH_3, CO, H_2, volatile organic vapors, dopamine, H_2O_2, glucose, etc [10–23].

By contrast, less attention has been paid to the researches on GN based sensitive materials for the detection of humidity, and usually low sensitivity was revealed. Guo et al. reported that GN obtained from laser-induced reduction of graphene oxide (GO) presented increased conductivity but decreased sensitivity to relative humidity (RH) with the enhancement in the reduction degree. Specifically, thoroughly reduced GO (RGO) exhibited impedance change of less than 90% between 11% and 95%RH, demonstrating poor sensitivity [24]. Pustelny et al. also found that GN based sensor showed resistance change of no more than 10% between 6% and 70%RH [25]. Chen et al. prepared a humidity sensor based on the bilayer GN with response magnitude of only ~20% between 35% and 98%RH [26]. In comparison, the composites of GN and polymers (mainly polyelectrolyte) exhibit enhanced sensitivity. However, higher response magnitude is usually achieved only in the environments with high humidity levels. Guo et al. found that the composite of RGO and poly(N-vinylpyrrolidone) demonstrated high sensitivity only when humidity was above 70%RH [27]. Lin et al. also reported that the composite of GN and polypyrrole exhibited no more than six-fold change in the impedance between 12% and 72%RH, while an impedance change of 138-fold was observed between 12% and 90%RH [28]. In particular, there have been few reports on the detection of low humidity (<10%RH) with GN based composites. Sreeprasad et al. prepared the graphene quantum dots (GQD) via complicated procedures, and revealed that the composite of GQD and polyallylminehydrochloride showed a 43-fold increase in the conductivity between 0% and 40%RH, indicative of good sensitivity in the low humidity range [29]. We also fabricated the composites of GN with sodium polystyrenesulfonate and GN with poly(dimethyl diallylammonium chloride) via the in-situ reduction of GO, and found that the composites revealed relatively good sensitivity as characterized by impedance increase of 300% and 1000% between 0.2 and 30%RH [30]. It is clearly seen that much more work is needed for the applications of GN based humidity sensors with

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desirable sensing characteristics, such as improved sensitivity and ability to detect very low humidity.

Here we reported humidity sensors based on RGO and crosslinked and quaternized poly(4-vinylpyridine) (QC-P4VP). QC-P4VP is a typical cationic polyelectrolyte humidity sensitive material featured with high humidity sensitivity, but poor conductivity under dry atmosphere [31]. Previously, we fabricated a series of composites of QC-P4VP with carbon nanotubes, carbon black, and polypyrrole, with improved sensing properties in the detection of low humidity [32–34]. Particularly, the sensor in the work presented a bilayer structure, with RGO film superimposed on the QC-P4VP film. Such a bilayer or even multilayer structure has been employed in the construction of a number of gas and humidity sensors with improved sensing properties (higher sensitivity, faster response, better stability, etc.) [35–39]. The QC-P4VP/RGO bilayer sensor exhibits much lower impedance compared with the sensor based on QC-P4VP alone in the low humidity range. Meanwhile, it maintains high response magnitude, which is superior to RGO based sensor. The bilayer sensor is featured with the ability to detect very low humidity (~0.18%RH) with good response magnitude. The concentration of the precursors of the sensitive materials, the deposition order and thickness of the sensitive films, temperature, and the structure of the interdigitated gold electrodes had great effect on the sensing properties of the bilayer sensor. A sensing mechanism of the bilayer-structured humidity sensor has been proposed.

2. Experimental

2.1. Reagents

4-Vinylpyridine was purchased from Acros and distilled under reduced pressure before use. Poly(vinyl alcohol) (PVA, model:1788) and poly(vinyl butyral) (PVB) (M_W: 170,000–250,000) were supplied by Aladdin Chemical Reagent Co. Chloroform, 1,4-dibromobutane (DBB), ether, hydrazine hydrate (85%), and N,N-dimethyl formamide (DMF) were all purchased from Sinopharm Chemical Regent Co., Ltd. Azobisisobutyronitrile (AIBN) was obtained from Shanghai Sihewei Chemical Co., Ltd., and purified by recrystallization before use. Graphene oxide (GO, 1.0 wt% aqueous dispersion) was obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. All the chemicals used in the work were of analytical grade and used as received unless otherwise noted.

2.2. Preparation of poly(4-vinylpyridine)

Poly(4-vinylpyridine) (P4VP) was prepared by a general radical polymerization with AIBN according to the reference method [31] (M_w: 87845; M_n: 47731; PDI: 1.840).

2.3. Fabrication of the composite humidity sensors

P4VP (24 mg/mL) and PVB (5 mg/mL) were dissolved in DMF by magnetic stirring. Afterwards, DBB (98.6 mg/mL) was added, and the resulting mixture was aged at room temperature for 12 h and designated as solution A. The addition of PVB into the mixture could improve the film-forming ability.

PVA (8 mg/mL) was dissolved in water by magnetic stirring, and mixed with aqueous solution of GO (1 mg/mL, 2 mg/mL, and 4 mg/mL). The mixture was cooled to 0–5 °C in ice-water bath, and added with hydrazine hydrate (the ratio of GO to hydrazine hydrate is fixed at 1 mg:12 μL) to obtain solution B. PVA was employed to enhance the film forming ability.

The humidity sensor based on QC-P4VP was fabricated by coating solution A on the interdigitated gold electrodes with an automatic dip-coating machine, and subsequent heating at 110 °C for 10 h for the crosslinking and quaternization reaction between P4VP and DBB. The bilayer humidity sensor was obtained by dip-coating solution B onto the surface of the sensor with a thin film of QC-P4VP, followed by heating at 110 °C for 10 h for the reduction of GO. For comparison, a sensor based on RGO was prepared from solution B. To examine the effect of the film thickness on the response of the bilayer sensor, a thin film of QC-P4VP was also obtained by coating solution A onto the interdigitated gold electrodes with a spin coater (KW-4A, Institute of Microelectronics, Chinese Academy of Sciences) and subsequent heat treatment. Two types of interdigitated electrodes with a ceramic substrate were used: Type I: size of 6 mm × 5 mm × 0.5 mm, and both the width and gaps of the gold tracks on the electrode were 40 μm; Type II: size of 12 mm × 5 mm × 0.5 mm, and both the width and gaps of the gold tracks on the electrode were 200 μm.

2.4. Characterization

Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vector 22 infrared spectrometer (KBr pellets). Ultraviolet–visible (UV–vis) spectra were recorded with a Varian Cary 100 Bio UV–vis spectrophotometer. Raman spectra were measured on RSJDbin-yvon LabRamHRUV system with a 514 nm wavelength laser in the range of 2000–500 cm^{-1}. Morphologies of the sensing films were investigated using a transmission electron microscope (TEM) (HT7700, Hitachi, accelerating voltage of 120 kV) and a scanning electron microscope (SEM) (s-4800, Hitachi, accelerating voltage of 3 kV). The determination of molecular weight and its distribution was carried out on a Waters 1515 chromatography calibrated with poly(methyl methacrylate) standard at 60 °C in DMF.

Humidity sensing properties of the sensors were investigated by recording their impedance responses to humidity at room temperature (~25 °C unless noted otherwise) using a home-made equipment [40]. The applied voltage and frequency were 1 V and 1 kHz, respectively. The sensors were placed in a chamber where humidity was controlled by adjusting the mixed ratio of dry and wet gases with the flowrate controllers and calibrated with a commercial hygrometer (Rotronic Hygroclip HC2-S3 with an accuracy of ±0.8%RH at 23 °C/±0.1 K). Dry and wet gases were obtained by passing the compressed air through silica gel and deionized water, respectively. For the measurement of electrical response in the low humidity range (0.15–15%RH), a dew point transmitter was used as the calibration (DMT242, Vaisala, Finland; dew point range: −60~60 °C; dew point of −60 °C is equivalent to 10.75 ppm or 0.008%RH at 23 °C). The response time transients were obtained by monitoring the real-time impedance response of the sensors when they were quickly transferred between different humidity sources ($MgCl_2$ for 33%RH and K_2SO_4 for 98%RH) [30,41]. The effect of temperature (from 20 °C to 40 °C) on the humidity sensing properties of the sensors was examined in a climatic chamber (STH-50S-A, Shanghai Shangqun Technology Co., Ltd.).

3. Results and discussion

3.1. Preparation and characterization of QC-P4VP/RGO composite

It is known that pristine GN usually does not disperse well in the solvents. Therefore the compatibility and dispersion of GN (usually obtained by the reduction of its precursor GO) in the polymer solution is of great concern while preparing thin film humidity sensors based on polymer/GN composite. A careful selection of the polymer (mainly polyelectrolyte) is necessary, and many polyelectrolyte sensitive materials are thus excluded, such as QC-P4VP.