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Facilely prepared composites of polyelectrolytes and graphene as the sensing materials for the detection of very low humidity

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ABSTRACT

Two polyelectrolytes, i.e., cationic poly(diallydimethylammonium chloride) (PDDA) and anionic sodium poly(4-styrenesulfonate) (PSSNa), were separately mixed with graphene oxide (GO) and hydrazine in solution, and heat-treated to result in composites of PDDA/graphene (GN) and PSSNa/GN, respectively. The composites were characterized by scanning electron microscopy, transmittance electron microscopy and Raman spectroscopy. Impedance-type humidity sensors were constructed by depositing the composite films onto interdigitated gold electrodes via dip-coating. The electrical response of the composite humidity sensors toward relative humidity (RH) was investigated at room temperature. It was found that the composites with higher content of GN exhibited lower impedance at low humidity levels. Both composite sensors could detect very low humidity (down to 0.2%RH), and showed good response magnitude in the low humidity range (relative impedance change of 300% and 1000% from 0.2 to 30%RH for PSSNa/GN and PDDA/GN, respectively). Moreover, the composites exhibited slight hysteresis similar to that of the polyelectrolytes alone, while their response time for desorption was even reduced. The sensing mechanism of the composites was explored by complex impedance spectra analysis, and the good sensing behavior at low humidity was proposed to the special electrical property and unique two-dimensional nanosheet structure of GN.

1. Introduction

Polymeric impedance-type (or sometimes called resistive-type) humidity sensors, which show intrinsic advantages of simple fabrication, low cost and high sensitivity, have seen rapid development thanks to the increasing concerns for humidity detection and control in recent years [1–8]. However, these sensors mainly employ polyelectrolytes as the sensing materials. Due to the poor conductivity of the polyelectrolytes in the absence of water molecules, their impedance at low relative humidity (RH) levels would be too high to be measured with normal electric circuit design. As a result, they are difficult to be used for the detection of very low humidity. To expand the detection range to very low humidity levels, and thus meet the requirements in the areas such as drying of some medicine and gases, production of lithium-ion batteries and transformers, supercapacitors, safe operation of gas insulated switchgear in power industry, etc., it is necessary to decrease the impedance of the polyelectrolyte-based humidity sensors at low humidity, while maintain acceptable sensitivity at the same time [9–11]. A general method for enhancing the conductance of the impedance-type humidity sensors is to prepare composites of polyelectrolytes and highly conductive materials. Carbon black (CB) nanoparticle, which is typical zero-dimensional nanomaterial with good intrinsic conductivity, has been used to form composite with poly(vinyl alcohol), doped poly(1,5-diaminonaphthalene) or even grafted to poly(ethylene glycol) and poly(4-vinylpyridine) to construct humidity sensors capable of detecting low humidity [12–15]. Recently, Zhang et al. prepared carbon quantum dots (CQD) containing a lot of functional groups such as hydroxyl and carboxyl groups. They found that the functional groups endowed the CQDs with good humidity sensitivity, but the conductivity was greatly damaged. Thus it showed poor conductivity at dry atmosphere (<7%RH) and could not detect very low humidity [16]. Moreover, carbon nanotubes (CNTs), which are well-known one-dimensional carbon-based nanomaterial, have also been employed for enhancing the conductivity of polymer-based humidity sensors at low humidity levels. It was reported that the introduction of CNTs into polyelectrolytes effectively enhanced the conductivity of the resulting composites, but the ability to detect very low humidity was not demonstrated [17,18]. Moreover, the impedance-type humidity sensors based on CNTs and the composites generally displayed greatly depressed sensitivity and the capability of low

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humidity detection was rarely disclosed. Yoo et al. fabricated CNT/polyimide composite humidity sensor with good sensing linearity, but the sensitivity was only 0.047/%RH [19]. Yu and coworkers obtained the composite of poly(ethyleneimine) and CNTs by layer-by-layer assembly, and reported a fast response and recovery time of 2 and 30 s, respectively. However the composite recorded resistance change of no more than two-fold from 5 to 85%RH, exhibiting much smaller sensitivity with respect to typical polyelectrolytes [20]. All these suggest that much more work is needed to develop impedance-type humidity sensors capable of detecting very low humidity with good sensing behaviors, such as acceptable sensitivity.

Graphene (GN) is a new-type of two-dimensional carbon-based nanomaterial. Due to its extraordinary electrical and mechanical properties, great attention has been paid to the preparation and application of the novel material since its discovery in 2004 [21–25]. The high surface-to-volume ratio, good conductivity and inherently low electrical noise made it an attractive candidate for the construction of highly sensitive chemical sensors, and its ability to realize single molecule detection has been reported [26]. The humidity responses of GN were also investigated. Ghosh et al. prepared GN and nitrogen and boron-doped GN, and measured their electrical response to humidity. It was found that the resistance of GN slowly decreased with increase in humidity, with relatively low sensitivity (no more than 80% from 4% to 84%RH). In addition, the recovery time was as long as a few hours [27]. Guo et al. prepared GN by reducing graphene oxide (GO) using the technique of two-beam-laser interference. It was revealed that the GN exhibited different conductivity and sensitivity depending on the reduction degree, and the sensitivity was much decreased in order to obtain high conductivity at low humidity [28]. Zhang et al. prepared a composite of GN and poly(N-vinylpyrrolidone) by solution reduction, and reported its positive response to humidity in the range of 30–90%RH. However, the composite still revealed quite low conductivity, and was not used to detect very low humidity [29]. Recently, Chang et al. fabricated the composite of GN and polypyrrole by in situ polymerization, and found that the composite exhibited a sensitivity of 138 over the range of 12–90%RH, but the sensitivity at low humidity range is so small (conductivity change of no more than 1.2 from 12 to 32%RH) that it would be unsuitable for accurate detection of very low humidity [30].

In this work, we prepared the composites of GN and polyelectrolytes and employed them as the sensing materials for the detection of very low humidity. The polyelectrolytes used are cationic poly(diallydimethyldiammonium chloride) (PDDA) and anionic sodium polystyrenesulfonate (NaPSS), which have been employed in the construction of impedance-type humidity sensors [31,32]. Considering the fact that GN is difficult to be dispersed in solutions, its derivative GO was used to form composite with the two polyelectrolytes, which was reduced to GN with hydrazine. Thanks to the stabilizing effect of the polyelectrolytes, uniform dispersions of reduced GO in PDDA or PSSNa solution were obtained and used to fabricate impedance-type humidity sensors by dip-coating. The humidity sensing properties of the composite sensors were investigated at room temperature, and the effect of the GN content on the humidity response was examined. Both composite sensors revealed good response magnitude in the low humidity range (0.2–30%RH). Moreover, other sensing properties, such as the hysteresis and response times, were not deteriorated after the introduction of GN. The composites showed promise as sensing materials of impedance-type humidity sensors for very low humidity detection. The sensing mechanism of the composites was explored, and their good sensing properties in low humidity span were proposed to relate to the special electrical properties and unique structure of the two-dimensional nanomaterial of GN.

2. Experimental

2.1. Reagents

Natural graphite flake (325 mesh, 99.8%) and sodium poly(4-styrenesulfonate) (PSSNa) (M.W. 70,000) were purchased from Alfa Aesar. Poly(diallyldimethyl ammonium chloride) (PDDA) (M.W. 200,000–350,000, 20 wt% in water) was obtained from Aldrich. Hydrazine hydrate (85%) was purchased from Sinopharm Chemical Regent Co., Ltd. H_2SO_4 (98%) was purchased from Quzhou Juhua Reagent Co., Ltd. P_2O_5 was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. $KMnO_4$ was purchased from Hangzhou Xiaoshan Reagent Co., Ltd. H_2O_2 (30%) was obtained from Linan Lanling Reagent Co., Ltd. Potassium persulfate was purchased from Shanghai Chemical Reagent Co., Ltd. Hydrochloric acid (36–38%) was obtained from Hangzhou Chemical Reagent Co., Ltd. All the chemicals used in this study were of analytical grade and used as received.

2.2. Preparation of PDDA/GN and PSSNa/GN and fabrication of the composite humidity sensors

Graphene oxide (GO) was prepared by a modified Hummers' method as described in the Ref. [33]. GO was dispersed in deionized (DI) water by ultrasonication. The obtained dispersion was slowly dropped into the aqueous solution of PDDA and PSSNa at 40 °C, respectively. After that, the mixture was ultrasonicated for another 30 min at room temperature. Finally, into the obtained homogeneous dispersion, was added hydrazine hydrate (85%), and the resulting mixture was heated at 95 °C for 12 h for the reduction of GO. In the process, the concentration of GO was set at 0.3 mg/mL, 0.9 mg/mL and 1.5 mg/mL, while the concentration of both polyelectrolytes was fixed at 30 mg/mL, and the ratio of GO to hydrazine hydrate (85%) was 1 mg:12 μL. As-prepared dispersion of GN in the solution of PDDA or PSSNa was dip-coated onto the surface of the interdigitated gold electrodes using an automatic dip-coating machine (the ascending and descending speeds were both 3.2 mm/s), followed by drying at 100 °C for 2 h to obtain the composite impedance-type humidity sensors based on PDDA/GN or PSSNa/GN. The size of the interdigitated electrodes with a ceramic substrate was 12 mm × 5 mm × 0.5 mm, and both the width and gaps of the 13 pairs of gold tracks on the electrode were 40 μm.

2.3. Characterization

Morphologies of the materials were observed using a scanning electron microscope (SEM) (s-4800, Hitachi, accelerating voltage of 3 kV) and transmittance electron microscopy (TEM) (JEM-1230, accelerating voltage of 60 kV). Raman spectra were obtained on RS JDbin-yvon LabRamHRUV system with a 514 nm wavelength laser in the range from 3500 cm^{-1} to 300 cm^{-1}.

Humidity sensitive properties of the sensors were investigated by recording their impedance response to relative humidity (RH) at room temperature (22–25 °C) using a home-made equipment. The diagram of the working principle of the measurement equipment is presented in Scheme 1. The applied voltage and frequency was 1 V and 1 kHz, respectively. R_0 and Z_x refer to the resistance of the standard resistor and the impedance of the sensor, respectively; V_i and V_0 are the applied voltage and measured voltage, respectively. The impedance of the sensor is calculated with the following equation: $Z_X = (V_{ir}/V_{0r}) \cdot R_0$, where V_{ir} and V_{0r} are the effective values of V_i and V_0, respectively. The sensors were placed in a chamber where humidity was controlled by adjusting the mixed ratio of dry and wet gases and calibrated with a commercial hygrometer (Rotronic Hygroclip HC2-S3 with an accuracy of ±0.8%RH at