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Bilayer-structured composite sensor based on polyaniline and polyelectrolyte for sensitive detection of low humidity

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ABSTRACT

A bilayer-structured composite humidity sensor based on quaternized and crosslinked poly(4-vinylpyridine) (QC-P4VP) and polyaniline (PANI) was fabricated by depositing thin films of QC-P4VP and PANI onto interdigitated gold electrode in sequence. The composite was characterized by Fourier transform infrared spectroscopy, Ultraviolet–visible spectroscopy, scanning electron microscopy, and atomic force microscopy. The composite sensor could sensitively detect very low humidity (down to ~1% RH) (impedance increase of ~860% from 15% to 1%RH). Furthermore, the sensor exhibited relatively fast response ($t_{90\%}$ of 24 s and 35 s for adsorption and desorption processes, respectively), small hysteresis (~3%RH) and good repeatability. In addition, the composite sensor revealed impedance change close to 10^3 from 1% to 98%RH, suggesting its capability of detecting full-range humidity with high sensitivity. The effect of the concentration of poly(4-vinylpyridine) and PANI, deposition sequence of the sensitive layers on the humidity sensing characteristics of the composite has been examined. The humidity sensing mechanism of the composite sensor was proposed by considering the electrical properties of QC-P4VP and PANI at different humidity levels and the special bilayer structure.

1. Introduction

Low humidity detection plays an important role in gas drying, production of transformer and lithium battery, quality control of insulating gases for safe operation of switchgear in power industry, etc. [1–7] However, the accurate measurement and control of low humidity (typically <relative humidity (RH) of 10%) are difficult for the widely applied polymer resistive-type humidity sensors, which are mainly due to their poor conductivity in dry atmosphere [2,5,8–10]. Therefore, their applications in a variety of fields were precluded. Efforts have been devoted to solving the problem by preparing the composites of polymer sensitive materials (primarily polyelectrolyte) with highly conductive materials, such as carbon black, carbon nanotubes, graphene, intrinsic conductive polymers, so as to enhance their conductivity [2,5,8–13].

Polyaniline (PANI) is one of the most intensively investigated conductive polymers employed as chemical sensitive materials [14–17]. There has been a number of reports on polyaniline and its composites with insulating polymers or inorganic semiconductors as humidity sensitive materials [13,18–21]. McGovern et al. found that the microsensor based on the composite of PANI and poly (vinyl alcohol) exhibited quite high humidity sensitivity (resistance change of more than three orders of magnitude from 30% to 95%RH), but its resistance was as high as ~10,000 MΩ at ~30%RH. By contrast, the composite of PANI with the copolymer of butyl acrylate and vinyl acetate showed higher conductivity, however, its humidity sensitivity over the entire humidity range was as low as ~800%. Moreover, its response time and recovery time were as long as 4–5 h and 24 h, respectively [18]. Parvatikar et al. fabricated the composite of PANI and WO_3 with good conductivity, but the resistivity decreased for no more than ~4 folds between 10%RH and 95%RH, indicative of quite low sensitivity [19]. Sajjan et al. reported the humidity sensor based on the composite of PANI and Cr_2O_3 featured with relatively fast response time and recovery time of 134 s and 213 s, respectively. However, the composite exhibited poor humidity sensitivity of no more than 87% [20]. Nohria et al. constructed the ultrathin film of PANI by layer-by-layer self-assembly featured with very fast response. Nonetheless, the resistivity changed for no more than 100% between 50%RH and 90% RH, revealing poor sensitivity [21]. We prepared the electrospun nanofibers of PANI and poly(vinyl butyral) with high humidity sensitivity and fast response. Nevertheless, its impedance at 20% RH was as high as ~10^7 Ω and could not be used to detect very low humidity [22]. Therefore, much more work is to be done to develop

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novel humidity sensing materials with both good conductivity and high sensitivity, which is necessary for the sensitive measurement of very low humidity.

It is proposed that the composite of polyelectrolyte and highly conductive PANI could not only display high sensitivity by taking advantage of the features of polyelectrolyte sensitive material, but also detect low humidity by virtue of the good intrinsic conductivity of PANI. Therefore, in this work, a bilayer structured composite humidity sensor has been constructed. The first layer is composed of a typical polyelectrolyte, i.e., quaternized and crosslinked poly(4-vinylpyridine) (QC-P4VP), which is known to exhibit high humidity sensitivity [23–25]. The second layer is water-processable PANI, which could exhibit high conductivity even in the absence of humidity by optimizing the ratio of monomer and doping agent. The effect of the concentration of QC-P4VP and PANI, the deposition order of the sensitive layers on the humidity sensing characteristics of the composite, especially in the detection of very low humidity, has been investigated at room temperature. The composite is featured with the ability to sensibly detect low humidity (1–15%RH), and even realize almost full-range humidity detection (1–98%RH) with high sensitivity. The sensing mechanism of the bilayer-structured composite has been explored.

2. Experimental

2.1. Reagents

Both aniline (Wulian Chem. Co.) and 4-vinylpyridine (Acros) were distilled under reduced pressure before use. Ammonium persulfate (APS) was purchased from Shantou Xilong Chem. Co. Poly(styrene sulfonic acid) (PSSA, Mw: 75,000, 30 wt% water solution) was obtained from Alfa Aesar. Poly(vinyl butyral) (PVB) (M.W. 170,000–250,000) and poly(vinyl alcohol) (PVA, model: 1788) were supplied by Aladdin Chemical Reagent Co. 1, 4-Dibromobutane (DBB), chloroform, acetone, and ether 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. All the chemicals used in the work were of analytical grade and used as received unless noted otherwise.

2.2. Preparation of polyaniline and poly(4-vinylpyridine)

Water-processable PANI was synthesized by a solution polymerization of aniline with APS as an oxidant and PSSA as a soft template according to our previous work [22,26]. Specifically, molar ratio of PSSA/aniline was controlled at 1/1. The PANI so prepared exhibited good conductivity and water solubility.

Poly(4-vinylpyridine) (P4VP) was prepared by a traditional solution polymerization with AIBN as the initiator [23]. A typical synthesis procedure is as follows: 22.7 mg of recrystallized AIBN was put into an ampoule, which was then repeatedly evacuated under vacuum and flushed with Ar for three times. Afterwards, 8.17 mL of chloroform and 3.83 mL of 4-vinylpyridine were injected into the ampoule, and the polymerization reaction was carried out in Ar atmosphere at 60 °C for 19 h. The resulting mixture was diluted with chloroform and precipitated in a large amount of ether, followed by vacuum filtering and drying under vacuum for 24 h to obtain white floccules of P4VP (M_w: 80,445, M_n: 48,813, PDI: 1.648).

2.3. Fabrication of the composite humidity sensors

P4VP and PVB were dissolved in DMF by magnetic stirring. Afterwards, DBB was added, and the mixture was aged at room temperature for 12 h. PVB was added into the solution to promote the formation of a complete and continuous film.

The humidity sensor based on QC-P4VP was fabricated by dip coating the mixture so prepared on the surface of interdigitated gold electrodes with an automatic dip-coating machine, followed by heating at 110 °C for 10 h to induce the crosslinking and quaternization reaction between P4VP and DBB. The composite humidity sensor was obtained by dip-coating the aqueous solution of PANI and PVA onto the surface of the sensor covered with the sensitive film of QC-P4VP, followed by heating at 100 °C for 2 h. PVA was employed to induce a crosslinking reaction between the dopant PSSA and PVA, and reduce the hysteresis [22,26]. The size of the interdigitated electrodes with a ceramic substrate was 6 mm × 5 mm × 0.5 mm, and both the width and gaps of the gold tracks on the electrode were 40 μm. The thickness of the composite films was ~6 μm as determined from their cross-section images.

2.4. Measurements

Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vector 22 infrared spectrophotometer (KBr pellets). Ultraviolet–visible (UV–vis) spectra were recorded with a Varian Cary 100 Bio UV–vis spectrophotometer. Morphologies of the sensing films were investigated with a scanning electron microscope (SEM) (s-4800, Hitachi, accelerating voltage of 3 kV) and an atomic force microscope (AFM) (SPI3800N) using a tapping mode. Molecular weight determination was carried out on a Waters 1515 chromatography calibrated with poly(methyl methacrylate) standards at 60 °C in DMF.

Humidity sensitive properties of the sensors were investigated by recording their impedance responses to relative humidity (RH) at room temperature (~25 °C unless noted otherwise) using a home-made equipment [5]. 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 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 of the sensors in the low humidity range (1–15%RH), a dewpoint transmitter was used as the calibration (DMT242, Vaisala, Finland; dewpoint range: −60 ~ 60 °C; dewpoint 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 (LiCl for 11%RH and K_2SO_4 for 98%RH) [5,8]. The complex impedance spectra of the sensors were recorded on a ZL5 intelligent LCR meter (Shanghai Haoshun Technology Co., Ltd.) at room temperature, with saturated salt solutions in their equilibrium state as the humidity sources [5,24].

3. Results and discussion

3.1. Characterization of QC-P4VP/PANI composite

Previously, we prepared the composite of QC-P4VP, with conductive polypyrrole (PPy) or carbon black, aiming at decreasing the impedance of the composite in dry atmosphere to facilitate the detection of low humidity [9,25]. The introduction of PPy or carbon black effectively enhanced the conductivity of the composite in the absence of water molecules, but the sensitivity of the composite was also sharply decreased. Moreover, the humidity sensing properties of the composite in low humidity range (typically <10% RH) have not been fully examined.

In the present work, we constructed a bilayer-structured composite humidity sensor based on QC-P4VP and PANI which