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Humidity sensors based on the composite of multi-walled carbon nanotubes and crosslinked polyelectrolyte with good sensitivity and capability of detecting low humidity

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ABSTRACT

Multi-walled carbon nanotubes (MWNTs) were dispersed in the matrix of quaternized and crosslinked poly(4-vinylpyridine) (QC-P4VP) to prepare a composite via solution blending and heat treatment. The composite was characterized by FT-IR spectroscopy and scanning electron microscopy. Thin film humidity sensors based on the composite were fabricated and their electrical responses to relative humidity (RH) were investigated at room temperature. The composite sensor showed much higher response magnitude than the sensor based on MWNTs (impedance increase of ~4700% from 7 to 90%RH). Meanwhile, its impedance at low humidity was significantly decreased with respect to that of QC-P4VP based sensor. Furthermore, it could detect very low humidity with good sensitivity (impedance change of 16%/%RH over 1–30%RH), and demonstrate its capability of realizing full-range measurement of humidity. The effect of content of MWNTs, poly(4-vinylpyridine) (P4VP) and the additive, molecular weight of P4VP, temperature and testing frequency on the humidity sensing properties of the composite sensors has been examined. A sensing mechanism was proposed by considering the MWNT conductive network in the polyelectrolyte matrix.

1. Introduction

Carbon nanotubes (CNTs) are one of the most important one-dimensional nanomaterials attracting extensive attention worldwide. Nowadays, CNTs have found applications in a broad spectrum of fields ranging from electronics and solar cells to humidity sensors [1–8]. In recent years, various types of humidity sensors based on CNTs and/or their composites have been reported, such as impedance-type (resistance type), capacitance-type, field-effect transistor, quartz crystal microbalance, and surface acoustic wave type [7,9–17]. Among them, CNT-based impedance-type humidity sensors are the most popularly examined. However, they suffer from the shortcomings of low sensitivity and slow response. Adjizian et al. found that pristine CNTs and B- or N-doped CNTs exhibited very long response time to humidity. The full recovery of the sensor baseline took about 2.5 h even when it was heated at 150 °C [18]. Yoo and coworkers [19] prepared the composite film of multi-walled carbon nanotubes (MWNTs) with polyimide and found that its resistance changed linearly with humidity variation, but the sensitivity was only 0.0047/%RH. Apparently, the CNT-based sensors showed much smaller sensitivity than polyelectrolyte-based humidity sensors, whose impedance typically changed for several orders of magnitude with humidity variation [20].

To conquer the drawbacks, efforts were done to modify CNTs by forming composites with inorganic semiconductors or polymers. Jiang et al. reported that the humidity sensor based on arrayed MWNT nests grown on arrayed nanoporous silicon pillars exhibited improved humidity sensitivity, and its relative change in resistance reached 362% between 11 and 85%RH. However, the composite showed very long response time (64 min) and recovery time (51 min) [21]. Zhang et al. prepared the composite of MWNTs and poly(vinyl alcohol). They found that the impedance of the composite did not change with humidity until 100%RH, thus composing a switch-type humidity sensor [22]. Yu et al. fabricated the composite film of poly(ethyleneimine)/MWNT by layer-by-layer assembly, and found that it showed a fast response of 30 s. Nevertheless, the relative impedance change of the composite between 5 and 85% was less than 100% [23]. Liu et al. also constructed the composite films based on CNTs and poly(dimethyldiallylammonium chloride)

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featured with fast response. However, the composite exhibited resistance changes of less than 100% between 25 and 75%RH [24]. Su and coworkers obtained the composite of MWNT/poly(methyl methacrylate) doped with KOH by in situ synthesis, and revealed that KOH doping substantially enhanced the sensitivity. But the composite exhibited very high impedance at low humidity, and could not be used to detect humidity at dry atmosphere [25]. Recently, Lee et al. demonstrated that flexible composite films of MWNTs and polyacrylic acid could show impedance change close to one order of magnitude over 30–90%RH, revealing good sensitivity. Nonetheless, the response time was still quite long, reaching 670 s and 380 s for humidification and desiccation processes, respectively [26]. Therefore, much more work is needed to obtain CNTs based humidity sensors with desirable sensory properties such as good sensitivity and acceptable response time.

In this paper, we reported an impedance-type humidity sensor based on the composite of MWNTs with quaternized and crosslinked poly(4-vinylpyridine) (QC-P4VP), which is a typical polyelectrolyte humidity sensitive material [27]. The composite showed good sensitivity and relatively fast response. In particular, it demonstrated the ability to detect humidity as low as 1%RH by exploiting the high intrinsic conductivity of MWNTs, and could thus realize full-range measurement of humidity. The effect of the contents of the composite, temperature and testing frequency on its sensing behaviors was studied. The sensing mechanism of the CNT-based composite featured with good humidity sensing properties was also explored.

2. Experimental

2.1. Reagents

4-Vinylpyridine was purchased from Acros and distilled under reduced pressure before use. MWNTs (outer diameter > 50 nm, length of 10–20 μm, 2 wt% in ethanol) were obtained from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. 4-Hydroxy-2,2,6,6-tetramethyl piperinooxy (THEMPO) was purchased from Alfa Aesar. Poly(vinyl butyral) (PVB) (M_w 170,000–250,000) was obtained from Aladdin. 1,4-Dibromobutane (DBB), absolute ethanol, ether and methanol were purchased from Sinopharm Chemical Regent Co., Ltd. Dibenzoyl peroxide (BPO) and azodiisobutyronitrile (AIBN) were obtained from Shanghai Shisihewei 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 poly(4-vinylpyridine) and fabrication of the composite humidity sensors

Poly(4-vinylpyridine) (P4VP) was prepared by a nitroxide-mediated living radical polymerization as described in Ref. [28]. Typically, 16.8 mg of BPO and 15.5 mg of THEMPO were added into an ampoule, which was then repeatedly evacuated and flushed with Ar for three times. Afterwards, 5 mL of 4-vinylpyridine was added, and the polymerization proceeded at 125 °C for 40 h under Ar atmosphere. The resultant was diluted with methanol and precipitated in ether, filtered and washed with ether, followed by vacuum drying to give a light-red solid (M_w: 38,081, M_n: 24,577, *MWD*: 1.54). ^{1}H NMR ($CDCl_3$) (ppm): δ = 8.65–7.96 (C*H*-N-C*H*), δ = 6.94–6.01 (—C*H*-C-C*H*), δ = 1.72–1.15 (—C*H*$_2$-CH-(C_5H_5N)).

For comparison, P4VP with high molecular weight was also prepared via the traditional radical solution polymerization [20]. Specifically, 5.88 mg of AIBN was added into an ampoule, which was then repeatedly evacuated and flushed with Ar for three times. Afterwards, 1 mL of 4-vinylpyridine and 6.2 mL of absolute ethanol were added, and the polymerization proceeded at 60 °C for 24 h under Ar atmosphere. The obtained mixture was precipitated in a large amount of water, and purified by repeatedly dissolved in ethanol and precipitated in water for three times, followed by vacuum filtering and drying under vacuum for 48 h to give a pink solid referred to as high-molecular-weight P4VP (HMW-P4VP) (M_W: 81,113, M_n: 41,397, MD: 1.95).

P4VP and PVB were dissolved in ethanol, then mixed with ethanol dispersion of MWNTs by magnetic stirring and subsequent ultrasonication for 0.5 h. Afterwards, DBB was added into the mixture and magnetically stirred for some time to obtain a homogeneous dispersion, which was aged at room temperature for 12 h.

The humidity sensors were fabricated by depositing the mixture so prepared on the surface of interdigitated gold electrodes with an automatic dip-coating machine, followed by heating at 110 °C for 11 h to induce the crosslinking and quaternization reaction between P4VP and DBB. 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 gold tracks on the electrode were 40 μm. The thickness of the composite films was ~2 μm as determined from their cross-section images.

2.3. Measurements

Fourier transformed infrared (FT-IR) spectra were obtained on a Bruker Vector 22 infrared spectrometer (KBr pellets). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker Advance2B spectrometer, operating at 400 MHz (solvent:$CDCl_3$ internal standard:tetramethylsiliane). Morphologies of the sensing films were observed using a scanning electron microscope (SEM) (s-4800, Hitachi, accelerating voltage of 3 kV). Molecular weight determination was carried out on a Waters 1515 chromatography calibrated with poly(methyl methacrylate) standards at 60 °C in N,N-dimethyl formamide (DMF).

Humidity sensitive properties of the sensors were investigated by recording their impedance response to relative humidity (RH) at room temperature (~20 °C unless noted otherwise) using a home-made equipment [29]. 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 over the span of low humidity (1–30%RH), a dewpoint transmitter was used as the calibration (DMT242, Vaisala, Finland; dewpoint range: −60 to 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) [28,29]. The effect of temperature (from 20 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. Characterization of MWNT/QC-P4VP composite

In this work, P4VP with different molecular weights was prepared by a nitroxide mediated living radical polymerization or via the traditional radical polymerization. The heat-induced reaction between P4VP and DBB resulted in QC-P4VP, as shown in Scheme 1.