



Nanocellulose-assisted dispersion of graphene to fabricate poly(vinyl alcohol)/graphene nanocomposite for humidity sensing



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ABSTRACT

In this study, nano-fibrillated cellulose (NFC) was used to stabilize the dispersion of chemical reduced graphene oxide (rGO) in aqueous system. Owing to the hydrophobic interactions between the rGO sheets and specific crystalline faces (hydrophobic (200) planes) of NFC as well as electrostatic repulsion between the NFC, a homogenous dispersion of NFC/rGO in water was obtained with good stability. Then the prepared NFC/rGO solution was simultaneously merged into water soluble polyvinyl alcohol (PVA) to obtain PVA/NFC/rGO composite freestanding films via a casting method. It was found that the conductivity of the composite films changed rapidly as changing of relative humidity (RH) and exhibited a good repeatability between RH at 50%–70%. Compared to PVA/rGO film without NFC, PVA/NFC/rGO film exhibited higher conductivity, sensitivity as well as faster response (lower hysteresis). Thus the prepared PVA/NFC/rGO films could serve as an effect humidity sensor. It was suggested that NFC played several roles in the composite films: (1) as compatibilizer to enhance the dispersion of rGO in PVA matrix, (2) as a bridge to enhance the load transfer and humidity transfer between PVA and rGO, and (3) as water absorber to enhance the sensitivity of humidity.

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1. Introduction

In recent years, humidity measurement and monitor have been paid more and more attention for its importance and necessity in many areas such as weather prediction, historic preservation, medical/healthcare product development, industrial manufacturing, agriculture and wearable or mobile electronics [1]. For the requirements of precision, electric hygrometer gains broader concern than the traditional hair hygrometer or psychrometer, due to its sensitivity of electrical signal along with the changing of moisture content in materials. Up to now, the sensitivity and prompt response of electric hygrometer remain to be improved to gain a better prospect of application. The structure of electric hygrometer contains humidity sensitive layer which absorbing/desorbing water molecules in the atmosphere air, and electronic transducer outputting electrical signal via sensing the variation of moisture content. For the humidity sensitive layer, polymers are the optimal choice to construct the humidity sensitive materials, since they can provide many novel advantages such as low cost, high sensitivity, fast response, flexibility, easy

processability, etc. [2] Abundant researches indicated that polyvinyl alcohol (PVA) is a good sensitive material [3–6]. To find out its cause, the good sensitivity of PVA originates from the massive hydroxyl groups existed in its molecular chains, which could interact with water molecules via hydrogen bonding. Due to its special structure, large surface area, high mechanical strength and excellent electrical properties [7–9], graphene has been deemed to be one of the most attractive candidates for transparent conductive substrates [10–12], super capacitors [13–15], lithium batteries [16,17], field-effect transistors [18,19], chemical sensor [20–23] and polymer nanocomposites [24–26]. Graphene as electronic transducer can improve the sensitivity of PVA-based humidity sensor effectively since conductivity of graphene can be influenced by the water molecules absorbed on its surface [27–29]. Nevertheless, the hydrophobicity of graphene nanosheets makes it hard to be dispersed in polar solvent or polymer matrix, which largely restrict its practical application. Therefore, to increase the miscibility with polymers, graphene was modified by numerous approaches. Researchers have demonstrated that both covalent and noncovalent functionalization methods could improve the dispersibility of graphene in the polymer matrix effectively [30–34]. Especially, Hwang et al. [6] reported that using poly(dopamine) modification on graphene oxide (GO) surface to enhance the dispersion of graphene as

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well as interfacial interaction between graphene and polyvinyl alcohol (PVA), to fabricate poly(dopamine)-treated graphene oxide/polyvinyl alcohol (dGO/PVA) composite film which exhibit good repeatable humidity sensitivity without sacrifice of long-term performance. Although the surface chemical or physical modifications of graphene, can improve the dispersion of graphene sheets in some extent, generally, they result in a decrease of conductivity and mechanical behavior of composite materials. Therefore, the fabrication of novel and high performance humidity sensor with higher sensitivity, stability and fast response remains a great challenge.

As a renewable and readily biodegradable natural polymeric material, nanofibrillated cellulose (NFC) extracted from abundant natural cellulose fibers with one-dimensional morphological structure, abundant hydroxyl groups on its surface, and biodegradable property, has been reported to exist hydrophobic interactions between carbon black, carbon nanotubes or graphene and the hydrophobic crystalline faces ((200) planes) of cellulose nanocrystals [35–37], which makes it possible that using NFC as a compatibilizer to improve the dispersion of carbon materials in polar solvents. Li et al. [38] and Ye et al. [36] have proved that NFC is an excellent green dispersant for two-dimensional materials as boron nitride (BN) and reduced graphene oxide (rGO) sheets, respectively, arising from the amphiphilic properties of NFC. Except that, Ye et al. [36] also confirmed when compared to polymeric stabilized rGO, the cellulose nanocrystal (CNC) decorated rGO showed better dispersibility in solvent. Furthermore, the synergistic effects with superior mechanical and electrical properties were observed for PEO/rGO composite films after adding NFC as modifier.

In this work, nano-fibrillated cellulose (NFC) was used to stabilize the dispersion of chemical reduced graphene (rGO) in water solution. In this way a simple and environmentally approach can be achieved to fabricate freestanding film of NFC-assisted rGO/PVA with excellent humidity sensitive performance. NFC can not only interact with rGO sheets via hydrophobic interaction between rGO sheets and specific crystalline faces (hydrophobic (200) planes) of NFC, but also forms numerous hydrogen bonding with PVA molecular chains through the hydroxyl on NFC surface, resulting in good dispersion of rGO in PVA matrix. Except that, the hydrogen bonding between NFC and PVA matrix can act as a channel for water molecules in the humidification and dehumidification process to improve the sensitivity and prompt response of the composite film. Compared to PVA/rGO film without NFC, PVA/NFC/rGO film exhibited higher conductivity, sensitivity as well as faster response (lower hysteresis) to humidity to use as humidity sensor.

2. Experimental section

2.1. Materials

Commercial graphite powder was purchased from Qingdao Black Dragon graphite Co., Ltd. Potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄ 98%), hydrogen peroxide (H₂O₂), sodium nitrate (NaNO₃), sodium hydroxide (NaOH), purchased from Kermel Chemical reagent plant (Tianjin, China). Micro-fibrillate cellulose (MFC, solid content, 25%) (Celish KY100-S, Daicel Chemical Industries, Ltd, Japan) is prepared from wood pulp by a number of homogenization progresses. TEMPO (2,2,6,6-Tetramethylpiperidine) was purchased from Sigma-Aldrich. PVA was 99% hydrolyzed with an average polymerization degree of 1700 (SINOPEC Sichuan vinylon works). All agents were used as received.

2.2. Preparation of nano-fibrillated cellulose (NFC) and graphite oxide (GO)

Micro-fibrillated cellulose (MFC) was used as raw materials and

treated with TEMPO-oxidized system [39]. The MFC (10 g) was pre-suspended in water (1000 ml) containing TEMPO (0.16 g) and sodium bromide (1 g). The TEMPO-mediate oxidation was activated by adding NaClO solution (12 wt%, 10 mmol per gram of cellulose). Keeping the system stirring at room temperature, during the oxidation procedure, 0.5 M NaOH was used to maintain the pH at 10–10.5 until no decrease in pH was observed. The TEMPO-oxidized cellulose was thoroughly washed with distilled water by filtration and stored at 4 °C before further treatment.

Graphite oxide was fabricated using commercial graphite powder as the raw material via a modified Hummers method [40,41].

2.3. Preparation of PVA/NFC/rGO nanocomposite films

For preparation of NFC-assisted dispersion of graphene in water, corresponding NFC and GO was dispersed in distilled water and treated with ultrasound for 20 min. We chose L-ascorbic acid (L-AA), which is mild, nontoxic and efficient reductant to reduce graphene oxide. Zhang et al. [42] have proved that L-AA was an effective reductant to remove the oxygen functionalities on GO surface and recover the electronic conjugation state of reduced GO significantly. L-ascorbic acid (L-AA) (10 times weight of GO sheets, the reductant need not be removed because Zhang et al. [43] has proved that the oxidized products of L-AA could act as stabilizer of the reduced GO aqueous suspension) was added under vigorous stirring at 90 °C for 15 min [44]. Then stored at room temperature for further usage.

The fabrication procedure for PVA/NFC/rGO composite free-standing film was as follows: PVA (2 g) was dissolved in distilled water (20 g) at 90 °C for 2 h. Corresponding NFC/rGO hybrid solution was treated with ultrasound for 20 min then gradually dropped into the PVA solution and carefully stirred for 2 h at 50 °C. After subsequently sonicated for 30 min, the homogeneous PVA/NFC/rGO solution was obtained then poured into an aluminum dish and slowly evaporated at 60 °C for film formation till its weight equilibrated. A series of PVA/NFC/rGO composite films with various rGO loading: 0%, 0.5%, 1%, 3% and 5% were similarly prepared. In all these samples, the NFC content was kept constant 3 wt%. There is an optimal density of NFC that can enhance strength and modulus without sacrifice toughness of nanocomposites. Researchers have suggested that the optimal content could vary from 3 wt% to 5 wt% approximately [45,46]. That is the reason why the content of NFC is fixed at 3 wt% in this work. For comparison, PVA and PVA/rGO composite films without NFC were also prepared according to the same procedure as reference samples.

2.4. Characterization

Fourier transform infrared analyses (FTIR) was performed on Nicolet FTIR spectrometer (Nicolet FTIR 6700, Thermo Electron Co., USA) at room temperature. All the samples were obtained as films through casting method in a glass dish at 60 °C for 48 h. X-Ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Co., UK) was carried out to demonstrate the change of functional groups GO and rGO surface before and after reduction, using focused monochromatized Al K α radiation (15 kV) at room temperature. The ultraviolet–visible spectra (UV–vis) was recorded on a UV-1800PC spectrophotometer at room temperature and the date was collected from 200 to 700 nm. The concentration of the NFC/rGO solution for the UV–vis test was 0.3 wt% at a pH of 7.4. The tensile experiments were carried out on an Instron 5567 universal testing machine by uniaxial tension. The films were tested with a cross-head speed of 5 mm/min and the load cell was 100 N with a gauge length of 20 mm. The specimen dimensions were 60 mm length,

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