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A novel flexible humidity switch material based on multi-walled carbon nanotube/polyvinyl alcohol composite yarn

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ABSTRACT

A yarn-like switch-type humidity sensing material is fabricated by infiltrating hydrophilic water-swellable polyvinyl alcohol (PVA) into a multi-walled carbon nanotube (MWCNT) yarn. The electrical resistance of the virgin humidity sensing material remains almost constant at low relative humidity (RH), and then increases sharply as the RH increases above 75%, showing a good humidity switch characteristic. The sensitivity of the sensing material can reach up to 1.89 at 100% RH. The flexible humidity sensing material shows an adjustable switch point (between 75% and 84% RH), excellent reproducibility, moderate hysteresis, and sufficiently high residual sensitivity (0.63) for repeated use. The promising multi-functional material may be used for real-time RH switch monitoring in flexible electronic devices, such as in intelligent textiles and other industrial applications.

1. Introduction

Polymer-based sensors are essential for the development of flexible electronic systems, including wearable electronics, smart textiles and multifunctional garments [1–5] of the future. In addition to the ability to sense the measurands, essential characteristics of these devices are mechanical compatibility with the system (e.g. textile products), low response time and hysteresis, light-weight, good stability and robustness over repeated uses [6]. Continuous humidity sensing, in general, and switch-type humidity sensing, in specific, are needed in wearable electronics to monitor humidity levels of the atmosphere [7] and/or the peripersonal space [8,9].

In recent decades, number of materials [10,11] have been studied for switch-type humidity sensing based on various transduction mechanisms, such as capacitive [12], resistive [13–18], optical [19] and mechanical [20,21]. Of all these, the polymer-based, resistive-type humidity sensing materials have received much attention, primarily due to their ease of preparation, low price, high sensitivity, fast response and simple application circuitry [6]. Most of the these are based on carbon black (CB) and hydrophilic, swellable polymers, including polyvinyl alcohol (PVA) [15,22], polyacrylic acid (PAA) [17] and hydroxyethyl cellulose (HEC) [18].

Carbon nanotubes (CNTs) are attractive for humidity sensing due to their stability, high electrical conductivity and sensitivity to water vapor doping [23,24]. In contrast to the most reported CB based switch-type sensing materials, CNT based humidity sensing materials are, in general, more sensitive and stable. For example, Fei et al. reported a humidity sensor based on MWCNT/PVA composite film with high sensitivity and good switching characteristics [14]. Qi et al. investigated a unique water sensor based on CNT/cellulose composite with reproducible and highly stable characteristics even after a 45 day application [18,25]. However, due to the existence of rigid surrounding materials (such as ceramic substrates, array of electrodes) and complex fabrication processes, the composites based switch-type sensors reported above are likely to be bulky, stiff, and expensive.

More recently, Devaux et al. fabricated a novel yarn-like relative humidity (RH) sensor based on PLA/CNT multifilament yarns using a melt spinning process [16]. The sensitivity of the sensor demonstrated excellent repeatability and fast reversibility from room RH to 100% RH. However, the potential difficulties in CNT dispersion, complex integration process and modest sensitivity limited its applications. A relatively facile method of forming long strands of CNT/polymer composites with yarn-like aspect ratio is to use CNT yarns directly spun through aerogel-spinning [26], carpet-drawing [27], or wet spinning methods [28]. Fan et al. fabricated a highly

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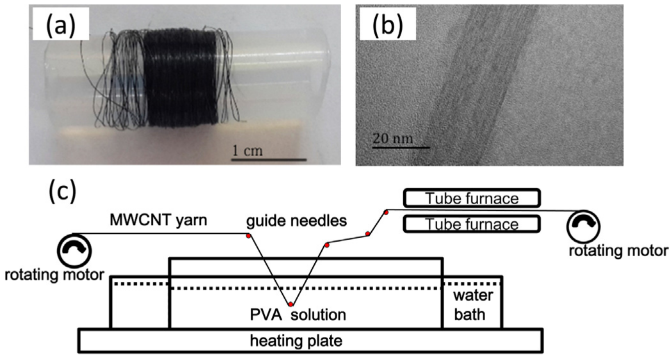

Fig. 1. Pure CNT yarn and experimental setup: (a) Pure MWCNT yarn collected on a plastic bobbin; (b) TEM image of the MWCNT yarn; (c) illustration of composite yarn fabricating setup.

scratch-resistant, conductive and high-strength CNT/PVA composite yarn by infusing PVA into continuous CNT framework [29]. To our knowledge, little has been reported on the humidity-resistance response behavior of CNT/PVA composites fabricated from CNT yarns.

In this study, we investigated a humidity switch yarn fabricated by dipping MWCNT yarn into a solution of PVA and drying. The essential sensing characteristics of these humidity switch materials such as moisture sensitivity, hysteresis, repeatability, and response time were evaluated.

2. Material and methods

Pure MWCNT yarn (Fig. 1a) was provided by Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences. The MWCNT yarn was spun directly by the chemical vapor deposition (CVD) synthesis zone of a furnace using a liquid source of carbon and an iron nano-catalyst [26]. As shown in Fig. 1b, the transmission electron microscopy (TEM, JEOLJEM–2100 at 200 kV) indicates that the MWCNT has a diameter of approximately 25 nm.

PVA, obtained from Sinopec Shanghai Petrochemical Company, has a polymerization degree of 1750 and an alcoholysis degree of 98%, and is highly swellable above 75% RH. The PVA solution was prepared by adding 1, 3, 5 or 7% of PVA into the mixture of distilled water and ethyl alcohol, with a magnetic stirrer stirring for 4 h at 90 °C. The MWCNT yarn was subsequently drawn through the PVA solution maintained at 30 °C, a speed of 5 cm/min, using a set-up shown in Fig. 1c. The stainless steel needles were to guide the yarn as well as to squeeze out extra polymer solution. Finally, the MWCNT/PVA composite yarn was dried at 60 °C and wound on a spool. The morphological features (diameter, twist angle, etc.) of the composite yarns were characterized by scanning electron microscopy (SEM, Hitachi TM3000 at 5 kV) and field emission SEM (FESEM, Hitachi S–4800 at 5 kV), as shown in Fig. 2. The composite yarn has a skin–core structure, including the outer MWCNT/PVA coating layer and the inner MWCNT core. The large aspect ratio of the MWCNT bundles and the network structures of the aerogel-spun MWCNT yarn, see Fig. 2d, make it possible for the thin MWCNT/PVA coupling coating to function on the whole yarn structure.

Sensory characteristics of the composite yarns were determined using a set-up, designed to record their electrical resistance with a digital multi-meter (Agilent, 34410A, USA) under different RH environments, maintained at isothermal condition at 25 °C, see Fig. 3a and b. The RH conditions inside the containers, ranging from 11–100%, were produced using various saturated salt solutions in its equilibrium state, including LiCl for 11% RH, CH3COOK for 23% RH, MgCl2 for 33% RH, K2CO3 for 43% RH, Mg(NO3) 2 for 54% RH, NaCl for 75% RH, KCl for 85% RH, and KNO3 for 94% RH [14,15]. In addition, distilled water was used for 100% RH. A piece (1 cm long) of composite yarn was put inside the container using sliver paste and copper wires as leads to connect the multi-meter. To allow the samples to reach their moisture equilibrium conditions, each sample was evaluated after conditioning in the required environment for at least 4 h. The repeatability and reversibility of the materials were experimented undergoing absorption-desorption dynamic cycles between 55 and 100% RH. Humidity dependent hysteresis of electrical resistance was measured by conditioning

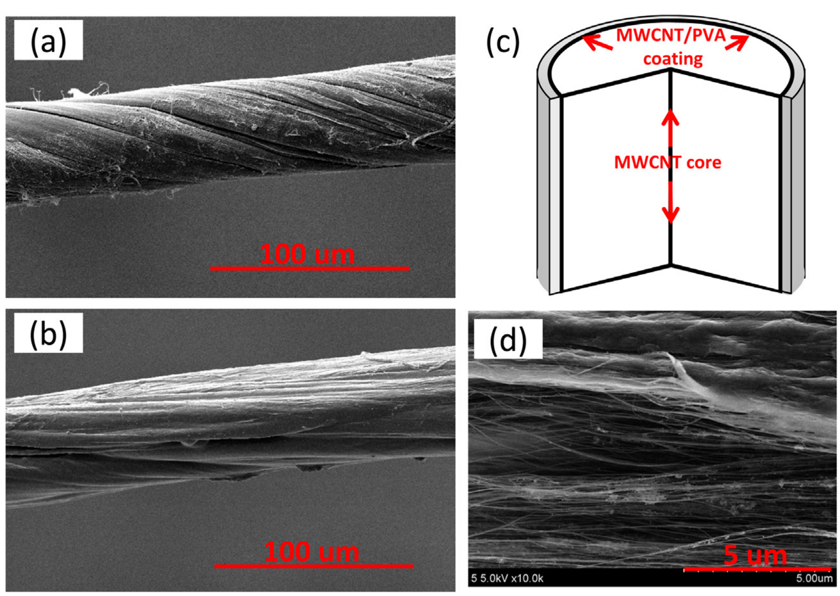

Fig. 2. Longitudinal morphologies of pure MWCNT yarn (a) and MWCNT/5% PVA composite yarn (b); skin–core structure (c) and an abrasion fracture specimen (d) of the composite yarn.