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Strain-gauge sensoring composite films with self-restoring water-repellent properties for monitoring human movements

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ABSTRACT

Flexible strain-gauge sensors are an essential constituent in smart electronic devices that can monitor the complex movements of people. We herein report a strain-gauge sensor with self-restoring water repellency, based on thermoplastic polyurethane (TPU)/multi-walled carbon nanotube composite films. TPU/carbon nanotube (CNT) composite films were simply fabricated by the filtration of CNT suspensions using electrospun TPU nonwovens as the filter paper. The strain-gauge sensors exhibited not only high sensitivity and durability, but also excellent self-restoring water repellency. The sensors performed well in monitoring a person's fingers, elbows, knees, and even neck movements. The self-restoring water repellency of the strain-gauge sensors originated from the hierarchical CNT networks on the TPU nonwovens. The "mesh-like" CNT networks would be cracked or broke under mechanical deformation, exposing the "feather-duster" structures underneath. The integrated hierarchical roughness mobilized the water droplets on the surface even under mechanical deformation. It is expected that the strain-gauge sensors will be applied in wearable electronic devices with super water-repellent properties. The work paves the possibility to fabricate high performance strain-gauge sensors that could be used in raining days or moist conditions.

1. Introduction

Flexible electronics, including strain-gauge sensors [1–6], flexible displays [7,8], stretchable circuits [9], and implantable medical devices [10,11], have attracted increasing attention over the past two decades owing to their wide potential applications. Various strain-gauge sensors for monitoring people's physical body movements have been developed. Pang et al. reported a type of highly sensitive strain-gauge sensor based on reversible nanoscale mechanical interlocking between platinum-coated nanoarrays supported on polydimethylsiloxane thin films [12]. A sensor that measures pressure (~ 5 Pa), shear (~ 10^{-3} N), and torsion (~ 2×10^{-4} N) has been realized. In addition, a flexible pressure sensor that has tissue paper filled with ultrathin gold nanowires between polydimethylsiloxane thin sheets was reported by Gong et al. [13]. The sensor was able to monitor pressure as low as 13 Pa with sensitivity better than 1.14 kPa^{-1}. Recently, Wang et al. fabricated a highly reliable strain-gauge sensor by incorporating single-walled carbon nanotubes into elastic cotton/polyurethane core-spun yarns [14]. The yarn sensor can bear strain as high as 300%, and be cycled nearly 300,000 times under 40% strain. Past decades have witnessed great progress in the development of highly sensitive and reliable strain-gauge sensors.

However, it should be noted that sensitivity and reliability are not the only factors to be considered in fabricating strain-gauge sensors, owing to the possibly complicated working environments, especially in raining days, or in moist conditions. Therefore, strain-gauge sensors with both high sensitivity and good water-repellency are important to electronic sensor devices [15,16]. Basically, the wettability of materials is controlled by surface topographies and chemical compositions [17,18]. Appropriate surface roughness and low-free-energy chemical compositions are two main factors of the wettability of materials. Lower surface energy leads to higher hydrophobicity [19,20] and surface roughness plays a crucial role in achieving a superhydrophobic state [21–23]. Great efforts have been made to fabricate superhydrophobic materials with low adhesion to water, by combining hierarchical surface roughness with low-free-energy chemical compositions [24–32]. Nevertheless, the hierarchical structures and low-free-energy coatings on the surface can be easily damaged when the surface undergoes mechanical deformations, such as bending, stretching, or shearing, thereby losing the superhydrophobic properties [33–35]. Several strategies have been proposed to deal with this issue; e.g., the introduction of microscale rigid pillars that withstand mechanical damage under abrasion [36], increasing the number of cross-linking sites or enhancing the cross-linking strength in coating components [37], and improving

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adhesion between substrates and coatings via physical and chemical methods [38]. However, all these approaches are only valid for the maintenance of the superhydrophobic state under low mechanical deformations. It is still a challenge to achieve high sensitive and reliable strain-gauge sensors with mechanical stable and durable superhydrophobic (water-repellent) properties [15].

In the present work, we report a simple and versatile path for the fabrication of a highly sensitive strain-gauge sensor with self-restoring water-repellency, by combining electrospinning with vacuum filtration. Thermoplastic polyurethane (TPU)/multi-walled carbon nanotube (MWCNT) composite films were simply prepared by the filtration of MWCNT suspensions using elastic TPU nonwovens as the filter paper. Interestingly, MWCNTs first anchored onto the surface of the solvent-swollen TPU fibers to form a “feather-duster” structure at low MWCNT loading. On the other words, the embed MWCNTs increased the interaction between TPU fibers and CNTs. With increasing MWCNT loading, carbon nanotubes (CNTs) connected with each other to weave into a surface “mesh-like” structure with the “feather-duster” structures underneath. Such a hierarchical structure accounts for the multifunctional properties of the prepared materials. The good elasticity of TPU and the high conductivity of CNTs make the TPU/CNT composite films good candidates for the fabrication of strain-gauge sensors. Moreover, the hierarchical CNT networks on the surface endow the TPU/CNT composite films with superhydrophobicity with low water adhesion. When undergoing mechanical deformation, the “mesh-like” CNT networks will be cracked or break into fragments with the “feather-duster” structures underneath being exposed, resulting in excellent self-restoring water-repellency. This work paves a new way to designing and fabricating of strain-gauge sensors with high-sensitivity, high-durability, and good self-restoring water-repellent properties.

2. Experimental section

2.1. Materials

TPU pellets (WHT-1295) were purchased from Wanhua Chemical Groups (China) and used without further treatment. M_w and M_w/M_n were 99,700 and 1.87, respectively. MWCNTs (VGCF-X) were provided by Showa Denko K. K. (Japan), as shown in Fig. S1. The diameter of MWCNTs is about 10 nm and the length of MWCNTs is about 1.5 μm. Dimethyl formamide (DMF) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). Ortho-dichlorobenzene (o-DCB) was purchased from Aladdin Chemical Reagent Co. Ltd. (China).

2.2. Sample preparation

Fig. 1 shows the fabrication process of TPU/CNT composite films. The TPU nonwovens were obtained by electrospinning a 25%/75% (w/w) TPU/DMF solution. The applied high voltage and polymer feeding rate were respectively 10 kV and 0.2 mL h^{-1} (under relative humidity of 65–75%). The aluminum foil was kept a constant 15 cm below the needle tip to collect TPU fibers for 10 h, the thickness of TPU nonwovens is about 0.3 mm. Uniform MWCNT suspensions were obtained by dispersing MWCNTs in dichlorobenzene followed by ultrasonication at 40 °C for 30 min. The MWCNT suspensions were then poured into a glass filter device, using TPU nonwovens as the filter paper to prepare the composite film. The MWCNT loading content can be easily controlled by changing the MWCNT mass per TPU nonwoven filter because all CNTs were captured on the filter during filtration. Finally, the TPU/CNT composite films were obtained after drying the films in a vacuum oven for more than 12 h.

2.3. Sample characterizations

The surface morphology of the TPU/CNT composite films was captured by a field-emission scanning electron microscope (Hitachi S-4800). The water contact angles (WCAs) and sliding angles (SAs) were measured by a drop shape analyzer (DSA 100) at ambient temperature, and the volume of the test droplet was 10 μL. Average values of the WCA and SA were obtained for five positions of the samples. The static electrical conductivity of the TPU/CNT composite films was measured according to a testing method for resistivity of conductive plastics with a four-point probe array (JIS K7194). To ensure accuracy, all TPU/CNT composite films were measured at least five times at different positions.

A sensory performance test was conducted on a Metrohm Autolab potentiostat/galvanostat (PGSTAT 128 N). Basically, strips of the TPU/CNT composited films were cut and fixed to a manual stretching device, and then stretched to strains of 50%, 100%, and 200%. To measure the sensing performance, the TPU/CNT composited films were cut into rectangles of 2×1 cm^2 and fitted with two copper electrodes for assembly of a device that monitors body movements, including finger movements, neck motions, elbow bending, and arm swings. The supplied DC voltage was 0.5 V and the relative current was recorded.

3. Results and discussion

3.1. Morphologies investigation of TPU/CNT composite films

Fig. 2 shows the morphological changes in the TPU/CNT composite film surface with increasing CNT loading. TPU nonwovens containing fibers with a diameter of about 1.9 μm, as shown in Fig. 2**a**, served as support materials. The TPU/CNT composite films were fabricated by filtering CNT suspensions under diminished pressure, using elastic TPU nonwovens as the filter paper. The TPU fibers were swollen by the solvent (DCB) and CNTs were anchored into the swollen TPU fibers during the filtration to form a “feather-duster” structure, as shown in Fig. 2**b** and **c**, when the CNT loadings were less than 24 μg cm^{-2}. It was found that CNTs were firmly anchored onto the TPU fibers and therefore essentially enhanced the mechanical stability of the surface structure of the TPU/CNT composite films. For samples with CNT loading higher than 24 μg cm^{-2}, as shown in Fig. 2**d**, the redundant CNTs began to come into contact with each other and transformed into hierarchical conductive meshes with the “feather-duster” structures underneath (as shown in Fig. S2). Scheme 1 illustrates the formation from the “feather-duster” to “mesh-like” structure with increasing CNT loading content. The distinctive topographies at the critical point

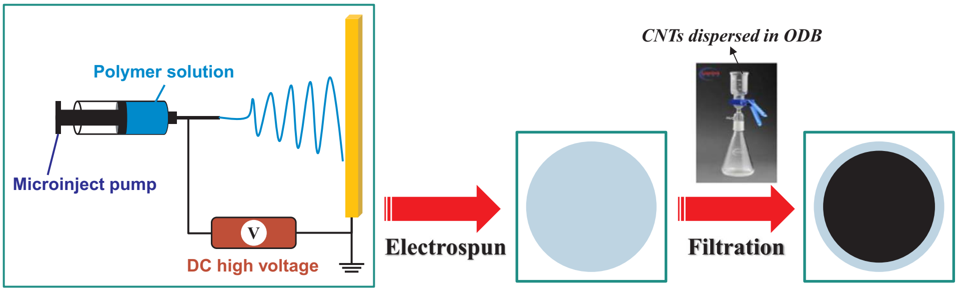

Fig. 1. Schematic illustration of the fabrication process of TPU/CNT composite films.