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Superhydrophobic and conductive properties of carbon nanotubes/polybenzoxazine nanocomposites coated ramie fabric prepared by solution-immersion process

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ABSTRACT

Nanocomposites coating consisting of pristine multiwall carbon nanotubes (MWNTs) and polybenzoxazine has been constructed onto ramie fabric through solution-immersion process. The adsorbed nanocomposites coating is a hierarchical three-dimensional interpenetrating network structure, and the surface coverage and density increase substantially with increasing repeated immersing cycles. Measurements of the superhydrophobicity and conductivity for the coated ramie fabrics show that the highest water contact angle reaches 152°, the lowest water sliding angle reaches 3°, and the corresponding sheet resistance is 3410 Ω sq^{-1}, which shows strong dependency on the number of repeated immersing cycles and concentration of MWNTs suspension. This work provides a facile pathway to design and fabricate nanocomposites coated natural cellulosic fabric for superhydrophobic and conductive applications.

1. Introduction

Over the past several decades, extensive research has been devoted to the design and fabrication of superhydrophobic surfaces, water contact angles (WCA) of which are higher than 150° [1,2]. Among many employed materials, carbon nanotube is one of the most interesting candidates because of its unique morphology and structure. Generally speaking, the cooperation of surface roughness at both micro- and nanoscales with low surface energy is essential for superhydrophobicity [3,4]. Hence, methods for forming aligned or hierarchical three-dimensional interpenetrating network structures are actively sought to achieve superhydrophobicity [5–8]. For instance, poly(tetrafluoroethylene) (PTFE) coated vertically aligned carbon nanotubes forest demonstrates WCA as high as 168°, which is contributed by the surface roughness templated by nanotubes forest and the low surface energy imparted by PTFE coating [9]. Another typical example is the hierarchical three-dimensional interpenetrating network structure constructed from carbon nanotubes and nafion by solution process, which shows the highest WCA of 168° and the smallest sliding angle of 3.3° [10].

In view of the excellent performance of carbon nanotubes for superhydrophobicity, researchers also explore its effect in natural biopolymer systems in recent years, such as cellulose fiber [11,12]. For example, Georoakilas et al. [13] prepared perfluorinated multiwall carbon nanotubes (MWNTs) coated cotton fabric with superhydrophobicity, WCA value of which is as high as 170°. By dip coating and UV irradiation process, Li et al. [14] prepared MWNTs/aromatic azide copolymer (poly(4-azidophenyl methacrylate-*co*-methyl acrylate)) nanocomposites coated cotton fabric, and the WCA value is higher than 150°. Obviously, these reported methods always involve prior chemical modification of carbon nanotubes or special treatment process for the sample preparation. Moreover, superhydrophobicity combined with other functional properties (such as conductivity [15–17] and magnetism [18]) is especially fascinating and of both fundamental and practical importance [12]. One representative combination is superhydrophobic conductive surface, which can remove static charges accumulated on the surface and shows promising application as electromagnetic interference shielding material [12,19,20].

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Although reports of studies exploring superhydrophobic properties of cellulose fiber have appeared, convenient methods for imparting both superhydrophobicity and conductivity to such substrate remain limited.

In this work, we present a simple but effective nanocomposites coating consisting of pristine MWNTs and polybenzoxazine, which was constructed onto flexible and porous ramie fabric step by step. Polybenzoxazine is a new kind of low-surface-free-energy materials, which shows somewhat cheaper and easier preparation process compared with fluoropolymers in recent investigations [21,22]. The objective of the present study is to vary the concentration of MWNTs suspension and the corresponding surface roughness and surface free energy, so as to control the hydrophobic and conductive properties for the coated ramie fabrics.

2. Experimental details

2.1. Materials

Plain ramie fabrics, purchased from Jiangxi Jingzhu Ramie Textile Co., Ltd. (China), were washed with detergent in deionized water several times, followed by drying under vacuum at 60 °C for 2 h. The benzoxazine monomer (3,3′-(((2,2-dimethylpropane-1,3-diyl)bis(oxy))bis(4,1-phenylene))bis(3,4-dihydro-2H-benzo[e][1,3]oxazine-6-carbonitrile), BOZ) was synthesized and used as previously described by our group [23]. Multiwall carbon nanotubes (MWNTs; purity, >95%; length, 10–30 μm; outer diameter, <8 nm) were purchased from Chengdu Organic Chemicals Co., Ltd. (China). N,N-dimethylformamide (DMF) and ethanol were used as received from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water with a resistance of 18 MΩ was used for all the experiments.

2.2. Preparation of polybenzoxazine and MWNTs/polybenzoxazine nanocomposites coated ramie fabric

For the preparation of BOZ solution, BOZ powders were added to DMF and stirred continuously until completely dissolved, and the concentration was set to 1.0 mg mL^{-1}. For the preparation of MWNTs/BOZ mixture suspension, dried MWNTs powders were sonicated in DMF for 1 h at room temperature using an ultrasonic cleaner (model JK-3200 B, 150 W, 40 kHz, Hefei Jinnike Machinery Co., Ltd., China) to form stable suspension, and the concentrations were 0.5 and 1.0 mg mL^{-1}, respectively. Thereafter, BOZ powders were added to the MWNTs suspension, and sonication was continued for another 1 h to form MWNTs/BOZ mixture. The concentration of BOZ was only 1.0 mg mL^{-1}.

As shown in Fig. 1(a), a typical sample preparation process is as follows: the ramie fabric was immersed into the BOZ solution or MWNTs/BOZ mixture suspension (fresh for each immersion process) for 10 min, washed twice with deionized water and once with ethanol (each for 1 min), dried under vacuum at 50 °C for 30 min, heated at 130 °C for 2 h (*Note*: the temperature was restricted to 130 °C for partial cure reaction to prevent degradation of ramie fabric), and cooled to room temperature naturally. This procedure describes a complete cycle, and it was repeated until the required number (n) of cycles was achieved. In this work, we denote briefly the treated ramie fabric that was immersed into the BOZ solution (BOZ: 1.0 mg mL^{-1}) for 20 cycles as $(1.0\ \mathrm{BOZ})_{20}$, MWNTs/BOZ mixture suspension (MWNTs: 0.5 mg mL^{-1}, BOZ: 1.0 mg mL^{-1}) for 20 cycles as $(0.5\ \mathrm{MWNTs}/1.0\ \mathrm{BOZ})_{20}$.

2.3. Measurements and characterization

Fourier transform infrared (FT-IR) spectra were obtained from KBr pellets using a Vector 22 spectrometer (Bruker) in the frequency region of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded by a Nicolet 5700 spectrometer (Thermo-Nicolet) using 32 scans in the frequency region of 4000–400 cm^{-1} at a 4 cm^{-1} resolution. Raman spectra were obtained using a Labor Raman HR-800 system (Jobin Yvon) by exciting a 514.5 nm Ar ion laser. The morphologies of the uncoated and coated ramie fabrics were investigated using an S-4800 field-emission scanning electron microscopy (FE-SEM, Hitachi) operated at 3 kV. Prior to analysis, the specimens were gold-sputtered for 45 s under a high vacuum. Transmission electron microscopy (TEM) images were collected by using a JEM 1230 TEM instrument (JEOL) operated at 80 kV. The water contact angles (WCA) and sliding angles (SA) were measured with an OCA 20 contact angle system (Dataphysics) at room temperature. For WCA measurements, water droplets (about 3.8 μL) were dropped carefully onto the surface of ramie fabrics. For SA measurements, water droplets (about 30 μL) were dropped onto the tilted surfaces from 5 mm height, and the tilting angles at which the water droplets rolled off the surfaces were determined as SA value. The average values of WCA and SA was obtained by measuring more than five different positions of the same sample. Sheet resistances (R_s) were measured by the standard four-probe technique using a RTS-4 four-probe conductive meter (Guangzhou 4 Probes Tech., China).

3. Results and discussion

3.1. Characterization of MWNTs/polybenzoxazine nanocomposites

To prepare polybenzoxazine and MWNTs/polybenzoxazine nanocomposites coated ramie fabrics, the BOZ solution and MWNTs/BOZ mixture suspension are firstly prepared. As shown in Fig. 2(a2, a3), the MWNTs/BOZ mixtures form stable black suspensions in DMF, without visible coagulated bundles of carbon nanotubes at the bottom of vials. In order to investigate the chemical structure changes, the MWNTs/BOZ mixture suspension with MWNTs concentration at 0.5 mg mL^{-1} was filtered as representative, washed with fresh DMF, heated at 130 °C for 2 h and characterized using TEM, FT-IR and Raman spectroscopy. It can be clearly seen from Fig. 2(b) that MWNT is well packed by nanoscale particles, which is believed to be ascribed to the partially cured benzoxazine monomer and mainly based on the π–π and CH–π interactions and attractive interactions [24–26]. As presented in Fig. 3, MWNTs/poly(BOZ) shows characteristic absorption bands belong to the partially cured benzoxazine structure at approximately 1508 (trisubstituted benzene ring stretching), 1246 (asymmetric stretching vibration of C—O—C), 1020 (symmetric stretching vibration of C—O—C) and 950 cm^{-1} (out-of-plane C—H) [23,27], respectively. Furthermore, the Raman spectra of MWNTs and MWNTs/poly(BOZ) present two peaks at around 1345 and 1575 cm^{-1} (see Fig. 4), which are believed to be assigned to D and G bands [28], respectively. It is well-known that the D and G bands are attributed to amorphous and crystalline graphitic carbon, respectively, and the integrated intensity ratio of D band to G band (I_D/I_G) can be used to determine the graphitization degree of carbon materials [29,30]. For MWNTs and MWNTs/poly(BOZ), the I_D/I_G values are 1.08 and 1.29, respectively. Meanwhile, the D and G bands of MWNTs/poly(BOZ) shifts to higher wavenumbers, which is mostly due to the interaction between absorbed poly(BOZ) and MWNTs [31–33].

3.2. Characterization of coated ramie fabric

As illustrated in Fig. 1(a), the poly(BOZ) and MWNTs/poly(BOZ) nanocomposites coated ramie fabrics are prepared through solution-immersion process, mainly including immersing, washing

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