Full paper - Functional carbon nanotube/cellulose composite fibers prepared from solution-spinning

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ABSTRACT

Electrically conducting fibers composed of cellulose and carbon nanotubes (CNTs) were spun using aqueous alkaline solution. The structure and properties of the resulting fibers were investigated. These flexible composite fibers exhibit sufficient mechanical properties and good electrical conductivity. Furthermore, these novel CNT/cellulose composite fibers have impressive multifunctional sensing abilities and are promising to be used as smart materials.

1 INTRODUCTION

Fibers and textiles are materials with applications in almost all our ordinary activities. A steadily growing area in applied nanomaterials research and information technology is concerned with the integration of functional materials into textiles, which are capable to respond to external stimuli (such as mechanical, thermal, chemical, and magnetic).[1-3] Wearable electronics and smart textiles could be served as novel communication platform, which has great potential application in many fields such as healthcare, work wear, sportswear, and military.[4] Cellulose based fibers extracted from natural plants have been used by humans to manufacture clothing and fabrics for many years, as they are deformable and soft, washable, durable, and breathable, thus ideal to be explored as a promising platform for wearable electronics.[5] As one of the most intriguing nanomaterials, on the other hand, carbon nanotubes (CNTs) possess excellent mechanical, thermal, and electrical properties permit a variety of potential technical applications.[6,7] Therefore, the combination of cellulose with the multi-functionality of CNTs may offer a large number of possibilities. However, cellulose and CNTs are both insoluble in water and common organic solvents, which complicates the combination as well as the processing of the two materials. To date, several attempts to prepare CNT/cellulose composites in some solvents for cellulose, such as lithium chloride/N, N-dimethylacetamide (LiCl/DMAc), ionic liquids (ILs) and N-methylmorpholine-N-oxide (NMMO) monohydrate, have been reported.[8,9]

Recently, a simple but efficient process was developed to dissolve cellulose by using aqueous NaOH/urea solution. In comparison to the solvents mentioned above, this solvent is more common and cheaper because the components are water, urea and NaOH. Particularly, water (about 80 wt% in this solvent) is also used widely for the dispersion of CNTs. It allows the CNTs to be dispersed more directly and efficiently in the system and further in regenerated cellulose.[10] By using this homogeneous aqueous system, we have fabricated functional and smart materials based on cellulose/CNT composites, including two-dimensional films and three-dimensional aerogels.[10,11] In the present study, quasi-one-dimensional CNT/cellulose composite fibers are produced through a simple wet-spinning process using NaOH/urea aqueous solution as solvent. The structure, physical properties and their sensitivity to external stimuli of the fibers are comprehensively investigated.

2 EXPERIMENTAL SECTION

2.1 Materials

Cotton linters (DP 500) as cellulose materials were supplied by Hubei Chemical Fiber Group Ltd. (Xiangfan, China). Multi-walled carbon nanotubes (MWCNTs, NC3150, purity +95%) with an average length of 1.5 μm and an average diameter of 9.5 nm and were purchased from Nanocyl S.A., Belgium. Non-ionic surfactant Brij76 (polyoxyethylene (10) stearyl ether), organic solvents and other

reagents of analytical grade were purchased from Sigma Aldrich (St. Louis, MO, USA).

2.2 Preparation of CNT/cellulose composite fibers

The CNT/cellulose aqueous dope was prepared according to our previous work.[10] Firstly, the MWCNT dispersion with MWCNT content of 1.0 wt% was prepared by sonication in surfactant (Brij76) solution. Secondly, the aqueous NaOH/urea/CNT (7/12/0-0.4) system was prepared by mixing MWCNT aqueous dispersion with urea, NaOH, and distilled water. The resulting mixture was pre-cooled to −12.0 °C. Then the cellulose was dispersed immediately into the mixture and stirred vigorously for about 5 min to obtain a CNT/cellulose dope. After degasification, the wet spinning process was carried out on a lab-scale apparatus, which is schematically shown in Fig. 1. An aqueous solution containing 10 wt% H_2SO_4/10 wt% Na_2SO_4 was utilized for coagulation at room temperature. By varying the amount of the CNT in dispersion and using different type of nozzles, we obtained a series of CNT/cellulose composite monofilament fibers and multifilament fibers (with CNT percent: 0 wt%, 2 wt% and 3 wt%, which were coded as RF0, RF2 and RF3, respectively). The dosing needle with diameter (Φ) of 0.50 mm was used to spin monofilament fibers; and stainless steel spinneret with 120 × 0.15 mm (Number × Diameter of hole) was used to spin multifilament fibers.

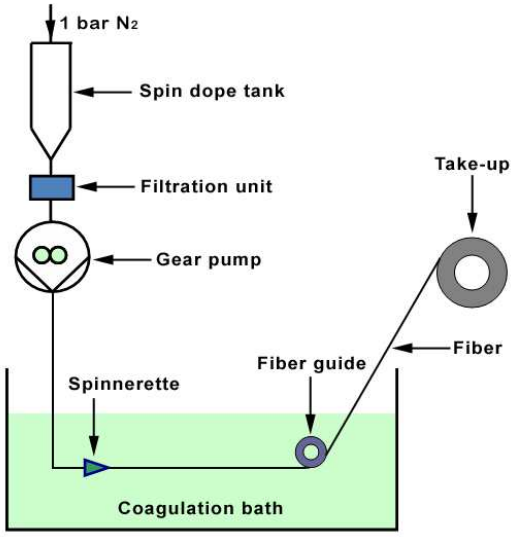

Fig. 1 Schematic diagram of the lab-scale wet-spinning apparatus.

2.3 Characterization of structure and physical properties

The morphology of the prepared fibers was examined by a scanning electron microscope (SEM, Ultra 55, Carl Zeiss SMT AG, Germany). The tensile tests of the composite fibers were carried out on a FAVIGRAPH semiautomatic equipment (Textechno Company, Germany), with an extension rate of 10 mm/min. The thermogravimetric analysis (TGA) for the compo-site fibers was carried out by using a TA Instruments TGA Q 5000 in nitrogen atmosphere, with the heating rate of 10 K/min from room temperature to 800 °C. Wide-angle X-ray diffraction (WAXD) experiments on the fiber samples were carried out using a single-crystal diffractometer STOE & Cie. The electrical volume resistivities of the composite fibers were measured by using a four-point test fixture in combination with a Keithley 2000 electrometer (Keithley Instruments GmbH, Germany) at 23 °C and 50% RH.

2.4 Characterization of sensing abilities

By using two-point setup with a Keithley 2001 multimeter, in-situ electrical resistance measurements were performed to monitor the sensing abilities of the CNT/cellulose composite fibers to temperature, relative humidity, tensile strain and even liquid water. To investigate the tensile strain/stress sensing abilities, the electrical resistance of composite fibers was recorded as the specimen underwent uniaxial tensile (or cyclic loading) using the FAVIGRAPH equipped with a 1 N load cell. The investigation of the resistance changes of fibers to temperature was performed with a

hot-stage (Linkam LTS350 Heating/Freezing, UK) in a nitrogen atmosphere from 100 to 0 °C with a cooling rate of 1 K /min. The resistance changes in dependence of the RH were examined by placing the specimen in a desiccator. The different desired RH (the values were shown in the following parentheses) were obtained through saturated aqueous solutions of different salts at 23.0 ± 1.0 °C: KCl (86%), NaCl (76%), $NaNO_2$ (65%), $Ca(NO_3)_2 \cdot 4H_2O$ (55%), K_2CO_3 (45%) and $CaCl_2 \cdot 6H_2O$ (35%).

To investigate the sensitivity of the fibers to liquid water, resistance values of specimen were collected by a computer-controlled liquid sensing setup with a sampling rate of 1 s. A measurement cycle consists of an immersion (wetting) and a drying step. The temperature during the immersion process was controlled by using a heating/cooling bath. The drying step was carried out in air (with 50% RH) at 23 °C. To investigate the sensing behavior of the composite fiber independently of their initial electrical resistance, the sensing response was normalized according to Eq. (1),

$$R_{rel} = (R_t - R_0) / R_0 \times 100\% \quad (1)$$

where R_0 is the initial electrical resistance of the fiber; R_t is the transient electrical resistance of fiber upon external stimuli, such as RH, tensile strain, and liquid water.

3 RESULTS AND DISCUSSION

3.1 Morphology and microstructure of the CNT/cellulose composite fibers

In the present work, CNT/cellulose composite fibers with different CNT loadings could be fabricated by using a home-made lab-scale wet-spinning apparatus (Fig. 1). Different type of continuous composite fibers, e.g. mono- and multi-filaments, were obtained. During the wet-spinning process, there are no obvious color changes or dark sediments in the coagulation bath and in the rinsing water. It indicates that there are hardly CNTs isolated from the CNT/cellulose dispersion solution during the spinning process. Therefore, the production process appears to be a simple, quick, efficient and eco-friendly method for the continuous fabrication of CNT/cellulose composite fibers. Fig. 2 shows exemplarily scanning electron microscopy (SEM) images of surface and cross-section of a CNT/cellulose composite fiber containing 3 wt% CNTs (RF3). Overall, the composite fibers exhibit smooth circular surfaces and uniform diameters. The diameters (Φ) of the monofilament and multifilament fibers are in the range of 85-95 μm and 16-21 μm (see Table 1), respectively, which can be controlled by the spinning process. The SEM results show that the CNTs are relatively well-dispersed within the cellulose matrix.

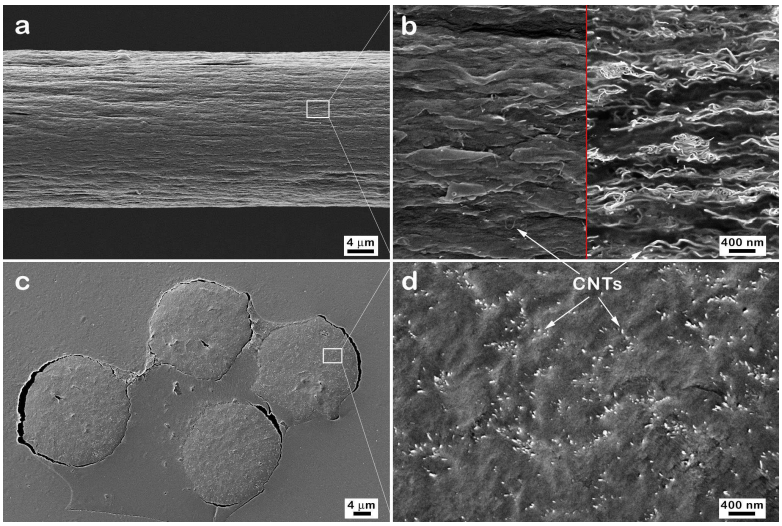

Fig. 2 Scanning electron microscopy (SEM) images of surface (a and b) and cross-section (c and d) of a CNT/cellulose composite multifilament fiber (RF3). The right side in b shows the charge contrast imaging SEM of the fiber surface.

As reported, charge (or voltage) contrast imaging SEM of CNT/polymer composites allows for visualization of CNT networks within insulating polymer matrix.[12] Fig. 2b shows both the

conventional topographic contrast (left) and the charge contrast imaging SEM micrograph (right) of the surface of CNT/cellulose composite fibers. Only few fragments of carbon nanotubes are visible in the surface image on the left side, meaning that most of them are inside the cellulose matrix rather than on fiber the surface. From the image on the right side, however, the CNTs network embedded in cellulose matrix can be clearly observed. Although some small clusters of entangled CNTs could be identified in the micrograph, the CNTs still appear in a relatively homogeneous state of dispersion. It also discloses that the CNTs overlap and align along the fiber axis.

The results of 2D WAXD for CNT/cellulose composite fiber clearly show that cellulose crystallizes in the energetically most stable type II polymorph independent of the MWCNT content. Diffraction peaks corresponding to MWCNTs have not been observed. From the equatorial 2Θ-scans, the cellulose II unit cell parameters, crystallite dimensions, and the crystalline cellulose fraction (i.e. the crystallinity) in the fiber samples have been obtained. Table 1 lists the calculated crystallinity and Hermans' orientation parameters.

3.2 Mechanical, thermal and electrical properties of the CNT/cellulose composite fibers

The mechanical properties obtained from tensile tests of the CNT/cellulose composite fibers are summarized in Table 1. These results disclose that the CNT/cellulose composite multifilament fibers exhibit relatively high tensile strength and strain-to-failure values (for RF2, one obtains values of 120 MPa and 9.4% respectively). Their tensile strength values are comparable to those for other man-made cellulose-based fibers, such as normal viscose filaments (150-320 MPa) and cuprammonium fibers (150-200 MPa).[13] Because these CNT/cellulose composite fibers are only primary product prepared from a simple home-made lab-scale wet-spinning apparatus, there is great potential to enhance the mechanical properties of the composite fibers by developing the apparatus and modifying the spinning conditions. In contrast to the mechanical characteristics, other fiber properties are improved by the incorporation of CNTs. As shown in Table 1, the decomposition temperatures T_d of the CNT/cellulose composite fibers are slightly higher compared to the pure cellulose fibers and suggest an enhancement of the thermal stability.

Table 1 Summary of the main results from wide-angle X-ray diffraction, tensile tests, electrical resistance measurements and thermal gravimetric analysis for CNT/cellulose composite fibers in comparison to the pure regenerated cellulose fiber.[a]

Samples	M, wt%	Φ, μm	ν_c	f_h	σ_b, MPa	ε_b, %	E, GPa	R, Ohm·cm	T_d, °C
Mutilfilaments, RF0	0	17(1)[b]	0.53	0.78	122.8 (23.5)	10.8 (3.5)	6.5 (1.0)	-	322
Mutilfilaments, RF2	2	19(2)	0.37	0.58	120.9 (25.0)	9.4 (2.5)	6.9 (0.5)	86	327
Mutilfilaments, RF3	3	19(2)	0.43	0.76	116.9 (30.6)	7.8 (3.2)	7.0 (1.6)	11	328
Monofilaments	0	88(3)	-	-	115.7 (20.0)	8.9 (3.0)	6.1 (0.9)	-	322
Monofilaments	1	90(3)	-	-	113.2 (18.0)	9.1 (3.0)	6.3 (0.8)	4×10^5	-
Monofilaments	2	91(4)	-	-	109.6 (16.8)	9.1 (3.0)	6.3 (0.7)	230	328
Monofilaments	3	91(4)	-	-	107.5 (23.1)	7.6 (3.5)	6.8 (1.8)	22	329
Monofilaments	5	90(5)	-	-	96.4 (25.8)	6.5 (3.2)	6.4 (2.0)	4	-
Monofilaments	8	89(5)	-	-	78.3 (29.0)	5.2 (3.6)	6.3 (2.5)	1	-

[a] Notes: M, CNT weight percent in fibers; Φ,diameter; ν_c, crystallinity; f_h, Hermans' orientation parameter; σ_b, tensile strength; ε_b, strain-to-failure; E, Young's modulus; R, volume resistivity; T_d, decomposition temperature.

[b] The values shown in parentheses are the standard deviations.

As expected, the conductivity of CNT/cellulose composite fibers increases with the increasing CNT loading. The CNT/cellulose fibers with 2 – 8 wt% CNT exhibit a volume resistivity in range of 230 – 1 Ohm·cm (i.e., a conductivity of 4.3×10^{-3} –1.0 $S\cdot cm^{-1}$). As reported, the CNT/cellulose composite fibers fabricated from ILs show an electrical conductivity of 8.3×10^{-3} $S\cdot cm^{-1}$ for fibers with 4 wt% CNTs.[9] The much lower resistivity of our fibers demonstrates that the CNTs disperse more efficiently in cellulose matrices when aqueous NaOH/urea instead of IL is used as solvent.

Interestingly, the volume resistivity of CNT/cellulose composite multifilament fibers is much lower than that of the monofilament fibers with the same CNT loading (Table 1). It indicates the distribution of CNT networks in cellulose matrix might be changed by using different type of spinnerets (with different hole diameter), and hence affects the conductivity of the fibers.

3.3 The sensitivity of the CNT/cellulose composite fibers

As mentioned above, the cellulose-based fibers possess good electrical conductivities due to the embedded CNT networks, and this property opens up a number of possibilities in practical applications. In this work, we mainly focus on their sensitivity to environmental conditions or external stimuli. Similar to CNT/cellulose composite films [10], fibers exhibit good and repeatable piezoresistivity. These impressive characteristics permit the CNT/cellulose composite fibers to be used as wearable strain gauges because they can easily fit to the body shape of human. The sensitivity of CNT/cellulose composite fibers to environmental temperature and humidity is demonstrated in Fig. 3. Over the investigated temperature range between 10 and 95 °C, the electrical resistance (R) of the fiber decreases monotonically as the temperature increases, i.e., the fiber exhibits a negative temperature coefficient which is also found in other CNT-based materials.[14] Interestingly, the R exhibits approximately a linear dependence on temperature, with a slope of –0.99 (KOhm·°C^{-1}) (Fig. 3a). Consequently, the CNT/cellulose composite fibers can also be used as thermistors due to their excellent temperature sensitivity. Fig. 3b shows the relative resistance (R_{rel}) of RF2 in dependence of the environmental humidity. Due to the large amounts of hydroxyl groups on molecular structure, cellulose is a hygroscopic, polar polymer and has good affinity to water. This sensing behavior is consistent with other CNT-based composites as humidity sensors, such as polymer/CNT-array composite film and CNT-cotton yarns.[15,16] Therefore, these CNT/cellulose composite fibers may even serve as humidity sensors.

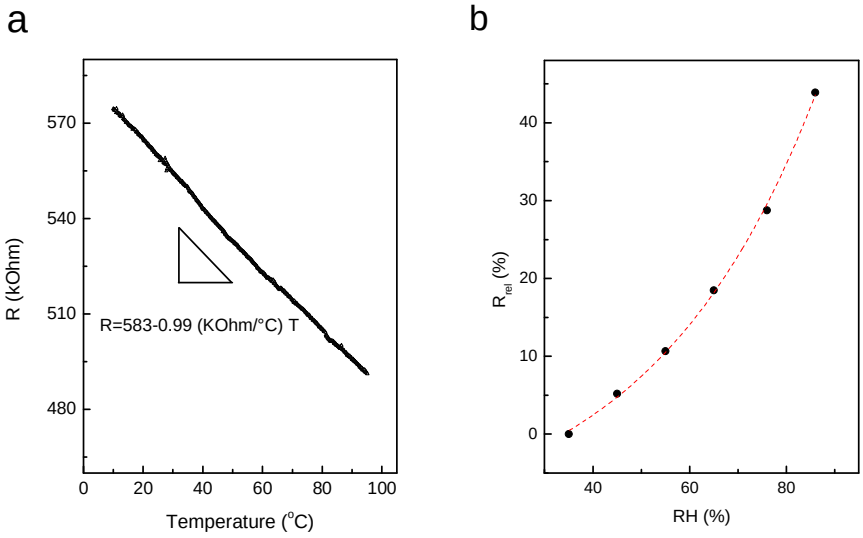

Fig. 3 Temperature and humidity sensing behavior of a CNT/cellulose composite fiber (RF2): a, dependence of electrical resistance on temperature; b, dependence of relative resistance change (R_{rel}) on relative humidity (RH) at 23 °C.

The humidity sensitivity of the CNT/cellulose compo-site fibers and the fact that cellulose is insoluble in water permits the design of smart water. To probe the sensitivity of CNT/cellulose composite fibers to liquids, the R_{rel} of the samples upon immersion in water was recorded as a function of test time. The typical resistive response of the CNT/cellulose composite fibers (exemplarily shown for the RF3 fiber, R = 12 Ohm·cm) to liquid water is depicted in Fig. 4a. Clearly, the R_{rel} value increases very rapidly after immersion in water, and reaches a high level of above 4700% only after about 10 s. This fast and reliable response demonstrates that CNT/cellulose composite fibers are very sensitive to liquid water. During the drying process of the fibers in air at ambient conditions for 70 s,

the R_{rel} value decreases almost to the initial base level (R_{rel} = 0), i.e., the CNT/cellulose composite fibers show good recovery properties. In addition, the sensing signals are quite reproducible and stable under successive wetting – drying cycles, i.e., the CNT/cellulose composite fibers are not only highly sensitive, but also well reversible and, therefore, ideally suited as water detectors. The CNT/cellulose composite fibers exhibit a positive liquid coefficient, which is similar to CNT/cellulose composite films as water sensors.[17] However, the CNT/cellulose composite fibers exhibit a much higher sensitivity to water than CNT/cellulose composite films (R_{rel} value of about 550%) with comparable CNT loadings. This may be attributed to the different distribution and alignment of CNTs in fiber matrix, which enhances the probability of disconnecting the CNTs by swelling of the cellulose matrix. In addition, the quasi-one dimensional nature and flexibility of the fibers is much more favorable for the design of water detection devices of arbitrary shape. Interestingly, for CNT/cellulose composite fibers with relatively high resistivity such as 230 Ohm·cm (RF2), a unique electrochemical "switch" sensing behavior is observed. That is, as shown in Fig. 4b, the electrical signals yield ON (or OFF) states as wetting (or drying) process performed. This fairly impressive water sensing property of CNT/cellulose composite fibers provides a simple and unique way to fabricate electrochemical sensors or switches which have the potential to be used in applications, such as, e.g., water detection systems or wearable electronics to monitor body sweat.

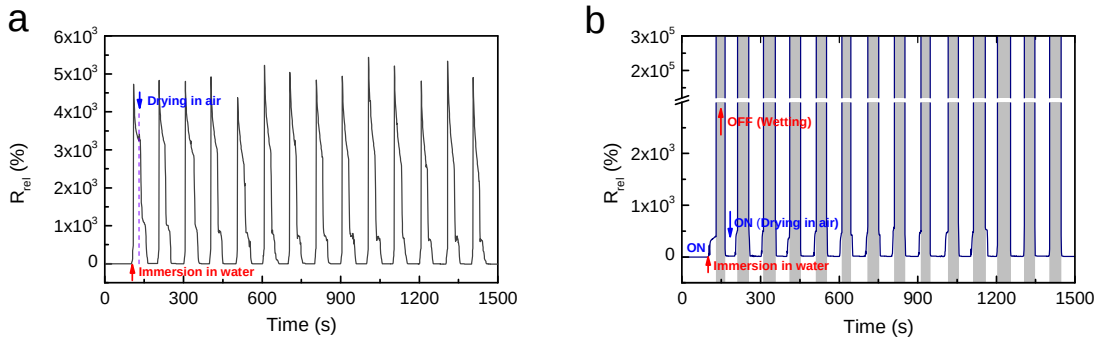

Fig. 4 CNT/cellulose composite fibers as unique water sensors: a, relative resistance change (R_{rel}) of RF3 (R = 12 Ohm·cm) during successive wetting - drying cycles in wa-ter/air at 20 °C (fiber acts as sensor); b, R_{rel} of RF2 (R = 230 Ohm·cm) during successive wetting - drying cycles in water/air at 20 °C (fiber acts as switch).

4 CONCLUSIONS

MWCNT/cellulose composite fibers were spun using an aqueous NaOH/urea system as solvent. The resulting fibers are light-weight, flexible and exhibit good mechanical properties. The embedded CNT network introduces a high electrical conductivity, with volume resistivities in the range of about 230 – 1 Ohm·cm for 2 – 8 wt% CNT loading. This intrinsic conductivity as well as the response of the fiber microstructure to external stimuli is fundamental for the impressive multifunctional sensing abilities of the composite fibers with respect to tensile strain, temperature and environmental humidity. In particular, these novel CNT/cellulose composite fibers are ideally suited to serve as highly sensitive, well reversible and reusable detectors or switches for liquid water. Based on their unique (structural) properties, the fibers may be processed into "wearable electronic devices" (textile sensors and actuators). Although the currently used spinning process yields in general composite fibers of high quality, some optimization is still necessary in order to enhance the electrical and mechanical properties of the composite fibers at high CNT loadings.

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