

Article

Smart Cellulose Fibers Coated with Carbon Nanotube Networks

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Abstract: Smart multi-walled carbon nanotube (MWCNT)-coated cellulose fibers with a unique sensing ability were manufactured by a simple dip coating process. The formation of electrically-conducting MWCNT networks on cellulose mono- and multi-filament fiber surfaces was confirmed by electrical resistance measurements and visualized by scanning electron microscopy. The interaction between MWCNT networks and cellulose fiber was investigated by Raman spectroscopy. The piezoresistivity of these fibers for strain sensing was investigated. The MWCNT-coated cellulose fibers exhibited a unique linear strain-dependent electrical resistance change up to 18% strain, with good reversibility and repeatability. In addition, the sensing behavior of these fibers to volatile molecules (including vapors of methanol, ethanol, acetone, chloroform and tetrahydrofuran) was investigated. The results revealed a rapid response, high sensitivity and good reproducibility for these chemical vapors. Besides, they showed good selectivity to different vapors. It is suggested that the intrinsic physical and chemical features of cellulose fiber, well-formed MWCNT networks and favorable MWCNT-cellulose interaction caused the unique and excellent sensing ability of the MWCNT-coated cellulose fibers, which have the potential to be used as smart materials.

Keywords: cellulose fiber; carbon nanotubes; smart fiber; piezoresistivity; vapor sensing

1. Introduction

Nowadays, the use of intelligent materials that are capable of reacting to environmental conditions or stimuli, such as mechanical, thermal, chemical, magnetic or others, is growing in the field of textiles [1–4]. Cellulose fibers obtained from natural plants have been used to manufacture fabrics and clothing for millennia. For their unique characteristics, such as being renewable, biocompatible, good mechanical property, and structural features, such as complicated surface morphology, functional groups, such as hydroxyl groups, and high porosity, which can easily be modified, cellulose fibers have attracted considerable attention [5,6]. On the other hand, carbon nanotubes (CNTs), which have excellent mechanical, thermal and electrical properties, are considered as one of the most interesting nanoparticles in the technology world today, due to the versatility of their potential applications [7,8]. Thus, the synergy between a flexible renewable substrate, such as cellulose fibers, and the interesting multifunctionality of CNTs offers a large number of possibilities.

Recently, surface modification of natural cellulose fibers with CNTs has been realized by using either covalent or non-covalent modification methods, such as coating/sizing technologies [6,9–11]. For instance, CNT network armors were fabricated on the surface of cotton fibers using a simple dip coating method [9]. By using carboxylic acids as crosslinking agents, CNT-coated cotton fabrics were fabricated [10–12]. These CNT-coated cotton textiles exhibit improved mechanical properties, flame retardancy, ultraviolet-blocking and water-repelling characteristics. Smart electronic yarns and wearable fabrics were developed from cotton threads by using a polyelectrolyte-based coating with CNTs. These materials can be used as wearable biomonitoring and telemedicine sensors, which are simple, sensitive, selective and versatile [13]. CNTs were also applied with a resin onto a cotton fabric to improve the thermal conductivity [14]. Jute fibers and corresponding epoxy-based composites with sensing abilities could also be realized by depositing multi-walled carbon nanotubes (MWCNTs) on the surfaces of jute fibers or fabrics [15]. These conductive MWCNT-jute fibers can be used as integrated sensors or surface-mount strain gauges to monitor crack initiation/propagation and stress/strain behavior in different composite structures [15]. These reported results are impressive, and therefore, the CNT-functionalized cellulose natural fibers will find a variety of applications in high performance fabrics and intelligent materials.

In contrast to these natural cellulose fibers mentioned above, the composition and structure of man-made fibers can be humanly shaped. This lends man-made fibers special properties and renders them useful for many different purposes. In our previous work, man-made cellulose fibers (viscose fibers) were used to prepare conductive MWCNT-coated cellulose fibers by a simple and scalable dip coating process [16]. For their uniform structure and controllable dimension, mechanical and other properties are stable and can be repeated well for CNT-coated viscose fibers, as well as the original ones. Additionally, the resultant MWCNT-coated cellulose fibers exhibit a rapid response, high sensitivity and good reproducibility for water, with a relative electrical resistance change of about 100%–8000%, depending on the initial resistivity. This unique sensitivity of MWCNT-coated cellulose fibers provides not only a reliable and efficient way to sense liquid water or aqueous solution, but also the potential to be widely used in other fields, such as smart textiles and wearable technology.

In the present paper, the microstructure of MWCNT-coated cellulose fibers and their sensing ability to other external stimuli will be further investigated, including the sensitivity, reproducibility and

stability of these materials as sensors, such as stress/strain sensors and vapor sensors. The correlations between the microstructures of MWCNT networks and sensing behavior will be discussed in detail.

2. Experimental Section

2.1. Materials

Cellulose fibers (commercial viscose fibers) with an average diameter of 20 μm were provided by Kelheim Fibers GmbH (Kelheim, Germany). Commercially available MWCNTs (NC3150, Nanocyl S.A., Sambreville, Belgium) with an average diameter of 9.5 nm and an average length of 1.5 μm were used. Organic solvents, non-ionic surfactant Brij76 (polyoxyethylene (10) stearyl ether) and other reagents were of analytical grade and obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of MWCNT-Coated Cellulose Fibers

The MWCNT-coated cellulose fibers were prepared according to our previous work [16]. Firstly, a certain amount of MWCNTs was added to a surfactant aqueous solution (Brij76). The ratio of surfactant to CNT was adjusted to 1.5/1 (w/w). The resultant mixture was then sonicated using a horn sonicator for 120 min to give a mixture without visible agglomerates. The dispersions with different MWCNT contents were thus prepared. Dip coating was then used to apply MWCNTs onto cellulose-based fibers. For each dipping, fibers were fixed on steel wire frames and immersed in the MWCNT dispersion for 5 min, following 30 min of drying in air. By varying the number of dipping repetitions and MWCNT content in dispersions, cellulose fibers coated with different amounts of MWCNTs were fabricated. In this work, MWCNT-coated cellulose fibers were prepared using dispersions with 0.5 wt% CNTs three times, if not stated otherwise. All of the fibers prepared were dried in a vacuum oven at 40 $^{\circ}\text{C}$ for 8 h before testing.

2.3. Characterization of Morphology and Microstructure

The surface of the MWCNT-coated cellulose fibers was investigated using a scanning electron microscope (SEM, Ultra 55, Carl Zeiss SMT AG, Oberkochen, Germany). The samples for SEM observation were coated by an approximately 5 nm-thick platinum layer.

The Raman spectra have been recorded using the confocal Raman microscope alpha 300 R (WITec GmbH, Ulm, Germany) equipped with a laser with an excitation wavelength of 532 nm. The samples were analyzed with a 20 \times objective and an integration time of 0.5 s. The laser power was 1 mW. To improve the signal-to-noise ratio, 200 accumulations were done. For a better comparison, each spectrum has been normalized to the highest peak in the range of 800 to 2000 cm^{-1} .

2.4. Characterization of Sensing Abilities

The electrical resistance of the single MWCNT-coated cellulose fibers was measured with a Keithley 2001 electrometer (Keithley Instruments GmbH, Germering, Germany) at 23 $^{\circ}\text{C}$ and 50% RH. The mean values of at least ten measurements for the fiber were calculated.

To investigate the piezoresistive effect, the electrical resistance was recorded as the specimen underwent uniaxial tensile or cyclic loading using the FAVIGRAPH semiautomatic equipment (Textechno Company, Mönchengladbach, Germany) equipped with a 1 N load cell. A Keithley 2001 multimeter having a measurement range from 10^{-6} to $10^9 \Omega$ was used to monitor the electrical resistance change of the specimens. The cyclic loading and unloading tension tests were conducted with an initial gauge length of 30 mm, a cross-head velocity of 0.2 mm/min and a strain amplitude of 3%. The specimen was fixed between two clamps coated with conductive silver paste (Acheson Silver DAG 1415M, Plano GmbH, Wetzlar, Germany) serving as electrodes. Simultaneous resistance, strain and load measurements were integrated with the time scale in a customized data acquisition package, TestPoint 2.0.

The vapor sensing behavior was investigated by recording the resistance change of samples during cyclic flows of diluted organic vapor and dry air according to [17]. The dimension of the part exposed to the target analyte is the same (length: 10 mm). The measurements were carried out based on a self-made measurement set-up, which is illustrated in Scheme 1S. A bubbler evaporation system was used to deliver the controlled concentration of volatile vapor to the detection chamber (25 mL) using dry air as the carrier and diluting gas. The temperature of the bubbler evaporation system was set to 25 °C if not stated otherwise. The same Keithley 2001 multimeter (Keithley Instruments GmbH, Germering, Germany) as used for tensile strain sensing was used to monitor the electrical resistance change of the specimens for vapor sensing. Resistance values were collected every 1 s. Common organic solvents, such as methanol, ethanol, acetone, chloroform and tetrahydrofuran (THF), were used to produce vapors for the target analytes, respectively.

In order to compare the sensing properties of specimens independently of their initial resistance, the sensor response was normalized according to Equation (1):

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

Here, R_0 is the initial resistance of the specimen; R_t is the transient resistance upon tensile loading for stress/strain sensing (or exposure to vapors for vapor sensing).

3. Results and Discussion

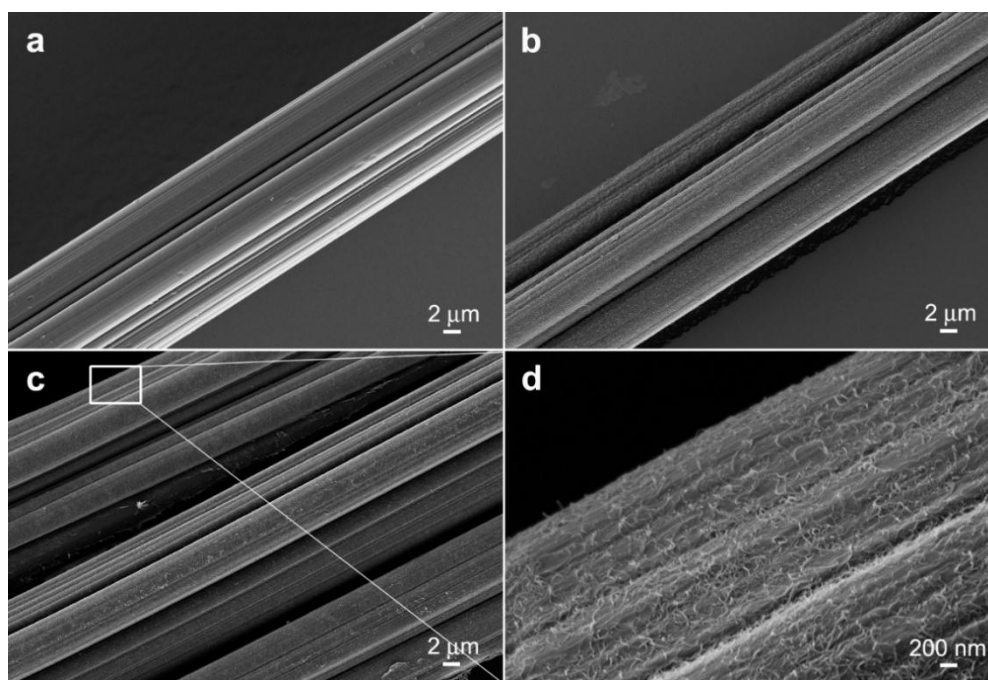
3.1. The Formation of Electrically Conducting MWCNT Networks on Cellulose Fiber Surfaces

The cellulose fibers (Figure 1a) used in this work are regenerated by the viscose process. Due to the hygroscopic nature of cellulose, the coating of CNTs on the cellulose fiber surfaces was much more efficient than their coating on a glass fiber surface, which was performed in our previous work [18,19]. As the SEM images show (Figure 1b–d), the interconnected MWCNT networks were formed on cellulose fiber surfaces after dip coating in the prepared CNT dispersions. This process is efficient for both cellulose monofilament fibers and multifilament fibers to be modified with MWCNTs. The color of cellulose fibers turned from white to light gray and further to black with the increasing amount of MWCNTs coated on the cellulose fibers. The measured resistance, as length normalized resistance, RL , of the single MWCNT-coated cellulose fiber could be in the range of 50–200,000 k Ω /cm, according to the CNT dispersions used and the number of dipping repetitions [16]. In order to reflect the quasi-one-dimensional nature of the fibers, we use length normalized resistance RL instead of resistivity for comparison. In addition, the mechanical properties of the CNT-cellulose fibers do not show obvious

changes compared with those of the original cellulose fibers. The resultant fibers have a good mechanical property and are still very flexible, which is important for the wearability of electronic fabrics, as published previously [16]. Thus, CNT-coated cellulose fibers with stable physical properties and controllable electrical conductivities were prepared through the simple dip coating process.

Once the MWCNT-coated cellulose fibers were dried, it was impossible to remove the CNTs coated from the fibers by exposure to solvents, heat or a combination of both. This could be a result of the efficient interaction of carbon nanotubes with cellulose-based materials. Due to a small amount of functional groups (such as $-OH$) on the surface of MWCNTs and hydroxyl groups of the cellulose molecule, hydrogen bonding could be created between MWCNTs and cellulose fibers, leading to the favorable CNT-cellulose interfacial bonding [16,20]. Additionally, the flexibility of the CNTs enabled an efficient coating on the surface of the cellulose fibers.

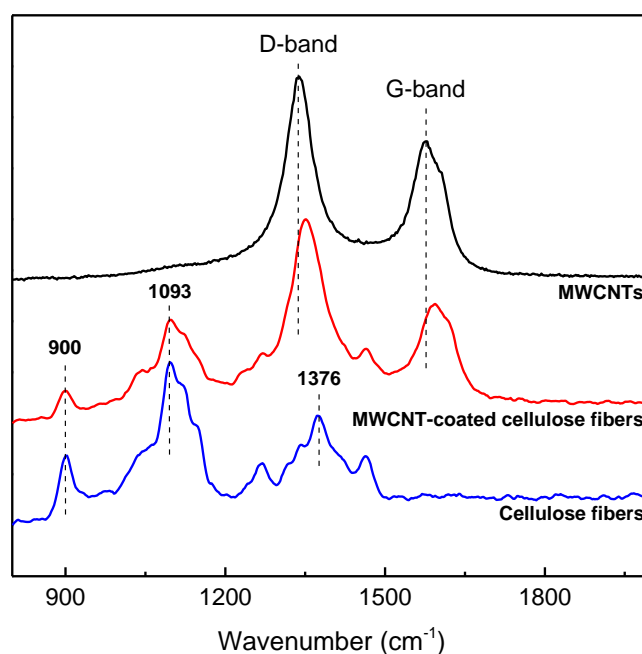
Figure 1. SEM images of the surface of (a) original cellulose fiber (viscose fiber) and MWCNT-coated cellulose fiber (b–d) dip coated with a 0.5 wt% CNT dispersion; (b) monofilament cellulose fiber; (c) multifilament cellulose fibers; and (d) well-formed MWCNT networks on the fiber surface.



In order to study the interaction between the MWCNTs and the cellulose fiber surface, Raman spectra of the pristine MWCNTs, cellulose fibers and MWCNT-coated cellulose fibers were recorded. Figure 2 shows the bands at about 900 cm^{-1} and 1093 cm^{-1} from the spectrum of cellulose fiber that are characteristic bands from cellulose I [21], which do not show an obvious change after MWCNT coating on the surface of the fiber. The Raman spectra of MWCNTs in the range of $800\text{--}2000\text{ cm}^{-1}$ are dominated by two peaks, D-band (at 1337 cm^{-1} , attributed to disorder induced by defects and curvature in the nanotube lattice) and G-band (at 1577 cm^{-1} , due to the in-plane vibration of the C–C bonds) [20,22]. The integral area ratios of the D-band and G-band (I_D/I_G) can be used to evaluate the extent of any carbon-containing defects [23]. Compared with that of MWCNTs (1.6), the value of I_D/I_G for MWCNT-coated cellulose fibers (2.2) increased. Besides the contribution from the bands (such

as bands at 1376 cm^{-1}) of cellulose fibers, it might indicate that the MWCNTs with more defects (or functional groups) are more easily coated on the surface of the cellulose fibers. Moreover, up-shifts in both D-band (from 1337 to 1351 cm^{-1}) and G-band (from 1577 to 1591 cm^{-1}) positions could be observed in the spectrum of MWCNT-coated cellulose fibers (Figure 2). These shifts suggest that strong non-covalent interactions, such as hydrogen bonds between cellulose fiber and MWCNTs, were created [22,23].

Figure 2. Raman spectra of the pristine MWCNTs, cellulose fibers and MWCNT-coated cellulose fibers.



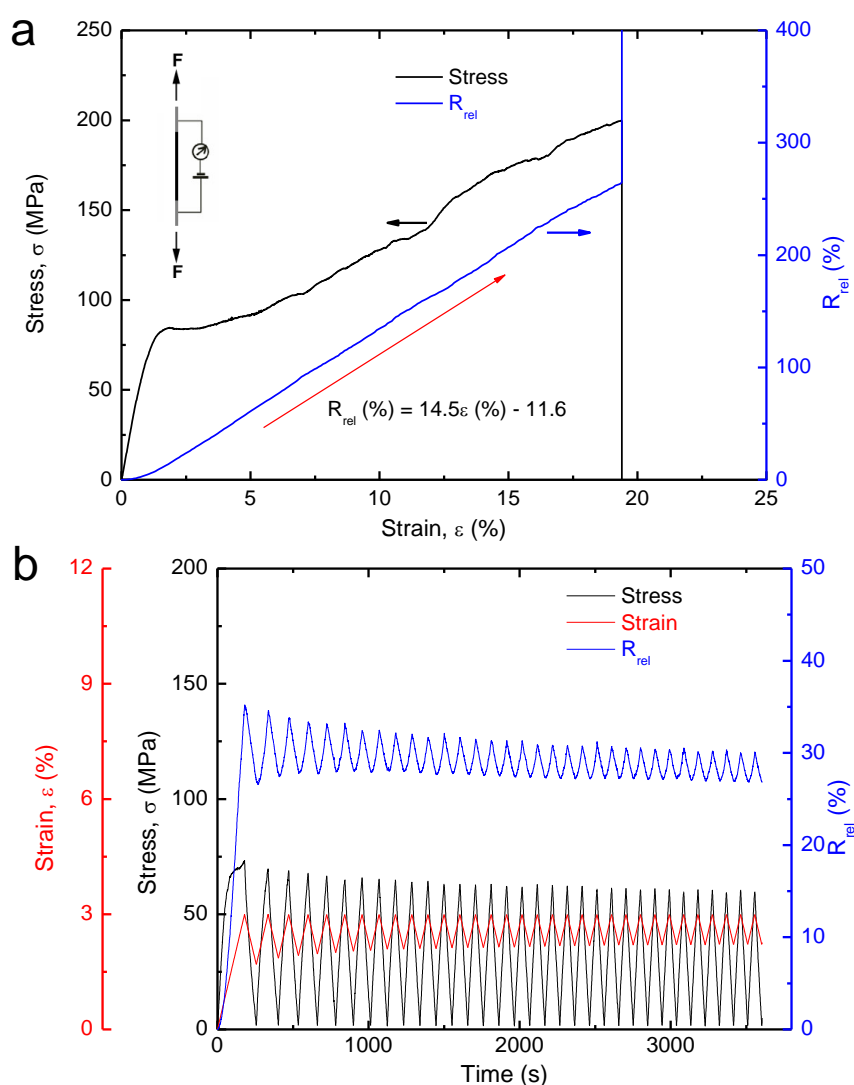
3.2. Piezoresistivity of MWCNT-Coated Cellulose Fibers

With well-formed MWCNT networks coated on the surface, the modified cellulose fibers provide the possibility to serve as smart fibers, such as sensing external stimuli. In this part, the piezoresistivity for strain sensing is investigated for MWCNT-coated cellulose fibers. Figure 3a shows the correlation of electrical resistance changes, mechanical stress and strain of MWCNT-coated cellulose fibers under stress up to fracture. At very low strains (below $\epsilon \approx 0.2\%$), the observed constant electrical resistance suggests that the change in the CNT network shape can be neglected. With increasing strain (ϵ), the relative electrical resistance change (R_{rel}) of the MWCNT-coated cellulose fibers increases monotonously and linearly, almost without noise. This linear strain-dependent electrical resistance keeps even after the yield and until the final fracture.

The strain sensing of MWCNT-coated cellulose fibers is mainly due to the piezoresistivity of the electrically-conductive network of carbon nanotubes on the cellulose fibers. When the MWCNT network is altered by mechanical deformation, a change in the resistivity occurs [24]. In general, the resistance change of CNT networks can be attributed to not only the stress-dependent resistivity of the nanotube structure, but also the stress-dependent change of the nanotube network geometry, nanotube-nanotube interspace, contact area and density (junction point per unit volume) [19]. Therefore, the resistance

change is normally explained by superposing a modified percolation-based scaling rule [25] (related to the linear resistance change region) with relationships describing tunneling resistance (related to the nonlinear resistance change region) [26]. In our case, the locally high concentration of MWCNTs on our cellulose fiber surface can be considered as overlapping at the contact locations, rather than being arranged in an end-to-end configuration. Thus, the percolation-based scaling rule, which accounts for the effects of the network geometry change, might be the dominant phenomenon, leading to the linear resistance change with strain. The tunneling resistance effect might not play a major role here.

Figure 3. The electrical responses to external stress/strain for MWCNT-coated cellulose fiber. (a) The relative electrical resistance change (R_{rel}) versus strain; and (b) the R_{rel} and tensile stress-strain versus time during cyclic tensile loading up to a fixed strain of 3%.



The linear correlation between R_{rel} and tensile strain (ϵ) can be described as an equation following:

$$R_{rel} = GF \times \epsilon + a \tag{2}$$

where GF is the abbreviation of gauge factor and stands for strain sensitivity, and the parameter, $a = \epsilon_0 \times GF$; ϵ_0 refers to the initial strain for the piezoresistivity effect of CNT networks [15,19]. According to the linear correlation in Figure 3a, the GF value for this MWCNT-coated cellulose fiber is

14.5, which is much higher than that of metal alloys used for conventional foil gages (0.74–5.1) [26]. It is noted that the linear correlation between fractional resistance and strain for this MWCNT-coated cellulose fiber is up to 18% strain until the final fracture. This linear strain range is much larger than that of CNT-coated natural fiber (about 1.5% strain) [15], CNT/cellulose composite films (7%–13% strain) [16] and other CNT/polymer composites (below 3% strain) [15,19,26]. For our MWCNT-coated cellulose fibers, furthermore, the R_{rel} value before the final fracture can be up to 200%–400%, which is much higher than that of most reported CNT-based materials. These results indicate that our MWCNT-coated cellulose fibers are more efficient and sensitive for use as stress/strain sensors.

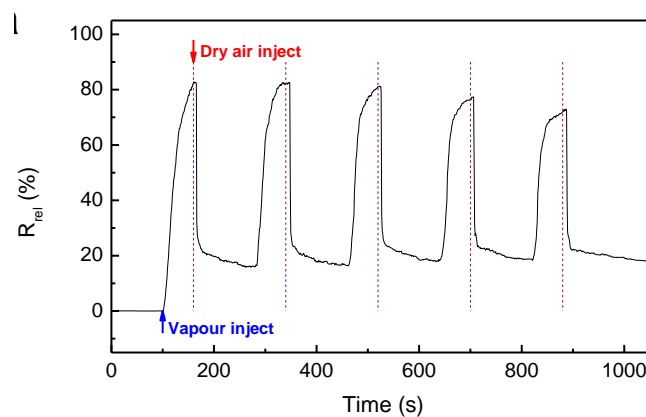
The repeatability of the piezoresistive behavior for MWCNT-coated cellulose fiber was checked under a cyclic tension condition. Figure 3b shows the typical correlation of R_{rel} , stress and strain of MWCNT-coated cellulose fiber under stress to a fixed strain of 3.0%. The R_{rel} increases linearly upon first tensile loading and then decreases linearly upon unloading to a level above the initial zero value, the same as that for fiber strain. This indicates that an irreversible deformation of cellulose fiber occurred under the tensile stress, leading to the irreversible change of the CNT networks coated on the surface. Reloading causes R_{rel} to increase again, and the subsequent cycles show relatively constant electrical resistance change with a small difference, indicating good reversibility and repeatability. It is noted that all of the R_{rel} show a highly linear change with almost the same slope upon tensile stress loading. These impressive characteristics indicate that our MWCNT-coated cellulose fibers are perfect for use as strain sensors. Thus, these sensory fibers can be woven together with other fibers for smart textiles and wearable technology, for example to be used to monitor the motion of muscles and limbs for rehabilitative and telemedicine applications. Moreover, our MWCNT-coated cellulose fibers can be used as integrated sensors or surface-mounted strain gauges to monitor crack initiation/propagation and strain/stress in different composite structures [15].

3.3. CNT-Coated Cellulose Fibers Used as Vapor Sensors

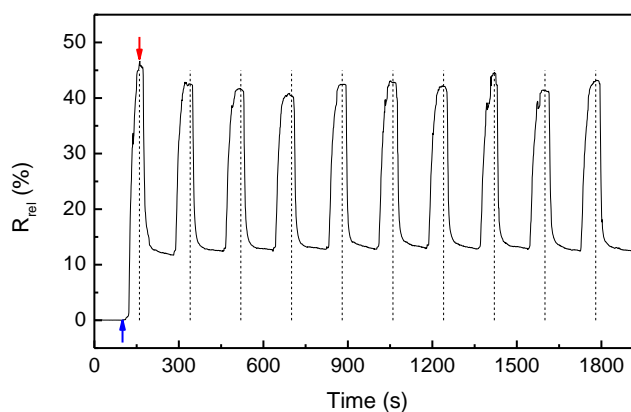
Due to their large adsorption capacity and the change of electrical resistance upon exposure to volatile molecules, MWCNT networks are good candidates for use as chemical sensors. We then further investigated the sensing ability of the MWCNT-coated cellulose fibers to volatile organic compounds (VOCs). In order to describe the vapor sensitivity of the MWCNT-coated cellulose fibers, the relative electrical resistance change (R_{rel}) of these exposed to gas pulses of solvent vapors was recorded as a function of time. Figure 4a shows the resistance response of MWCNT-coated cellulose fibers to diluted ethanol vapor (7%). Prior to the exposure to the target analyte, the resistance was recorded for 100 s under dry air to get a stable initial resistance value. Then, MWCNT-coated cellulose fiber was exposed to five cycles of alternating gas pulses of diluted ethanol vapor and dry air. Clearly, upon exposure to ethanol vapor, an instant sharp increase of resistance was observed. The R_{rel} reaches a value of about 20% after immersion for only 10 s. After 60 s, the R_{rel} value of the fibers reaches 82%. In addition, the R_{rel} value decreases during the following 120 s for the recovery of the MWCNT-coated cellulose fibers in dry air (Figure 4a). The recovery of the R_{rel} value starts at 3–5 s after injecting of dry air into the detecting chamber due to the time consumption for fully expelling ethanol vapor. Finally, the resistance response curve shows a 15% hysteresis to the initial resistance value due to the remaining solvent vapor on the sample after the ethanol vapor is withdrawn. Therefore, the reversibility of resistance change is

evaluated starting from the second cycle. The fiber exhibits fast and reproducible responsiveness as characterized by the significant increase in R_{rel} of about 80%, indicating its good sensing ability of ethanol vapor.

Figure 4. (a) Typical resistance response (R_{rel}) of MWCNT-coated cellulose fiber to ethanol diluted vapor (7%) for five cycles; (b) the resistance response (R_{rel}) of MWCNT-coated cellulose fibers to diluted acetone vapor (30%) for ten cycles.



(a)



(b)

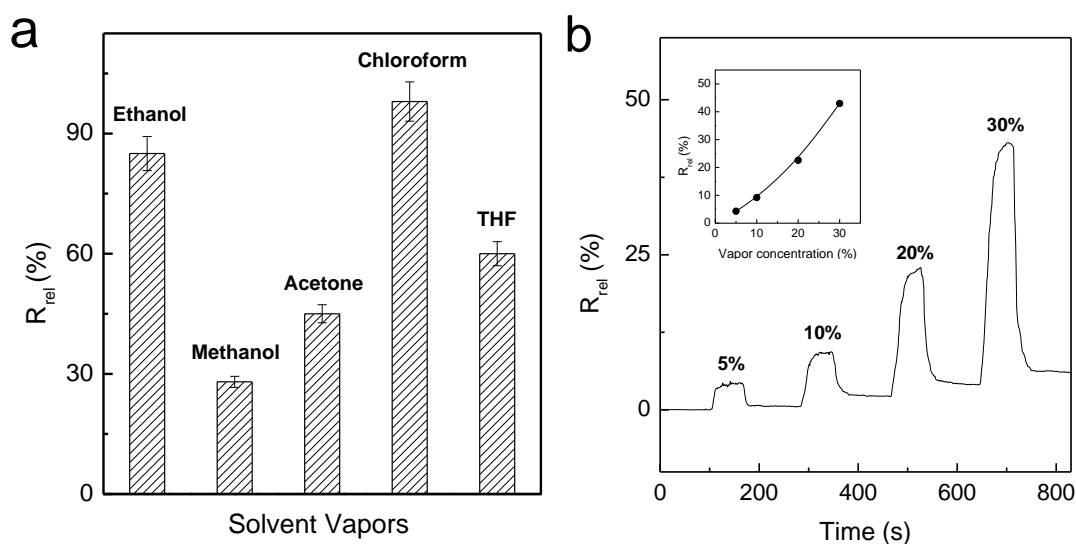
In order to have a fair comparison of the fiber for the solvent vapors, the exposure time and recovery time were restricted to 1 and 2 min, respectively, for all of our gas sensing experiments (unless otherwise marked). Figure 4b shows the resistance response of MWCNT-coated cellulose fiber to diluted acetone vapor (30%) for ten cycles. Similar to that for ethanol vapor, it can be noticed that the signals are also quite stable and reproducible for all of the cycles, with an R_{rel} value of about 42%. These results further verify the reliability and reproducibility of our fiber to serve as vapor sensors.

It should be noted that the MWCNT-coated cellulose fibers exhibit a positive vapor coefficient for ethanol and acetone vapors, which is also found in other CNT-based sensory materials for vapor sensing [17,27–30]. As reported previously, the change of resistance of CNT-based materials as sensors for vapors is mainly due to two reasons. One reason is the adsorption of electron-donating VOC molecules, compensating for the hole carriers in semiconductive MWCNTs and causing the increase of electrical resistance [27]. Another probable reason is that the adsorption of VOC molecules also directly causes the swelling of the polymer, resulting in the change in the microstructure of MWCNT networks

in the matrix or on the surface [17,28,29]. As a result, in our cases, it can be deduced that the resistance responses of MWCNT-coated cellulose fibers for VOC can be attributed to the adsorption of VOC molecules by both the cellulose fiber and the CNT networks. Compared to the CNT-based composites, furthermore, the unique distribution of CNT networks on the fiber surface provides a large, well-defined surface area and the capacity to make contact more directly and efficiently with analytes, leading to the rapid response and high sensitivity for MWCNT-coated cellulose fibers as vapor sensors.

Figure 5a shows the relative resistance response (R_{rel}) of the MWCNT-coated cellulose fibers after exposure to various solvent vapors (saturated vapor concentration at 25 °C, Table S1) for 60 s. For the different effects on the electrical resistance of nanotubes, as well as the swelling of cellulose fiber by adsorption of different VOC molecules, the resistance response of the fibers to these vapors is different. Thus, it is possible to monitor different vapors using our modified fibers by evaluation of their electrical resistance response. Figure 5b displays the relative resistance changes of the MWCNT-coated cellulose fibers upon sequential exposure to various acetone vapor concentrations. This fiber exhibits a good sensing ability for acetone vapor with a low concentration, such as 5%. It can also be observed that the changes of the resistance had an exponential relationship with the vapor concentrations, which is similar to other CNT-based materials as vapor sensors [17].

Figure 5. (a) The resistance response (R_{rel}) of the MWCNT-coated cellulose fibers after exposure to various solvent vapors (saturated vapor concentration at 25 °C, Table S1) for 60 s; (b) the resistance response (R_{rel}) of the MWCNT-coated cellulose fiber upon sequential exposure to various acetone vapor concentrations (the inset presents the exponential relationship between acetone vapor concentration and R_{rel}).



Based on the results mentioned above and our previous works [16], it can be concluded that MWCNT-coated cellulose fibers exhibit excellent sensing abilities for various external stimuli, such as stress/strain, solvent liquids and solvent vapors. It was noted that these fibers also show good reproducibility and repeatability during sensing tests, which further demonstrate that the coating of CNTs on cellulose fiber is rather stable without detachment after cyclic stress or exposure to solvent liquids or vapors.

4. Conclusions

Using a simple dip coating process, electrically-conductive MWCNT-coated cellulose fibers were fabricated. Strong non-covalent interactions between the cellulose fiber and MWCNTs were created, leading to favorable CNT-cellulose interfacial bonding. The network formation of the MWCNTs on the surface not only provided good conductivity to the modified fibers, but also led to excellent sensing abilities to external stimuli, in the combination with the intrinsic physical and chemical features of cellulose fiber. As stress/strain sensors, these MWCNT-coated cellulose fibers exhibited a highly linear and repeatable electrical resistance correlation to tensile strain, with good reversibility and repeatability. Additionally, the useful linear strain range for the fiber is about 18% strain with a GF value of 14.5. As chemical vapor sensors, our fibers exhibit a simple, sensitive and selective sensing ability for chemical vapors, indicating their potential to be designed as a new type of electronic nose (e-nose) for VOCs and other gases. Based on their unique structure and impressive characteristics, MWCNT-coated cellulose fibers as smart materials are promising and should be further investigated and introduced to other fields, such as smart textiles and wearable technology.

Acknowledgments

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Author Contributions

Haisong Qi conceived of the research, organized the experiments, interpreted the results and wrote the manuscript. Edith Mäder was the corresponding author who initiated the project and finalized the manuscript for submission. Jianwen Liu was responsible for SEM and tensile measurements. All authors read and approved the final manuscript.

Supplementary Materials

The scheme (Scheme S1) of the experimental setup for vapor sensing and the saturated vapor concentration of VOCs (Table S1) are given as supplementary data.

Supplementary materials can be accessed at: <http://www.mdpi.com/2079-6439/2/4/295/s1>.

Conflicts of Interest

The authors declare no conflict of interest.

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