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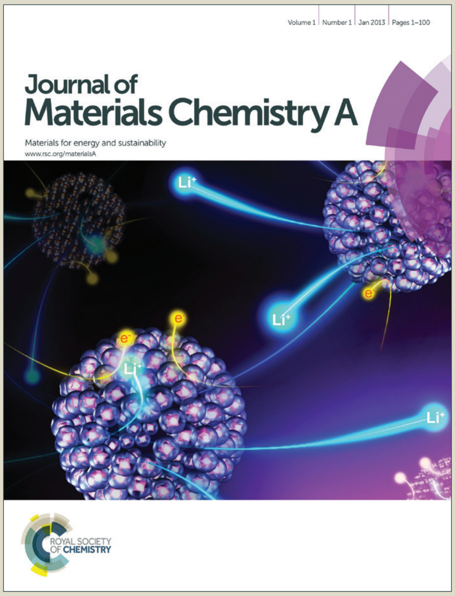

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PAPER

Cellulose fibres with carbon nanotube networks for water sensing

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Electroconductive cellulose-based fibres were fabricated by depositing multi-walled carbon nanotubes (MWNTs) on the surface using a simple and scalable dip coating. The morphology, mechanical properties and conductive properties of the resultant MWNT-cellulose fibres were investigated by scanning electron microscopy, tensile test and electrical resistance measurement, respectively. The resistance (R_L) of the single MWNT-cellulose fibre can be controlled in a wide range of 50 - 200,000 kΩ/cm by varying the condition of dip coating. The sensing behaviour of these fibres to liquid water was investigated in detail. The results showed that they exhibit rapid response, high sensitivity and good reproducibility to water, with a relative electrical resistance change of about 100 - 8000% depending on the initial resistance. It was proposed that the disconnection of MWNT networks caused by swelling effects of the cellulose fibres is the dominant mechanism. Moreover, the sensitivity of the MWNT-cellulose fibres to electrolyte solution was also investigated.

1 Introduction

Water or humidity sensors are widely applied in detecting water leaks, process control, industries production, biomedical and environment monitoring [1-3]. Devising an efficient and reliable method of water sensing has attracted considerable attention in recent years. A number of attempts involved materials and transduction techniques for water sensors were reported, including ceramic sensing materials, semiconducting sensing materials, polyelectrolyte-based resistive sensors and fluorescence water sensors [4-7]. However, it still remains challenging to develop a water sensor which provides a complete set of favourable characteristics, e.g., rapid response, good stability, high reproducibility and simple measurement.

It's well-known that water is the resource vital for the survival of all species on earth. Plants such as grass will wither in drought condition. Conversely, a drought-stricken lawn can become green quickly after the rains have returned. That is, the plants are "sensitive" to water. As the components in plants, the natural biopolymers can absorb water and might offer the candidates for the real liquid detecting. Cellulose, which is the structural component of the primary cell wall of green plants, has been widely used by our society in diverse fields such as textiles and paper [8,9]. Because of the large amounts of hydroxyl groups on the molecular structure, cellulose has good affinity to water and exhibits sensitive volumetric change. By embedding conductive fillers (e.g. carbon nanoparticles or metal particles) in cellulose matrix to form electric pathways, furthermore, we can convert the dimension change of this electrically insulating polymer into electrical signals. In our previous work, electroconductive carbon nanotube (CNT)-cellulose composites were fabricated through a blending process [10]. In the case of those materials used for liquid water sensing, the swelling of the cellulose matrix on contact with water disrupts the electron transport between CNT networks and causes the electrical resistance of materials to increase [10]. This direct transduction of chemical information into an electrical signal when combined with existing low power microelectronics and sensing technology makes CNT-cellulose composites attractive materials for liquid sensing.

Besides the blending method mentioned above, conductive cellulose-based materials could also be fabricated by dip coating [11-15], which has more benefits as following: firstly, the fabrication process is simple and scalable, similar to those widely used for dyeing fibres or fabrics in the textile industry; secondly, it is more effective in creating conductive CNT-to-CNT junction network where the CNTs are not encapsulated by polymer chains, leading to remarkably low CNT loadings compared to the previously reported percolation threshold values for composites [16]; thirdly, the original properties of cellulose-based materials could be preserved. In addition, the CNTs covered on the surface can contact directly and quickly to chemicals, which make them more sensitive to gases or liquids compared with composites.

In the present work, therefore, we deposited multi-walled carbon nanotubes (MWNTs) directly onto cellulose fibres through dip coating to fabricate conductive MWNT-cellulose fibres. The sensitivity, reproducibility and stability of these materials as water sensors were discussed in detail. Factors that influence the conductivity and the sensing behaviour were also investigated.

2 Experimental

2.1 Materials

Commercially available MWNTs (NC3150, Nanocyl S.A., Belgium) with an average diameter of 9.5 nm and an average length of 1.5 μm were used. Commercial viscose fibres with average diameter of 20 μm were provided by the Kelheim Fibres GmbH (Kelheim, Germany). Glass fibres with an average diameter of 12 μm utilized in this work were manufactured by a continuous spinning process at our institute. Non-ionic surfactant Brij76 (polyoxyethylene (10) stearyl ether) and NaCl were obtained from Sigma Aldrich.

2.2 Preparation of MWNT-cellulose fibres

Firstly, homogeneous MWNT dispersions were prepared as introduced in our previous work [10,15]. A certain amount of MWNTs was added to 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 MWNT content (0.05 wt%, 0.1 wt%, 0.2 wt%, 0.5 wt% and 1.0 wt%) were thus prepared.

Dip coating was then used to apply MWNTs onto cellulose-based fibres. As one time of dipping, fibres were fixed on steel wire frames and immersed in MWNT dispersion for 5 min, following with 30 min drying in air. By varying the number of dipping repetitions (such as 1, 3, 5 and 10) and MWNT content in dispersions, cellulose fibres coated with different amount of MWNTs were fabricated. Among them, MWNT-cellulose fibres coded as CF01, CF02, CF03 and CF04 is prepared using dispersions with 1.0 wt%, 0.5 wt%, 0.2 wt% and 0.05 wt% CNTs for 3 times, respectively. Similarly, MWNT-coated glass fibres were prepared using dispersions with 1.0 wt% CNTs for 10 times. All the fibres prepared were dried in a vacuum oven at 40 °C for 8 h before liquid sensing test.

2.3 Characterization

The surface and cross section for samples was investigated using a scanning electron microscope (SEM, Ultra 55, Carl Zeiss SMT AG, Germany). The samples for SEM observation were sputtered by approximately 5 nm thick platinum layer. Optical microscopes (Nikon Optiphot-2, Keyence VHX-600) were used to *in-situ* detect the width patterns of cellulose fibres swelling in water.

The mechanical properties of the fibres were measured on a FAVIGRAPH semiautomatic equipment (Textechno Company, Germany). The extension rate was set at 20 mm/min. All data were collected under the same conditions: 23 °C and 50% relative humidity (RH). The average values were calculated with 50 specimens for each fibre.

The electrical resistance of the single MWNT–cellulose fibres was measured with a Keithley 2001 electrometer (Keithley Instruments GmbH, Germany) at 23 °C and 50% RH. In order to reflect the quasi-one dimensional nature of fibres, we use length normalized resistance (R_L) instead of resistivity for comparison. And R_L was evaluated by means of equation (1):

$$R_L = R / L \qquad (1)$$

R and L are the measured electrical resistance and length of the fibres, respectively. And the units of resistance used here are Ohm/cm. The mean values of at least ten measurements for every fibre were calculated.

A two-probe setup with a Keithley 2001 and a DC power supply (ELV PS 7000) was used to obtain the current-voltage (*I–V*) curves while the specimens were kept in a desiccator with silica gel to avoid the influence of moisture. The MWNT–cellulose fibres were contacted with the electrodes using electrically conductive silver paint (Acheson DAG 1415 M). Compared to the resistance of specimens, the contact resistance is very small and can be ignored.

2.4 Liquid sensing test

A Keithley 2001 multimeter was used to monitor the electrical resistance change of the samples. As shown in Fig. S1, resistance values were collected by a computer, whereas the sampling rate was 1 s. The relative change of electrical resistance (R_{rel}) was evaluated by means of equation (2):

$$R_{rel} = (R_t - R_0) / R_0 \times 100\% \qquad (2)$$

R_0 is the initial resistance of the specimen before immersion; R_t is the transient resistance upon exposure to water at time t.

A measurement cycle consisted of an immersion and drying step. The immersion (wetting) was carried out under controlled temperatures using a heating/cooling bath. For the drying step the test fixture was lifted up and the remaining solvent drops were wiped off by tissue carefully. The drying took place in air at 23 °C and 50% RH. The samples were tested in distilled water and NaCl aqueous solution, respectively.

3 Results and discussion

The deposition of MWNTs onto cellulose fibres shows that the colour of cellulose fibres turned from white to light gray or black depending on the treatment condition. Although it is hard to determine accurately, the amount of CNT loaded on cellulose fibres is very small by dip coating. According to our previous work, the amount of CNTs coated on glass fibres is below 1×10^{-3} wt% [16]. As shown in SEM image in Fig. 1a, there is only a thin CNT layer on the surface of the cellulose fibres. It is clearly exhibited that the interconnected MWNT networks are uniformly formed. The measured resistance (R_L) of the single MWNT–cellulose fibre is in the range of 50 - 200,000 kΩ/cm depending on the condition of dip coating. As shown in Fig. S2 and S3, the conductivity of the patterns increases with increasing of CNT content in dispersions and number of dipping repetitions, respectively. This is because that the better percolation of the deposited CNTs could be obtained when more dipping repetitions or higher CNT content dispersions used. In principle, it would be true that a threshold or saturation value of electrical properties could be reached with extensive overlapping MWNT networks after a high number of dipping repetitions or using dispersions with high CNT content.

Fig. 1b shows the current–voltage (*I–V*) characteristics of a single CNT-cellulose fibre. Same as that of CNT-glass fibre [16], they are linear over a wide range of voltages (0-30 V) and symmetric to voltage polarity with high reproducibility, suggesting ideal Ohmic contacts between nanotubes as well as electrodes. However, the incorporation of CNTs with the cellulose fibres was much more efficient than their adsorption on glass fibres, which was tried in our previous work [16,17]. Furthermore, exposure of the produced MWNT-cellulose fibres to water imitating washing did not appreciably affect the electrical properties, which will be described in the later part of this paper. It could be a result of the efficient interaction of carbon nanotubes with cellulose-based

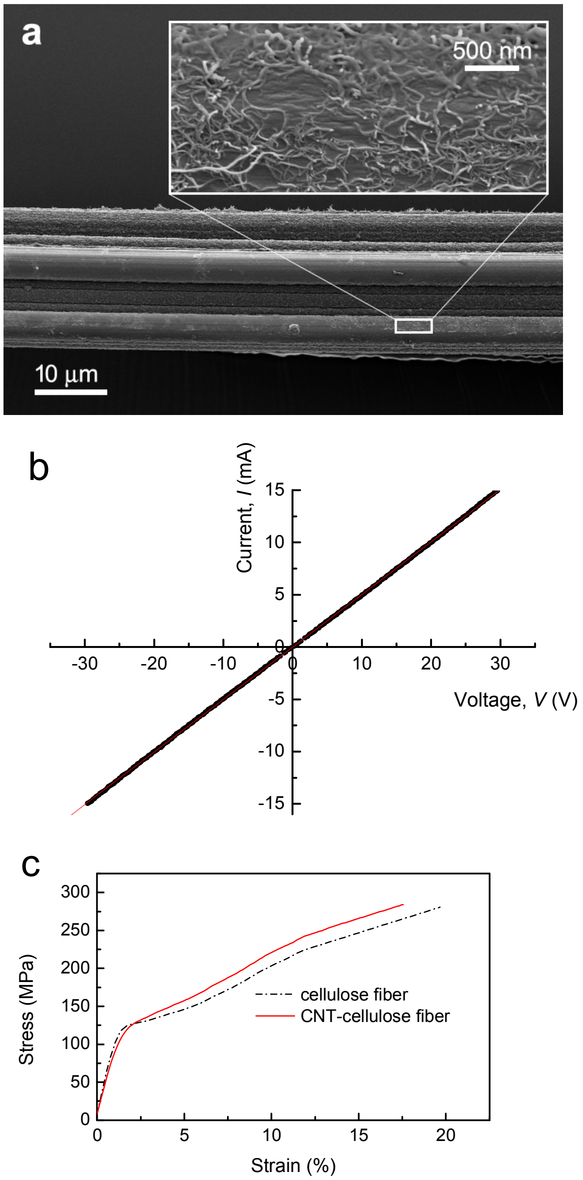

Fig. 1. The MWNT–cellulose fibre (CF01) prepared by dip coating: (a) SEM image of the fibre (the inset shows the CNT networks on the surface of fibre); (b) current–voltage (*I*–*V*) characteristics (with linear red dash lines for eye guide); (c) stress-strain curve of the treated fibres compared with the original ones.

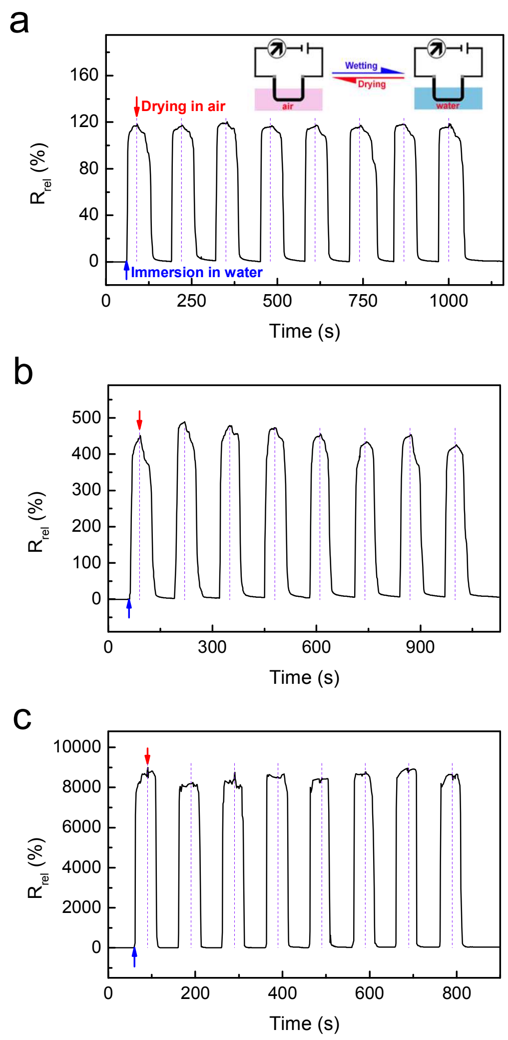

Fig. 2. Relative resistance change (R_{rel}) as a function of time during wetting/drying cycles in water/air at 20 °C for MWNT-cellulose fibres with different resistivity (R): a, CF01 (R_L = 179 kΩ/cm); b, CF02 (R_L = 621 kΩ/cm); c, CF03 (R_L = 1160 kΩ/cm).

materials. Due to a small amount of functional groups (such as –OH) on the surface of MWNTs and hydroxyl groups of the cellulose molecular, hydrogen bonding could be created between MWNTs and cellulose fibres, leading to the favourable CNT-cellulose interfacial bonding [18]. Additionally, the flexibility of the CNTs allows them to conform to the surface of the cellulose fibres.

As one of the important fundamental properties, the mechanical properties of the MWNT-cellulose fibres have no significant change compared with that of the original cellulose fibres (stress - strain curves are shown in Fig. 1c). Even though the cellulose fibres became slightly stiffer after being coated with CNTs, it is still very flexible, which is important for the wearability of electronic fabrics or other applications. Thus, cellulose-based fibres with controllable electrical conductivities while preserving original physical properties were prepared through a simple process of dip coating.

In order to describe the liquid sensitivity of these MWNT-cellulose fibres, the R_{rel} of the samples immersion in water as a function of time was recorded. Fig. 2a shows the typical resistive response of MWNT-cellulose fibres (CF01, R_L = 179 kΩ/cm) to liquid water. Clearly, the R_{rel} increases very rapidly and reaches a very high value of 100% after immersion in only 5 s. These fast and reliable responses indicate that the MWNT-cellulose fibres are very sensitive to liquid water. During the following time, the increase of R_{rel} is relatively slow and reaches about 117% after 30 s of immersion. Obviously, the MWNT-cellulose fibres exhibit a positive liquid coefficient, which can be also found in conductive polymer composites (CPCs) for vapours or liquids sensing [10, 19-25].

Normally, the resistance change ($\Delta R = R_t - R_0$) of CNT-based materials for gases (including vapours) or liquids sensing is mainly depended on two parts: (1) molecules absorption on CNT

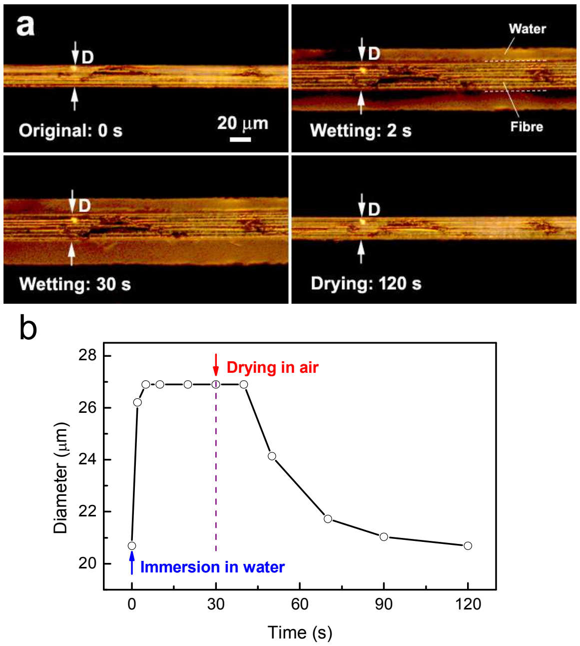

Fig. 3. Optical microscope images (a) of the MWNT-cellulose fiber (CF01) swelling/deswelling cycle in water/air at different time (the scale bar is same for all), with the changing of the diameter (D) of fibre during the cycle (b).

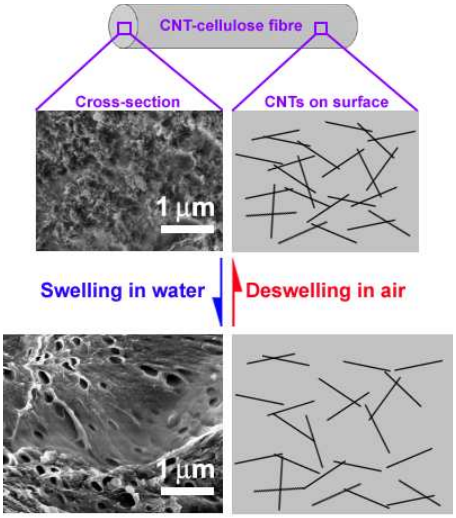

Fig. 4. The schematic of CNT–cellulose fibre for liquid water sensing, with the disconnection/connection of contact CNTs on surface driven by the swelling/deswelling of cellulose fibre.

(ΔR_A): the adsorbed molecules by CNTs change the carrier concentration in the outer graphene layer, which is responsible for electrical transport, leading to the increase (or decrease) of electrical resistance; and (2) CNTs network disruption causes by matrix swelling (ΔR_S): the swelling of polymer matrix due to their adsorption of solvent molecules results in the disruption of the electron transport between CNT networks and causes the electrical resistance to increase. That is, $\Delta R = \Delta R_A + \Delta R_S$. In the case of CNT alone as gas sensors [26,27], as well as some CNT-based materials prepared by depositing CNTs on paper (or polymer) surface as humidity or organic vapour sensors [28-30], ΔR_A is the dominant phenomenon. However, ΔR_S usually plays a major role when sensory CPCs or some CNT-based materials severed as vapours and liquids sensors [10, 19-25, 31].

As described above, in our case, the coated CNTs on cellulose fibre surface can be considered as extensive nanotube overlapping networks. It is deduced that the resistance responses of CNT-cellulose on water could be attributed to the adsorption of water molecules by both, cellulose fibre (ΔR_S) and CNT layers (ΔR_A). Optical microscope images (Fig. 3a) exhibit the swelling behaviour of the MWNT-cellulose fibres (CF01) exposed to water. It can be observed that the highly hygroscopic swelling of the cellulose fibre has already occurred in the initial 2-5 s, with the diameter (D) of the fibre increasing from about 20.8 µm to 26.5 µm (Fig. 3b). The SEM images (Fig. 4) of the cross-section of MWNT-cellulose fibre further prove the swelling behaviour of cellulose-based fibres in water. This enlargement of fibre volume caused by the swelling increases the nanotube-nanotube distance of neighboured CNTs above the tunnelling or hopping distances, leading to the sharp increase of the resistance, as described in Fig. 4. On the other hand, the adsorbed water molecules on the surface of CNTs also affect the electrical resistance [10,16,18]. To prove the dominant mechanism of the liquid sensing behavior of our materials, glass fibers coated with MWNTs were employed, and the relative resistance changes of them in the first exposure cycle in water are shown in Fig. 4S. Without the fibre swelling in water, however, the R_{rel} value of MWNT-glass fibre are only 3~4%, which are much lower than those of MWNT-cellulose fibres. Moreover, it exhibits a negative change of resistance after immersion in water. Thus, the swelling of cellulose fibres exposed to water (ΔR_S) is the dominant mechanism, while ΔR_A has no contribution to the positive liquid coefficient.

It is noted that, during the following 60 s for the drying of the fibres in air at ambient conditions (Fig. 2a), the R_{rel} value decreases to the same level as that of initial baseline ($R_{rel} = 0$). It indicates the MWNT-cellulose fibres have a good recovery as water sensors. The optical microscope images in Fig. 3a also show that the fibre has recovered to its initial state after drying, with the diameter reverting to its initial value. That is, the structure and properties of cellulose fibres remain unchangeable after the wetting/drying cycle. This feature is mainly due to that cellulose does not dissolve but only swells in water. On the other hand, it also demonstrates there exists favourable CNT-cellulose interfacial bonding, which results in the good stability of the materials. Compared with that of CNT-based sensory CPCs for liquid sensing [10,23-25], the usual response/recover time of our MWNT-cellulose fibres are much shorter, which are only several/tens seconds. Moreover, as shown in Fig. 2a, the response signals are quite stable and reproducible under cyclic wetting and drying process. All the R_{rel} values increase (or decrease) almost to the same level during the wetting (or drying) process. It indicates their good repeatability. Thus, our MWNT-cellulose fibres are not only sensitive, but also well reversible and reproducible for water sensing. These unique and perfect properties of the MWNT-cellulose fibres as water sensors have advantages for practical applications.

As mentioned above, there exists an overlapping mechanism in water sensing behavior of MWNT-cellulose fibres. The CNT loading on fibre surface might influence the disconnection of contact CNTs, which further influences the liquid sensing

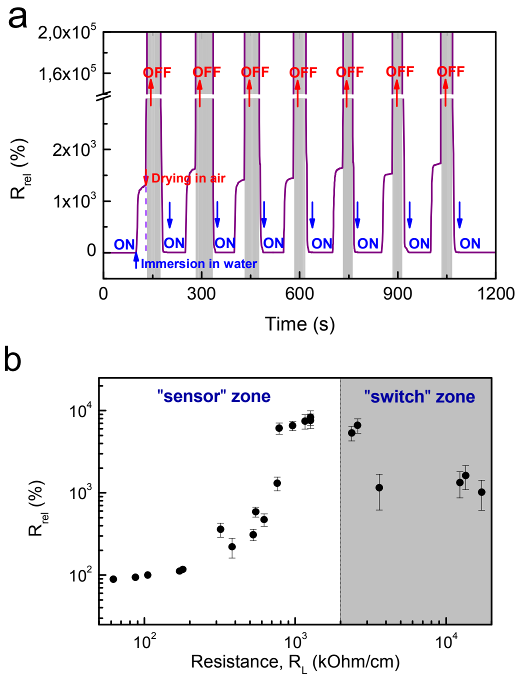

Fig. 5. (a) Relative resistance change (R_{rel}) of the MWNT-cellulose fibres (CF04, R_L = 13.5 MΩ/cm) as a function of time during wetting/drying cycles in water/air at 20 °C ; (b) the correlation of R_{rel} (immersion for 30 s at 20 °C) with resistance of different MWNT–cellulose fibres.

behaviour. We then monitored the sensing ability of MWNT-cellulose fibres with different resistance (R_L). Fig. 2b and c show the sensing behaviour of MWNT-cellulose fibres with higher resistance of 621 kΩ/cm (CF02) and 1160 kΩ/cm (CF03), respectively. They exhibit the same basic profile of such curves, which is characterized by a rapid increase in resistance with increasing immersion time. However, the amplitudes of their responses are much larger than those of CF01. Especially, CF03 exhibits high R_{rel} value of about 8000 %, which are almost two orders of magnitude higher than those of the CF01. That is, the R_{rel} value increases with the increase of resistance (R_L) of materials. This character is in good agreement with the percolation theory, same as CNT-cellulose composites for liquid sensing [22]. Driven by the highly hygroscopic swelling of cellulose fibre, the conductive CNT networks on the cellulose fibre surface tend to readily disconnect at less dense nanotube network structure. It further confirms that the ΔR_S is the dominant phenomenon for the high sensitivity of the MWNT-cellulose fibres to water. As shown in Fig. 2b and c, furthermore, both CF02 and CF03 show good repeatability in following responses under cyclic wetting/drying process. It indicates MWNT-cellulose fibres have good stability and high reproducibility as well as high sensitivity in a wide range of conductivity. This again demonstrates the capability of our CNT-cellulose fibres to be used as water sensor.

Interestingly, for MWNT-cellulose fibres with relatively high resistance such as 13.5 MΩ/cm (CF04), an alternative function–the electrochemical “switch” is found, where the electrical signals turn ON and OFF states with a variation of wetting and drying process (shown in Fig. 5a). During the first cycle wetting, the highly hygroscopic swelling of cellulose fibre leads to the rapid increase in resistance when exposed to water, with R_{rel} value as high as 1700 % after 30 s of immersion. However, the resistance jumps to “infinity” (out of measurable range, 2 GΩ) when MWNT-cellulose fibre removed from the water. That is, the CNT networks on fibre surface as conductive pathways are completely disconnected and the switch presents the “OFF” state on this moment. It demonstrates that the electrically conducting MWNT-coated cellulose fibre could change into electrically insulating fibre by the swelling of the cellulose fibre if the MWNT loading is low enough. During the drying process, subsequently, the swollen cellulose fibre is shrinking and the disconnected nanotubes are approaching each other. When the fibre swelling is less than certain critical value, some of disconnected carbon nanotubes reconnect to rebuild ohmic contacts or approach very near to each other to form tunneling current, and the switch turns into “ON” state. The conversion of ON-OFF states occurred at almost same time of all cycles. It indicates that this “switch” can be efficiently controlled by the wetting-drying of MWNT-cellulose in water. Therefore, the swelling-shrinking of MWNT-cellulose fibres during wetting-drying cycle results in the efficient “break-junction” (disconnection-connection of MWNT network) mechanism, which provides the possibility to fabricate the electrochemical “switch” in a simple and unique way.

It should be noted that the “OFF” state of the switch occurred at the beginning of drying process. However, it can be deduced that the CNT network are already completely disconnected by swelling of fibre during the immersion process. In fact, distilled water is almost pure but it will still have some conductivity (0.0001-0.001 mS/cm). And the measured transient resistance (R_t) during wetting process is not only the resistance of CNT-fibre, but also that of water which is in parallel connection with it. That is,

$$1/R_t = 1/R_{fibre} + 1/R_{water} \tag{3}$$

Compared with that of R_{fibre}, normally, the value of R_{water} is much high and can be ignored, as discussed previously for CF01 CF02, and CF03. In the case of CF04 immersed in water, however, R_{water} can not be ignored because R_{fibre} is comparable or even larger than R_{water}. Especially, the measured resistance (R_t) is actually the R_{water} when CNT networks were completely broken during immersion process (such as 25-30s after immersion). Thus, the value of measured R_{water} is about 400 MΩ according to $R_{t=30s}$ in this case.

Fig. 5b summaries the relative resistance change of the MWNT-cellulose fibres with different initial R_L. It can be divided into “sensors” zones and “switch” zone according to the sensing behaviour. For R_L being lower than 2 MΩ, the MWNT-cellulose fibres are mainly exhibit sensor behaviour. And the R_{rel} increases with the R_L of the materials. When R_L is higher above 2 MΩ, however, the MWNT-cellulose fibres can be served as simple and efficient electrochemical water “switches”.

Usually, water found natural environment or used in our ordinary life contains many other substances, including some ions which will increase the conductivity of the water. What is the influence of the ions on the sensitivity of CNT-cellulose fibres to such water might also attract much attention. Here, the sensing behaviour of MWNT-cellulose fibres to electrolyte solution was

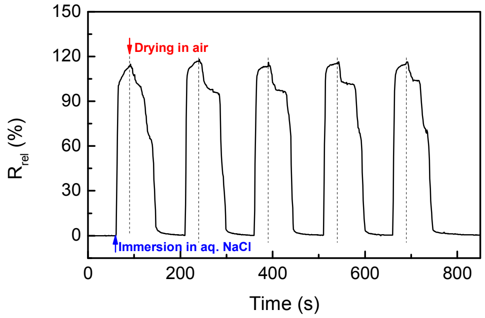

Fig. 6. Relative resistance change (R_{rel}) of the MWNT-cellulose fibres (CF01) during wetting/drying cycle in 1.0 wt% NaCl aqueous solution at 20 °C.

investigated using one example. Fig. 6 shows the typical resistive responses of MWNT-cellulose fibres (CF01) to 1 % NaCl aqueous solution. Similarly, they exhibit a rapid increase in resistance with increasing immersion time when immersed in NaCl aqueous solution, as well as reversible and reproducible sensing behaviour in the following drying process and repeated cycles. This character of the MWNT-cellulose fibres further broadens the field of practical applications. For example, it is possible to monitor the sweating from human body by using our MWNT-cellulose fibres in smart textiles. However, there is slight decrease in signal amplitudes compared with those of distilled water (Fig. 2a). As shown in Fig. 5S, furthermore, the amplitudes of the response decrease with the increase of concentration of NaCl in solution, especially for fibres with high initial resistance. This is because NaCl aqueous solution has much better conductivity than distilled water. According to equation (3), the value of R_{water} (here is the resistance of NaCl aqueous solution) cannot be ignored compared with R_{fibre} in this case. In our future work, further examination of the influence of different electrolyte solutions (e.g., the concentration, types of ions and so on) on the sensing behaviour of MWNT-cellulose fibres would be thoroughly investigated.

4 Conclusions

Electrically conductive MWNT-cellulose fibres have been prepared through a simple and efficient way by dip coating. The uniformly formed MWNT networks on the surfaces of fibres provide efficient conductive pathways, leading to the controllable resistance (R_L) of the MWNT-cellulose fibre in a large scale of 50 - 200,000 kΩ/cm. These conductive MWNT-cellulose fibres are demonstrated to be used as highly sensitive, well reversible and reproducible sensor for water, with a relative electrical resistance change of 100 - 8000%. For the overlapping mechanism of MWNT-cellulose in water sensing, the relative electrical resistance change increases with the increase of their initial resistance. And the MWNT-cellulose fibres with high resistance can even be served as simple and efficient electrochemical water "switches". Moreover, these functional fibres exhibited good sensibility to electrolytes aqueous solution. The unique sensibility of MWNT-cellulose fibres provides the potential to sense liquid water or aqueous solution in a reliable and efficient way, which can be widely used in water monitoring or other fields such as smart textiles and wearable technology.

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Notes and references

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Graphical Abstract

Cellulose-based fibres with unique and efficient sensing abilities to liquid water were realized by depositing multi-walled carbon nanotubes (MWNTs) on the surfaces of the fibres using a simple and scalable dip coating.