รายงานวิจัยฉบับสมบูรณ์

โครงการ: การศึกษาคุณสมบัติทางไฟฟ้าของท่อนาโนคาร์บอนแบบผนังสองชั้นที่เตรียมในรูปแบบฟิล์มบาง (~ 50 นาโนเมตร) ซึ่งใช้ตัวทำละลายเชิงชีวภาพโดยมีองค์ประกอบของน้ำเป็นหลักเพื่อการนำไปประยุกต์ใช้ทางด้านอิเล็คทรอนิกส์ในอนาคต

โดย นายพีรพงศ์ ยศประยูรศักดิ์ และคณะ

พฤษภาคม 2563

สัญญาเลขที่ MRG6080079

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โครงการ: การศึกษาคุณสมบัติทางไฟฟ้าของท่อนาโนคาร์บอนแบบผนังสองชั้นที่เตรียมในรูปแบบฟิล์มบาง (~ 50 นาโนเมตร) ซึ่งใช้ตัวทำละลายเชิงชีวภาพโดยมีองค์ประกอบของน้ำเป็นหลักเพื่อการนำไปประยุกต์ใช้ทางด้านอิเล็คทรอนิกส์ในอนาคต

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สนับสนุนโดยสำนักงานคณะกรรมการการอุดมศึกษา และสำนักงานกองทุนสนับสนุนการวิจัย

<u>โครงการ</u>

การศึกษาคุณสมบัติทางไฟฟ้าของท่อนาโนคาร์บอนแบบผนังสองชั้นที่เตรียมในรูปแบบฟิล์มบาง (~ 50 นาโนเมตร) ซึ่งใช้ตัวทำละลายเชิงชีวภาพโดยมีองค์ประกอบของน้ำเป็นหลักเพื่อการนำไปประยุกต์ใช้ทางด้านอิเล็คทรอนิกส์ในอนาคต

The study of electrical properties of double-walled carbon nanotubes dispersed in the environmental-friendly water-based solution prepared in dimension of thin films (~ 50 nm) for the future electronic applications

Abstract

A highly conductive paper is demonstrated using double-walled carbon nanotubes (DWCNTs) simply coated on cellulose fibers by filtration technique from an aqueous suspension. The DWCNT material in this work was non-covalently functionalized by hemicellulose, as a dispersant, which enabled their dispersibility in water. The electronic properties of DWCNT network on cellulose paper were investigated. The measurements show relatively good electrical conduction of the as-prepared samples with the lowest sheet resistance of about 178 Ω/□. Moreover, the flexibility of the DWCNT paper while bending at different conditions was examined and their relative conductivity was observed with a little deviation, indicating of great foldable properties. The results demonstrate that hemicellulose works well as a water-based dispersant without significant effect on the electrical properties of the DWCNT films on cellulose paper and can be further improved toward green and flexible paper-based electronic applications.

Keywords: Carbon nanotubes, Hemicellulose, Paper-based, Bending, Conductive paper

บทคัดย่อ

กระดาษที่มีความสามารถในการนำไฟฟ้าได้ถูกสร้างขึ้นด้วยการใช้วัสดุท่อคาร์บอนนาโนทิวบ์แบบผนังสองชั้นด้วยวิธีการเคลือบบนกระดาษเซลลูโลสโดยเทคนิคการกรอง ซึ่งสารละลายของท่อคาร์บอนนาโนทิวบ์ถูกเตรียมในน้ำด้วยการผสมสารช่วยละลายที่สกัดจากวัสดุชีวภาพคือเฮมิเซลลูโลส ชิ้นงานตัวอย่างที่ถูกสร้างขึ้นมาจะถูกวัดค่าทางไฟฟ้า ซึ่งจากผลการทดสอบพบว่าชิ้นงานตัวอย่างมีความสามารถในการนำไฟฟ้าได้ดี โดยค่าความต้านทานแบบแผ่นที่วัดได้มีค่าน้อยสุดประมาณ 178 Ω/□ นอกจากนั้นชิ้นงานตัวอย่างที่เตรียมบนกระดาษเซลลูโลสได้ถูกตรวจสอบคุณสมบัติความยืดหยุ่นด้วยการพับชิ้นงานที่เงื่อนไขต่างๆ ซึ่งจากผลการทดสอบพบว่าชิ้นงานตัวอย่างสามารถทนการพับงอได้ค่อนข้างดีโดยที่ความสามารถในการนำไฟฟ้ามีการเปลี่ยนแปลงเพียงเล็กน้อย ซึ่งแนวทางนี้อาจจะมีความสามารถในการนำไปประยุกต์ใช้งานกับงานวิจัยด้านอื่นในลักษณะการใช้งานเป็นขั้วไฟฟ้าจากกระดาษในอนาคตได้

Keywords: คาร์บอนนาโนทิวบ์, เฮมิเซลลูโลส, วัสดุพื้นฐานจากกระดาษ, สภาพโค้งงอ, กระดาษนำไฟฟ้า

Executive summary

Since carbon nanotubes (CNTs) have been discovered, they have a lot been studied as well as characterized in different essential properties for instance mechanical, optical and importantly electrical properties. In morphological details, CNTs are carbon-based materials that basically have a tubular structure with very high aspect ratio (length/diameter). They have been categorized into two main groups according to the number of walls which they contain, namely singled-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT). The SWCNT consists of only one layer throughout its composition while the MWCNT comprises of many walls along its structure. We can also particularly consider a nanotube configuration which composes of two carbon lattice layers as a double-walled carbon nanotube (DWCNT). Obviously, the diameter of CNTs depends on the number of their walls and can be as small as ~ 1-2 nm for SWCNTs. On the other hand, MWCNTs can be fabricated with the diameter range around 10-50 nm. Currently, with a variety of advanced techniques and tools, researchers are able to achieve the growth process for CNTs with an approximate length of centimeters, and thus resulting in a very large aspect ratio.

CNTs can be considered as a one-dimensional (1D) system and the charge transport properties have been widely studied at both room- and low temperature. In general, CNTs can be semiconducting or metallic, depending on their diameter and chirality, and these electronic behaviors clearly direct the applications. In the view of sensing, semiconducting CNTs are mostly exploited due to their great sensitivity to many physical, biological and chemical factors surrounding them. These external variables will definitely affect the nanotube electronic transport and the resistance change (or other electrical parameters) can be used as a sensing indication for each application. While talking about metallic CNTs, the utilization as conductive channels or thin films is most likely leading the race among other applications using metallic CNTs owing to their perfect electronic transport which is known as ballistic – specifically to be no resistance.

Besides, the practical configuration of CNT devices can be divided simply by the number of nanotubes in such device. CNTs can be utilized in different configurations such as individual tubes (single tubes separately), i.e. in the study of individual SWCNT field-effect transistors

(SWCNT-FETs), or networks, i.e. conductive thin films and composites. However, one major problem of fabricating these samples is the difficulty to prepare the well-dispersed CNT suspension because nanotubes tend to aggregate in solution by the effect of Van der Waal force. Once they re-combine as a black powder, the ultra-sonication will be necessary to separate them but of course damage the CNTs too. This problematic case will decrease the CNT transport quality no matter what configuration it is (individuals or network) due to not only forming as a bulky aggregate but also containing huge amount of amorphous carbon – badly conductive material indeed. This issue evidently leads to poor conductivity of CNT devices as well as relatively low efficiency. Therefore, a lot of efforts have been still carried on searching some either biological molecules (i.e. surfactants) or chemical solvent in order to dissolve carbon nanotubes well into solution as well as to increase their solubility.

The outer shell of CNTs plays very essential role in solubilizing themselves into any solution. Normally, CNTs are synthesized in a black powder form and intrinsically behave as a non-polar substance which is at some point difficult to deal with daily-life solutions (i.e. water, methanol, ethanol and so on). Therefore, it is absolutely required to dissolve CNT powder into a particular solution before using and also needed to disperse them well in such a way of separating all carbon nanotubes nicely and keeping them away from aggregation.

Since DWCNTs are slightly bigger than SWCNTs – resulting them in smaller band gap closely to metal, whereas much tinier than MWCNTs – making them able to densely pack in a film, then this project will only study the DWCNTs and mainly focus on the networked CNTs which will be fabricated as the conductive thin films. Their electrical properties will be measured and their morphologies will also be characterized at room temperature. The key point for having CNT thin film greatly conducted is the dispersion of CNTs in solution. Hence, if we could find the proper dispersive agents as well as the optimization of CNT concentrations and sample preparation methods, these can contribute to highly conductive CNT thin films which will be very useful for electronic applications in the future.

Carbon nanotubes (CNTs) have been well-known in their great electrical properties of both metallic and semiconducting behaviors. The ordinary way to use CNTs can be simply done through the deposition method in which CNTs are dissolved in a specific solvent and the solvent used in general is a polar chemical. In order to obtain the devices having great electrical transport, CNTs are necessary to be dispersed nicely and homogeneously in such solution. The problems of using chemicals as a solvent, however, are not only the danger of itself but also the aggregation of CNTs even though we have used a polar solvent. When the aggregation of CNTs occurs, the ultrasonication technique will be required to separate these bundles before the next use. In fact, the ultrasonication process has been known as a destructive mechanism that can damage and also cut the CNTs into shorter pieces. These effects will finally decrease the electrical properties of CNT devices.

The key idea of this project is to find the practical surfactants (acting similarly as solvent) which are able to disperse carbon nanotubes nicely and homogeneously in solution. Additionally, the challenge of this idea is to find the biomolecules that can dissolve CNTs into water and do not decrease their electronic properties. Besides and importantly, the selected biomolecules must stop the aggregation process, in which the ultrasonication is then unnecessary. In fact, carbon nanotubes cannot easily be dissolved in water but there is a possibility with the help of surfactants.

Research Details

Experimental

- **Materials**

DWCNTs with the purity of > 50 wt%, having an average length of 2 μm and approximately 2-3 nm in diameters, were purchased from Unidym Co. (USA). The hemicellulose, obtained as xylan molecules, was purchased from Symrise Bio Actives GmbH (Germany) and used as a dispersive material. The deionized water (DI) was used as media solution for CNT/HC complex. Cellulose filter paper (Whatman #5) was employed as a substrate for all experiments.

- **Methods**

Preparation of water-based CNT/HC suspension

The method for preparing CNT/HC dispersion has been previously reported and briefly as; 100 mg of DWCNTs and 1 ml of 2-propanol were mixed into 100 ml of DI water, followed with ultrasonication for 1 min. A 100 mg of hemicellulose was added into a mixture by four portions of each 25 mg and the sonication was performed for 4 min between each addition. A collected 10 ml of this dispersion was diluted with 390 ml of water and kept sonicating for 4 min. Then, the diluted suspension was used for entire experiments.

Preparation of CNT-coated cellulose paper

A cellulose filter paper was firstly prepared with the size of 10 x 20 mm2 and employed as the substrate. Since simple, quick and inexpensive methods are widely considered for paper electronics, the filtration technique was selected in this work. The CNT/HC dispersion was then filtered onto cellulose paper and followed by drying in ambient condition.

- **Characterization techniques**

Scanning and Transmission electron microscopy

The surface morphology of CNT paper was obtained by the field emission scanning electron microscope (JSM-7001F FE-SEM) with the acceleration voltages of 3-10 kV. The TEM images were carried out by a JEOL JEM-2100 TEM under the acceleration voltage of 200 kV.

Raman spectroscopy

The Raman spectra of CNT paper at room temperature were obtained by a JOBIN YVON HORIBA T64000 RAMAN SPECTROMETER, acquired with a 532 nm excitation laser and the scanning range of 50-2000 cm^{-1} by the spectral resolution of 1 cm^{-1}.

Electrical properties

Prior to the electrical conduction measurements, a CNT-coated cellulose paper was cut into a size of 2 x 20 mm^2 and then contacted both ends with the adhesive copper tape where a tiny amount of silver paint was used to help for complete contacts due to the surface roughness of cellulose paper, as shown in Fig.1.

The electrical conduction of as-prepared CNT cellulose paper was measured with two-terminal probe technique by national instruments (NI) equipped with NI PCIe-6341, BNC-2090A and SR570 low noise current preamplifier as the current-voltage (I-V) characteristics, while the sheet resistance was carried out by four-point probe technique with Keithley 2400 source-meter. In addition, the electrical measurement for the flexibility test was performed by a digital multimeter (HIOKI DT4212).

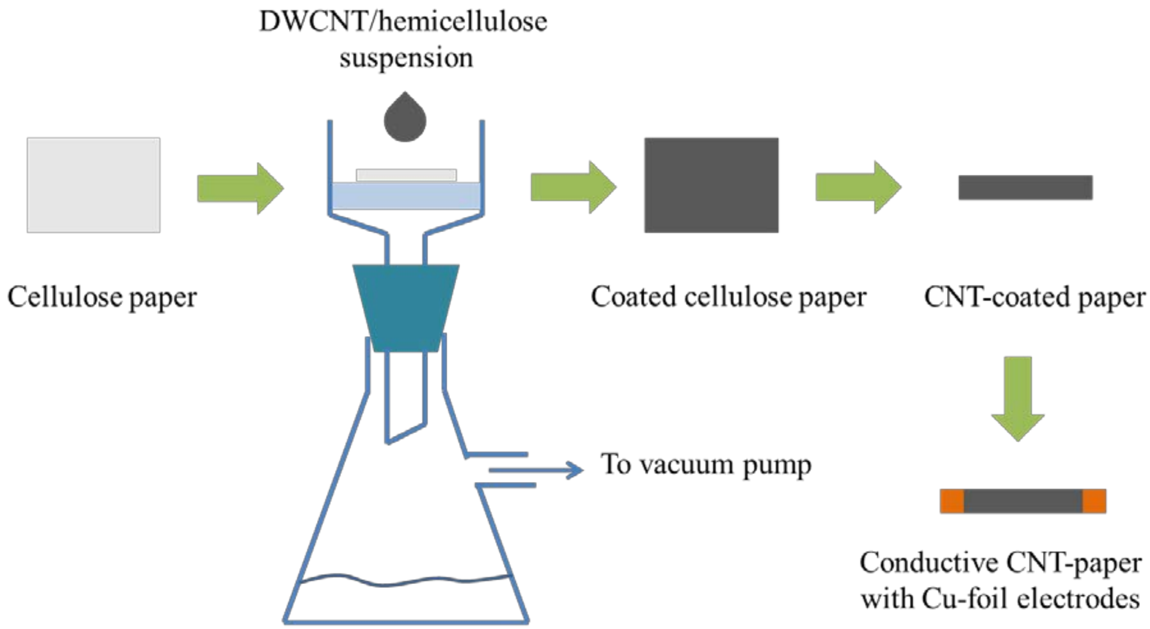

Fig. 1. Schematic of a simple fabrication for CNT films on cellulose paper.

Results and discussion

The optical photograph of the as-prepared sample is displayed in Fig. 2(a) and the morphologies of the CNT papers examined by scanning electron microscopy are shown in Fig. 2(b-c). The SEM images indicate that the formation of the filtrated CNTs on cellulose paper is highly dense as well as firmly entangled with the cellulose fibers. Moreover some hair-like structures of CNTs can be observed at the edge of the cut CNT paper as illustrated in Fig. 2(b). Transmission electron micrograph of the DWCNTs (Fig. 2(d)) reveals their inner diameter of approximately 3.1 nm and outer diameter of about 3.8 nm, as well as the tube walls of nanotube (indicated by red arrows) are clearly observed with the double concentric-walled structure.

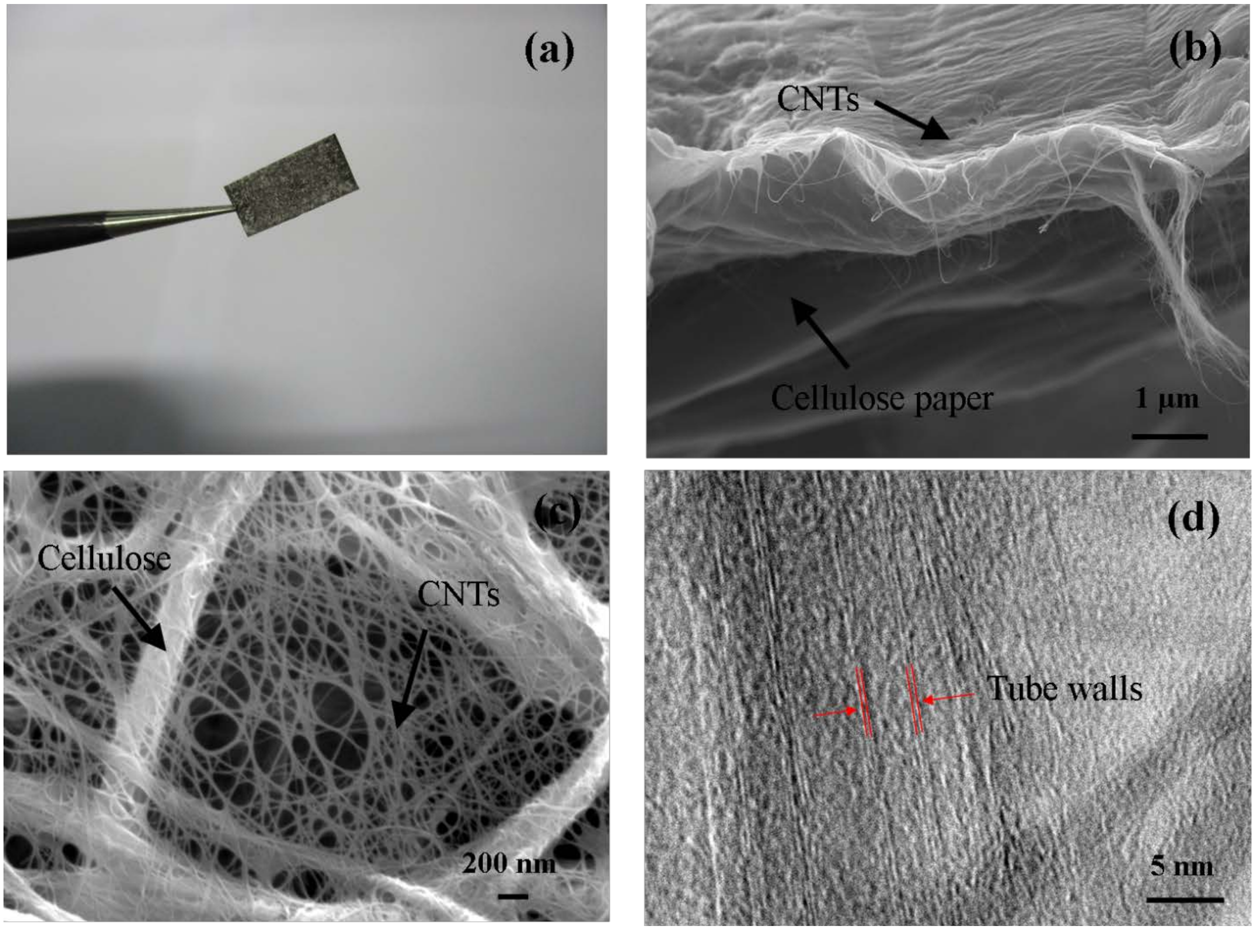

Fig. 2. (a) Photo image of the CNT network on paper. SEM images of the CNTs filtrated on cellulose paper with (b) perspective view and (c) top view. (d) TEM image revealing double tube walls of CNT.

The Raman spectrum of CNTs coated on cellulose paper is shown in Fig. 3 with the measured peaks at approximately 1582.5 cm^{-1} (G-band), 1335.5 cm^{-1} (D-band), 272.3 cm^{-1} and 161.5 cm^{-1} (radial breathing mode, RBM). The G-band is typically corresponding to the vibration characteristics of CNTs while the D-band can be considered as the defect-induced band or amorphous carbon, and thus can be used to analyze the crystallinity of CNTs. A very high intensity of G-band over the D-band indicates that the structure of CNTs is highly graphitic and crystalline with very little defects. The RBM peaks in Raman spectroscopy are typically found in

DWCNTs and this feature depends inversely on the nanotube diameter, where the RBM frequencies above 250 cm^{-1} and below 250 cm^{-1} are associated with the inner and outer tubes, respectively. Here, the estimation of the inner and outer tube diameters for RBM peaks at 272.3 cm^{-1} and 161.5 cm^{-1} is acquired to 0.85 nm and 1.50 nm, respectively.

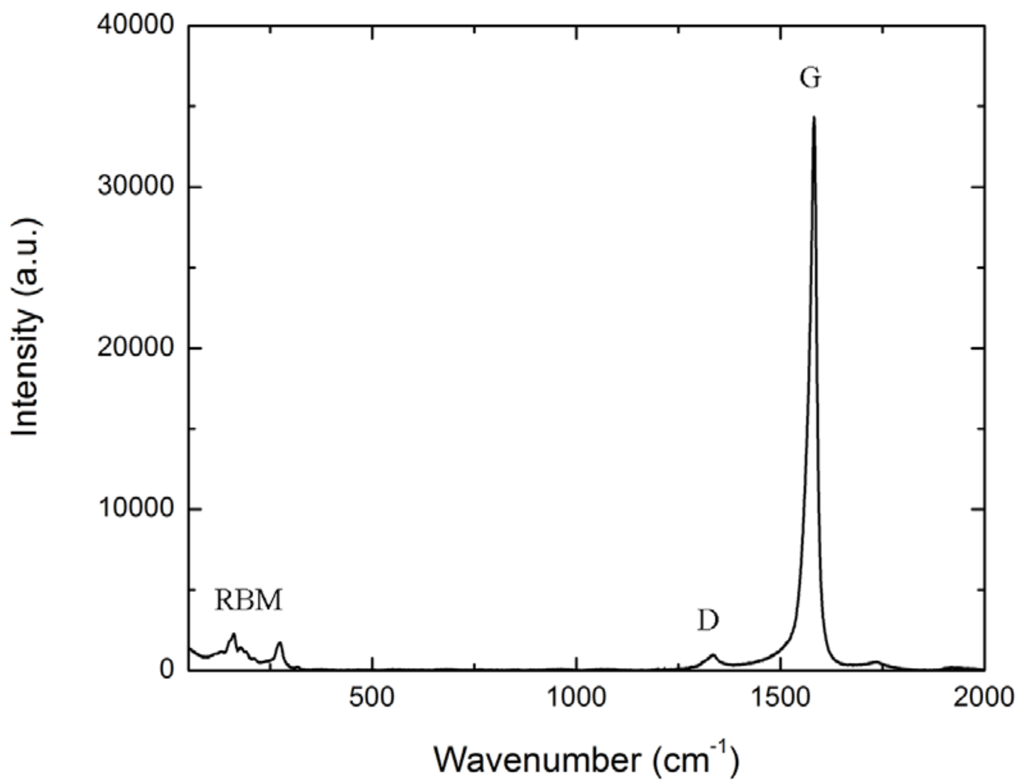

Fig. 3. Raman spectrum of DWCNT/HC complex on cellulose paper.

Fig. 4 shows the current-voltage (I-V) characteristics of a conductive CNT paper and a bare cellulose paper measured at ambient condition. The electrical measurements were performed by 2-probe technique as illustrated in the inset of Fig. 4 with the sweeping voltage range of ±100 mV. The conducting CNT paper shows an ohmic I-V response with the resistance of approximately 157 Ω, whereas no current was monitored in a bare cellulose paper, implying the insulating properties. Since the electrical resistance of the processed cellulose fibers is relatively small and constant over the applied voltages, the CNT/HC complex material can be utilized as a conducting paper with a low power operation.

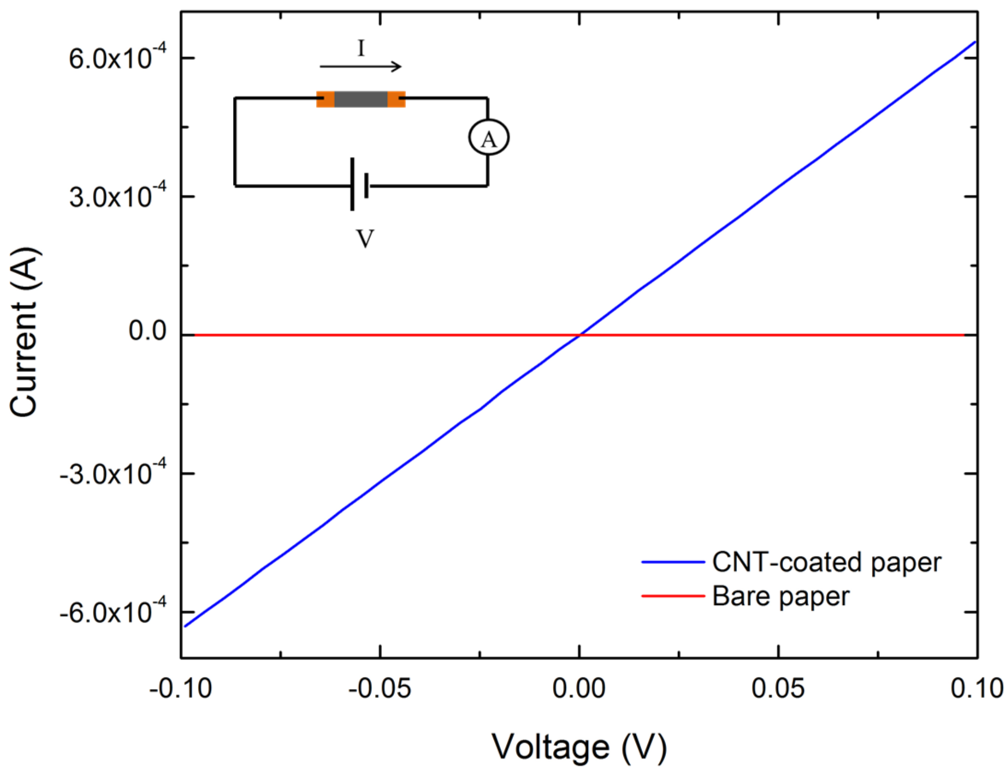

Fig. 4. The current-voltage (I-V) characteristics of an unprocessed paper and a CNT paper. Inset: A schematic of the electrical measurement setup.

The flexibility of conductive CNT papers was investigated by folding and unfolding at different angles as illustrated in Fig. 5(a), in which the nanotube networks are folded inwards and outwards for positive and negative angles, respectively. Fig. 5(b-c) shows the electronic capability of as-prepared conducting cellulose paper connected to LED lamp and a 3V battery pack while being flat and bent. The LED emission is somewhat bright due to low sheet resistance of approximately 178 Ω/□. The effect of bending on electrical conduction of CNTs on cellulose paper was measured and compared with the initial conduction before started folding.

Fig. 5(d) displays the relative resistance (R/R_o) of a conductive CNT paper measured as a function of bending angle where the complete loop of the same device was performed by $0^{\circ} \longrightarrow +180^{\circ} \longrightarrow 0^{\circ} \longrightarrow -180^{\circ} \longrightarrow 0^{\circ}$. The deviation of relative resistance is up to 2% under one complete folding rotation, indicating the foldable properties of the CNT paper with a very little change in electrical conduction. Furthermore, the relative resistances of the conductive cellulose paper were investigated as a function of bending turns (at $\pm180^{\circ}$), as shown in Fig. 5(e). The increase of relative resistance is about 5% and 4% after folded by 100 turns at $+180^{\circ}$ and -180°, respectively. This reveals that the CNT films on cellulose papers can endure at least up to 100 bending cycles with no tearing of the cellulose fibers.

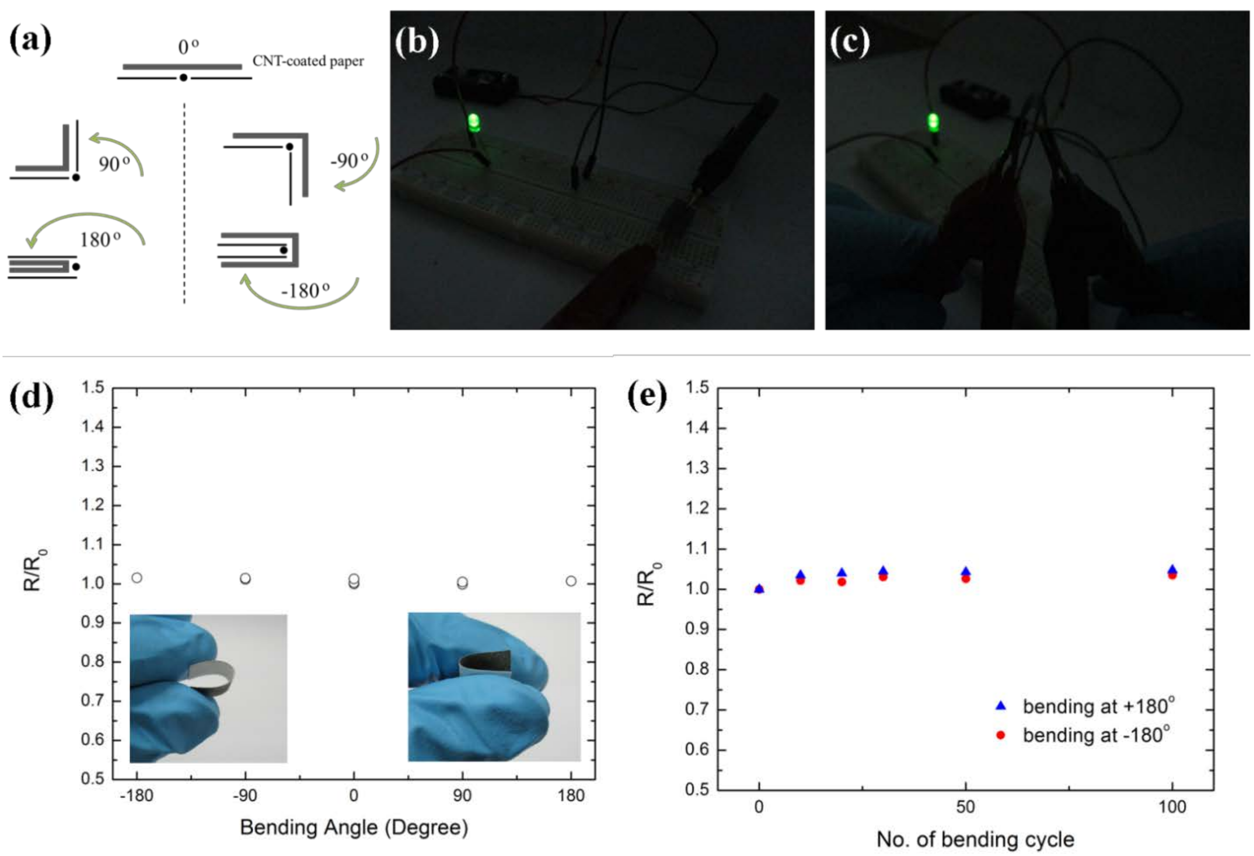

Fig. 5. (a) A schematic illustration of a CNT paper bending at different angles. The lighting of green LED wired to a straight (b) and a curved (c) CNT paper. (d) The measured relative resistance (R/R_o) of the CNT paper folded at different specific angles. Inset: Demonstration of

CNT sample folding at -180° (left) and +180° (right). (e) The measurement of relative resistances of the CNT paper as a function of bending cycle.

As a result, the electrical conduction of the networked films from CNT/HC complex material on cellulose paper is relatively high, which is comparable to pure CNT materials [27-28]. This indicates that the presence of hemicellulose in CNT network on paper does not significantly alter the conduction process between the interconnected nanotube junctions. Moreover, the surface roughness and porosity of the paper tend to accommodate the CNTs tightly, thus leading to firmly adhesion on paper [29]. This can assist the CNT/HC complex material to entwine with the cellulose fibers so that the densely packed CNT/HC films are highly conductive as well as flexible and foldable with a little change in their electronic conduction.

Conclusions

The aqueous dispersion of CNT/HC complex was simply prepared in an environmental-friendly approach without chemical functionalization on nanotubes. The densely packed and uniform films of a water-based CNT/HC suspension were easily fabricated on cellulose paper by a filtration method. The electrical conduction of the CNT films on cellulose fibers shows a linear I-V response with a relatively high conductivity comparable to pure CNT materials, implying of no effect from hemicellulose as an electrical insulating layer in this material. The flexibility of CNT-coated papers was demonstrated by folding in different angles and several numbers of bending cycles, in which the electronic conduction slightly changes relative to their initial value. This conductive CNT film on paper substrate is flexible and biodegradable, as well as can be extended to other paper-based applications, especially for the utility as a green conductive paper electrode.

Conductive and flexible cellulose paper from carbon nanotubes in aqueous solution using hemicellulose dispersant

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Keywords: carbon nanotubes, hemicellulose, paper-based, bending, conductive paper

Abstract

A highly conductive paper is demonstrated using double-walled carbon nanotubes (DWCNTs) simply coated on cellulose fibers by filtration technique from an aqueous suspension. The DWCNT material in this work was non-covalently functionalized by hemicellulose, as a dispersant, which enabled their dispersibility in water. The electronic properties of DWCNT network on cellulose paper were investigated. The measurements show relatively good electrical conduction of the as-prepared samples with the lowest sheet resistance of about 178 Ω/□. Moreover, the flexibility of the DWCNT paper while bending at different conditions was examined and their relative conductivity was observed with a little deviation, indicating of great foldable properties. The results demonstrate that hemicellulose works well as a water-based dispersant without significant effect on the electrical properties of the DWCNT films on cellulose paper and can be further improved toward green and flexible paper-based electronic applications.

1. Introduction

Carbon nanotubes (CNTs) have been attractive in a wide range of research areas owing to their remarkable mechanical, optical and electrical properties [1-2]. CNTs can be basically utilized in different configurations such as individual tubes and networks [3-4]. The various potential applications of CNTs as supercapacitors, perovskite solar cells, sensors as well as conductive and reinforcing filler materials have been reported in recent years [5-8].

Since CNTs are very small and difficult to deal with a single or a few tubes, they are often used not only as thin films but also to mix with other substances for making composite materials in several applications, such as thin-film transistors and CNT-cellulose composites [9-10]. Moreover, the cellulose fibers can also be employed as a paper substrate for the green electronic devices due to their naturally flexible, disposable and biodegradable properties [11-12]. Especially in nowadays, the key point of utilization in electronic-based applications has turned towards eco-friendly, point-of-care and low-cost devices [13-14]. As has been demonstrated in various works [15-17], the CNT-based devices fabricated on cellulose paper substrates have been implemented for potential paper-based applications such as flexible energy storage devices, conducting papers and gas sensors.

However, one of the major problems for fabricating these samples is the difficulty to prepare the well-dispersed CNT suspension because of their aggregation by van der Waals forces between each nanotube which can affect their performance when being used in actual devices [18-19]. Previously, a typical method for dispersing CNTs has been commonly achieved via hazardous organic solvents i.e. chloroform, dichlorobenzene and dimethylformamide [20], which requires expensive equipment and can be harmful to users. Thus, a lot of efforts have been carried out by mixing various biological dispersants, such as hydrophobin and cellulose nanofibrils, into water-based CNT solution in order to increase the solubility and dispersibility as well as, at the same time, being environment-friendly [21-23].

In this paper, we report the electrical conduction properties of double-walled carbon nanotubes (DWCNTs) dispersed in aqueous solution by using hemicellulose (HC) as a dispersant material. Here, the amount of DWCNTs and HC used for dispersing is comparable, thus forming as complex suspension. The networked films of a water soluble CNT/HC complex were prepared on cellulose paper substrate as a green flexible conductive paper.

2. Experimental

2.1 Materials

DWCNTs with the purity of > 50 wt%, having an average length of 2 μm and approximately 2-3 nm in diameters, were purchased from Unidym Co. (USA). The hemicellulose, obtained as xylan molecules, was purchased from Symrise Bio Actives GmbH (Germany) and used as a dispersive material. The deionized water (DI) was used as media solution for CNT/HC complex. Cellulose filter paper (Whatman #5) was employed as a substrate for all experiments.

2.2 Methods

2.2.1 Preparation of water-based CNT/HC suspension

The method for preparing CNT/HC dispersion has been previously reported as in Ref. [24]. Briefly, 100 mg of DWCNTs and 1 ml of 2-propanol were mixed into 100 ml of DI water, followed with ultrasonication for 1 min. A 100 mg of hemicellulose was added into a mixture by four portions of each 25 mg and the sonication was performed for 4 min between each addition. A collected 10 ml of this dispersion was diluted with 390 ml of water and kept sonicating for 4 min. Then, the diluted suspension was used for entire experiments.

2.2.2 Preparation of CNT-coated cellulose paper

A cellulose filter paper was firstly prepared with the size of 10 x 20 mm^2 and employed as the substrate. Since simple, quick and inexpensive methods are widely considered for paper electronics, the filtration technique was selected in this work. The CNT/HC dispersion was then filtered onto cellulose paper and followed by drying in ambient condition.

2.3 Characterization techniques

2.3.1 Scanning and Transmission electron microscopy

The surface morphology of CNT paper was obtained by the field emission scanning electron microscope (JSM-7001F FE-SEM) with the acceleration voltages of 3-10 kV. The TEM images were carried out by a JEOL JEM-2100 TEM under the acceleration voltage of 200 kV.

2.3.2 Raman spectroscopy

The Raman spectra of CNT paper at room temperature were obtained by a JOBIN YVON HORIBA T64000 RAMAN SPECTROMETER, acquired with a 532 nm excitation laser and the scanning range of 50-2000 cm^{-1} by the spectral resolution of 1 cm^{-1}.

2.3.3 Electrical properties

Prior to the electrical conduction measurements, a CNT-coated cellulose paper was cut into a size of 2 x 20 mm^2 and then contacted both ends with the adhesive copper tape where a tiny amount of silver paint was used to help for complete contacts due to the surface roughness of cellulose paper, as shown in Fig.1.

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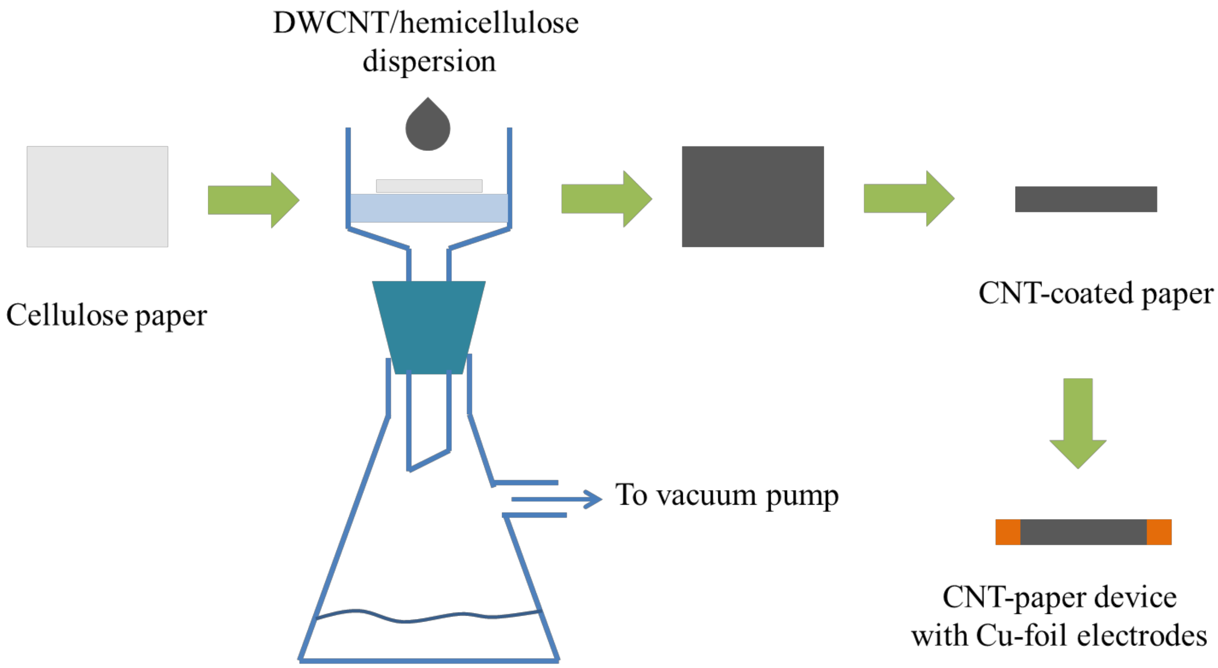

Fig. 1. Schematic of a simple fabrication for DWCNT/HC films on cellulose paper.

3. Results and discussion

The optical photograph of the as-prepared sample is displayed in Fig. 2(a) and the morphologies of the CNT papers examined by scanning electron microscopy are shown in Fig. 2(b-c). The SEM images indicate that the formation of the filtrated CNTs on cellulose paper is highly dense as well as firmly entangled with the cellulose fibers. Moreover some hair-like structures of CNTs can be observed at the edge of the cut CNT paper as illustrated in Fig. 2(b). Transmission electron micrograph of the DWCNTs (Fig. 2(d)) reveals their inner diameter of approximately 3.1 nm and outer diameter of about 3.8 nm, as well as the tube walls of nanotube (indicated by red arrows) are clearly observed with the double concentric-walled structure.

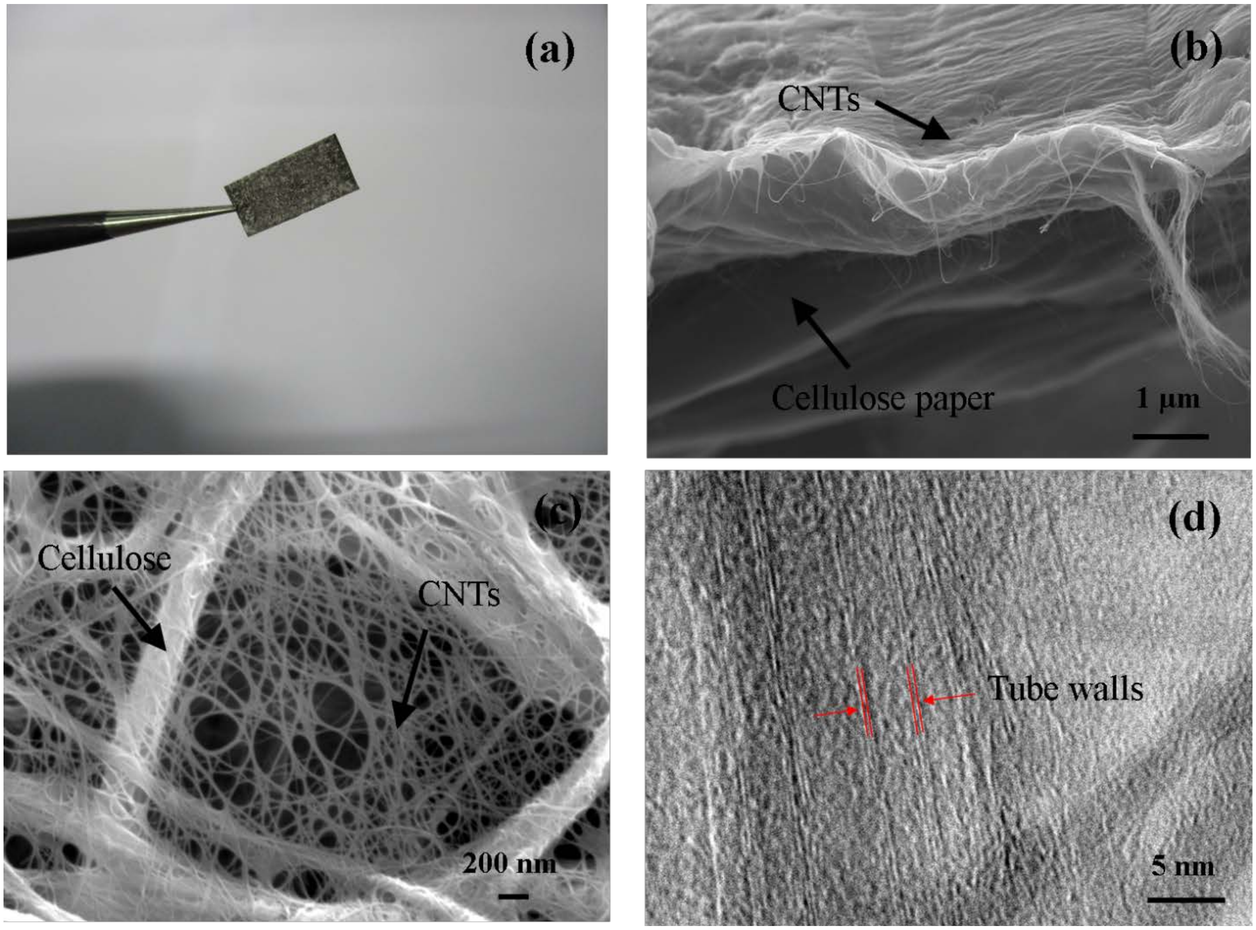

Fig. 2. (a) Photo image of the CNT network on paper. SEM images of the CNTs filtrated on cellulose paper with (b) perspective view and (c) top view. (d) TEM image revealing double tube walls of CNT.

The Raman spectrum of CNTs coated on cellulose paper is shown in Fig. 3 with the measured peaks at approximately 1582.5 cm^{-1} (G-band), 1335.5 cm^{-1} (D-band), 272.3 cm^{-1} and 161.5 cm^{-1} (radial breathing mode, RBM). The G-band is typically corresponding to the vibration characteristics of CNTs while the D-band can be considered as the defect-induced band or amorphous carbon, and thus can be used to analyze the crystallinity of CNTs [25]. A very high intensity of G-band over the D-band indicates that the structure of CNTs is highly graphitic and crystalline with very little defects. The RBM peaks in Raman spectroscopy are typically found in DWCNTs and this feature depends inversely on the nanotube diameter, where the RBM frequencies above 250 cm^{-1} and below 250 cm^{-1} are associated with the inner and outer tubes, respectively [26]. Here, the estimation of the inner and outer tube diameters for RBM peaks at 272.3 cm^{-1} and 161.5 cm^{-1} is acquired to 0.85 nm and 1.50 nm, respectively.

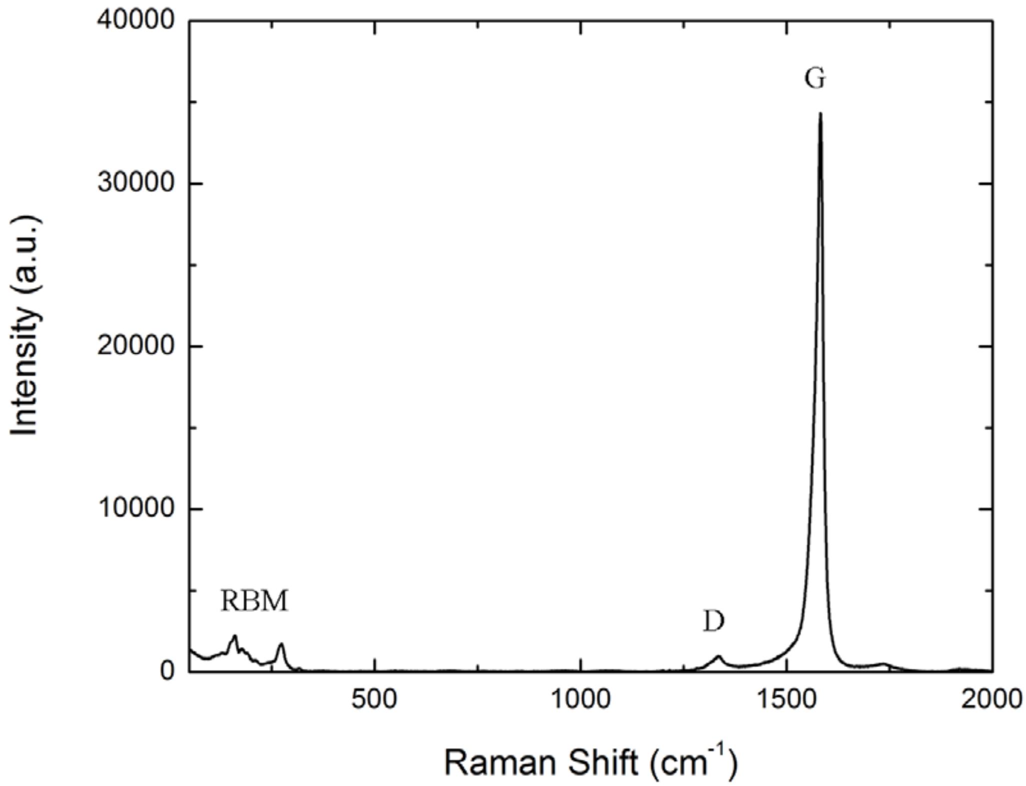

Fig. 3. Raman spectrum of DWCNT/HC complex on cellulose paper.

Fig. 4 shows the current-voltage (I-V) characteristics of a conductive CNT paper and a bare cellulose paper measured at ambient condition. The electrical measurements were performed by 2-probe technique as illustrated in the inset of Fig. 4 with the sweeping voltage range of ±100 mV. The conducting CNT paper shows an ohmic I-V response with the resistance of approximately 157 Ω, whereas no current was monitored in a bare cellulose paper, implying the insulating properties. Since the electrical resistance of the processed cellulose fibers is relatively small and constant over the applied voltages, the CNT/HC complex material can be utilized as a conducting paper with a low power operation.

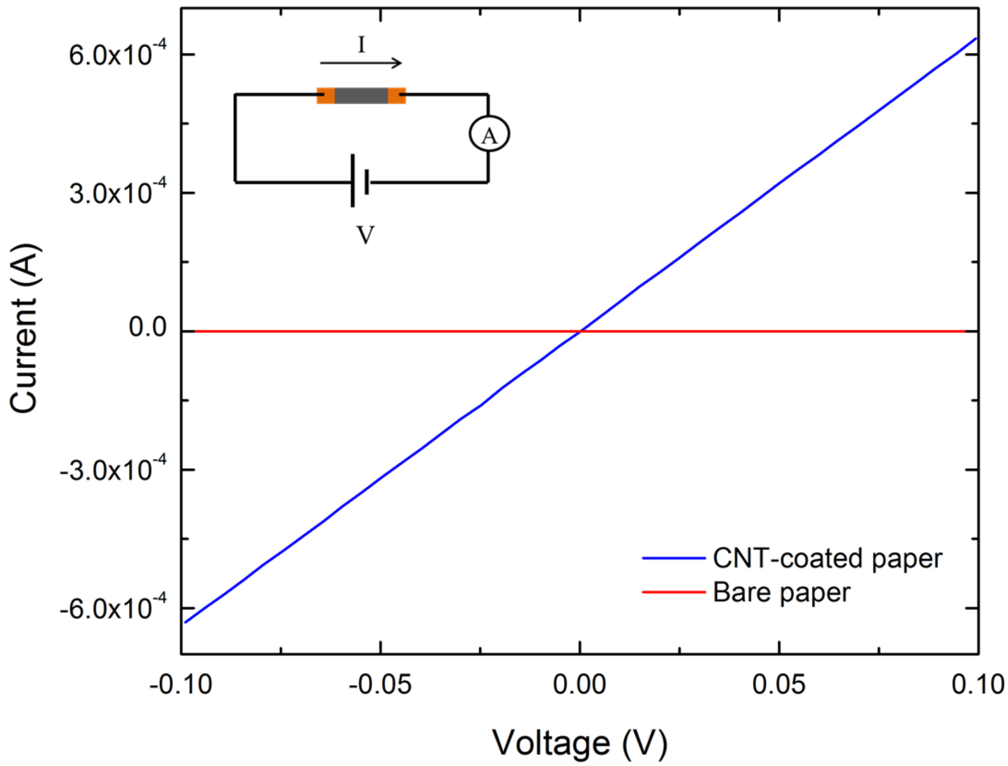

Fig. 4. The current-voltage (I-V) characteristics of an unprocessed paper and a CNT paper. Inset: A schematic of the electrical measurement setup.

The flexibility of conductive CNT papers was investigated by folding and unfolding at different angles as illustrated in Fig. 5(a), in which the nanotube networks are folded inwards and outwards for positive and negative angles, respectively. Fig. 5(b-c) shows the electronic capability of as-prepared conducting cellulose paper connected to LED lamp and a 3V battery pack while being flat and bent. The LED emission is somewhat bright due to low sheet resistance of approximately 178 Ω/□. The effect of bending on electrical conduction of CNTs on cellulose paper was measured and compared with the initial conduction before started folding. Fig. 5(d) displays the relative resistance (R/R_o) of a conductive CNT paper measured as a function of bending angle where the complete loop of the same device was performed by $0^o \rightarrow +180^o \rightarrow 0^o \rightarrow -180^o \rightarrow 0^o$. The deviation of relative resistance is up to 2% under one complete folding rotation, indicating the foldable properties of the CNT paper with a very little change in electrical conduction. Furthermore, the relative resistances of the conductive cellulose paper were investigated as a function of bending turns (at ±180^o), as shown in Fig. 5(e). The increase of relative resistance is about 5% and 4% after folded by 100 turns at +180^o and -180^o, respectively. This reveals that the CNT films on cellulose papers can endure at least up to 100 bending cycles with no tearing of the cellulose fibers.

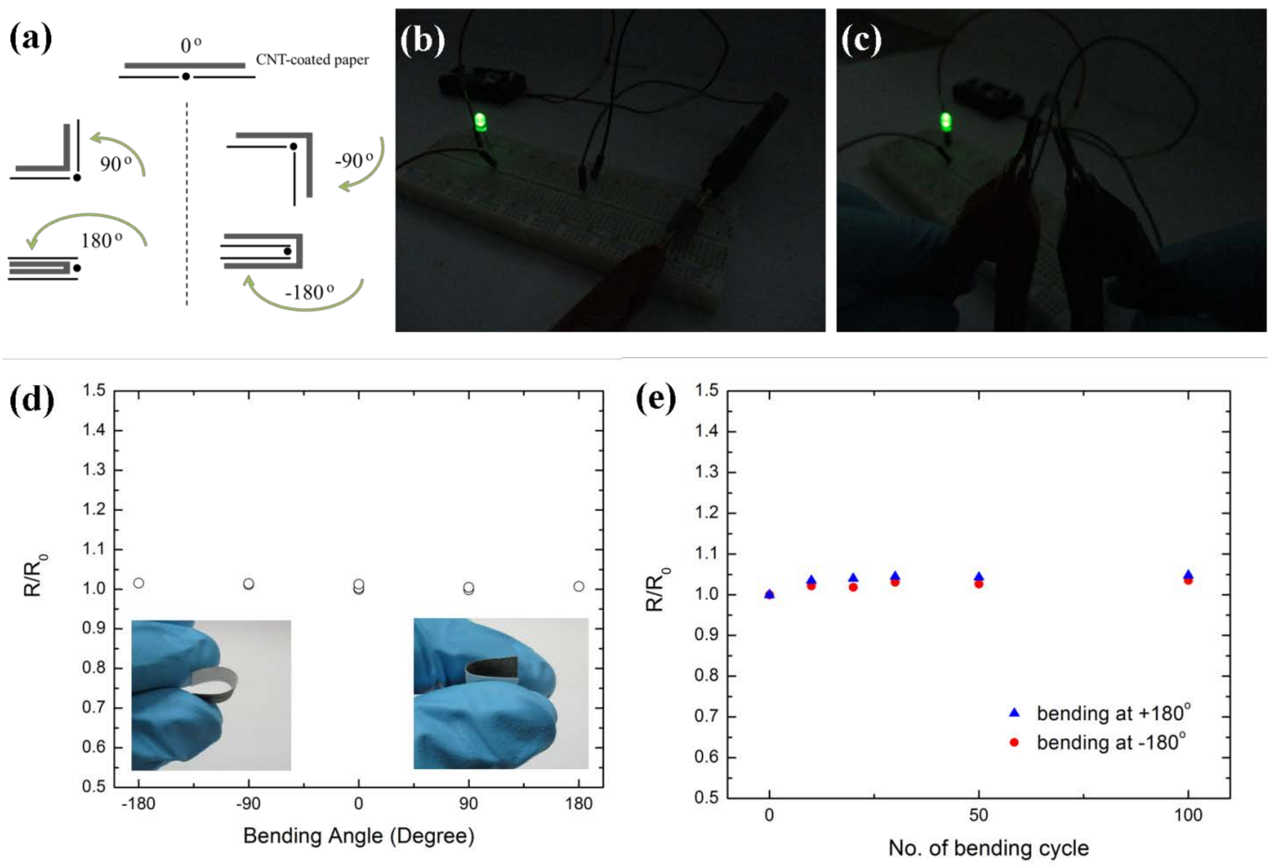

Fig. 5. (a) A schematic illustration of a CNT paper bending at different angles. The lighting of green LED wired to a straight (b) and a curved (c) CNT paper. (d) The measured relative resistance (R/R_o) of the CNT paper folded at different specific angles. Inset: Demonstration of CNT sample folding at -180^o (left) and +180^o (right). (e) The measurement of relative resistances of the CNT paper as a function of bending cycle.

As a result, the electrical conduction of the networked films from CNT/HC complex material on cellulose paper is relatively high, which is comparable to pure CNT materials [27-28]. This indicates that the presence of hemicellulose in CNT network on paper does not significantly alter the conduction process between the interconnected nanotube junctions. Moreover, the surface roughness and porosity of the paper tend to accommodate the CNTs tightly, thus leading to firmly adhesion on paper [29]. This can assist the CNT/HC complex material to entwine with the cellulose fibers so that the densely packed CNT/HC films are highly conductive as well as flexible and foldable with a little change in their electronic conduction.

4. Conclusions

The aqueous dispersion of CNT/HC complex was simply prepared in an environmental-friendly approach without chemical functionalization on nanotubes. The densely packed and uniform films of a water-based CNT/HC suspension were easily fabricated on cellulose paper by a filtration method. The electrical conduction of the CNT films on cellulose fibers shows a linear I-V response with a relatively high conductivity comparable to pure CNT materials, implying of no effect from hemicellulose as an electrical insulating layer in this material. The flexibility of CNT-coated papers was demonstrated by folding in different angles and several numbers of bending cycles, in which the electronic conduction slightly changes relative to their initial value. This conductive CNT film on paper substrate is flexible and biodegradable, as well as can be extended to other paper-based applications, especially for the utility as a green conductive paper electrode.

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