Improving mechanical and electrical properties of oriented polymer-free multi-walled carbon nanotube paper by spraying while winding

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ABSTRACT

In this study, a new method is introduced for fabricating carbon nanotube (CNT) paper, in which the solvent is sprayed on the CNT sheet while it is wound on a rotating mandrel. As the solvent evaporated, the capillary force pulls CNT closer together, resulting in a CNT paper with a high degree of alignment and a high packing density. Three batches of multi-walled CNTs with different wall thicknesses, tube diameters and lengths are utilized for synthesizing highly oriented CNT papers. It is found that CNTs with smallest diameter of 8 nm form strongest CNT paper with a tensile strength of 563 MPa and a tensile modulus of 15 GPa, while that made with CNTs of 10 nm diameter shows the highest electrical conductivity of 5.5×10\(^{-4}\) S/m.

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1. Introduction

Due to the unique structure and extraordinary properties, carbon nanotubes (CNTs) have drawn much attention during the last two decades. For individual CNTs, the tensile strengths are in the range of 10–63 GPa, and Young’s moduli between 0.27 and 1.47 TPa [1–3]. The combination of their exceptional mechanical properties and electrical conductivity [4–6] makes CNTs very promising materials in various applications [7,8]. For the same reason, CNT paper formed by CNT network possesses great potential for actuator, capacitors, battery electrode and reinforcement for composites [9–16]. However, traditional methods for fabricating CNT paper involve dispersion and filtration of suspended tubes, usually single-walled carbon nanotubes, accompanied with crookedness and agglomeration of CNTs in the CNT paper, limiting their strength and electrical conductivity [17,18]. To sufficiently utilize the unique properties of CNTs, a desirable CNT paper structure with compacted long and aligned nanotubes is critical.

Many new approaches have been developed to fabricate the highly oriented CNT paper by utilizing the vertically aligned CNT (VACNT) array. For example, Wang et al. have used a “domino pushing” method by pushing down the VACNT array to the aligned CNT paper [19]. The electrical conductivity along the alignment of the CNT paper is 2.0×10\(^{-4}\) S/m. Similarly, by shear pressing the VACNT array of about 1.4 mm height, Bradford et al. made the aligned CNT preform with tensile strength of 16 MPa and electrical conductivity of 1.2×10\(^{-4}\) S/m parallel to the alignment of the CNTs [14]. However, in the above methods, the size of the CNT paper is limited by the size of the substrate supporting the VACNT during its synthesis. Recently, anisotropic A4 sheet CNT paper were obtained by Inoue et al. through firstly winding the draw-out CNT web (10 m/s drawing speed) from the 2.0-mm-high drawable VACNT array and then ethanol spray was applied to densify the structure afterwards [20]. This approach allows the aligned CNT in the draw-out web transformed into the CNT paper, forming a compact structure without disrupting the alignment. The CNT paper has a tensile strength of 75.6 MPa and electrical conductivity of 7.56×10\(^{-4}\) S/m [20]. However, the strength of the CNT paper produced using this method is still relatively low compared with that of the component CNTs. Since the intermolecular bonds are the only forces holding the CNTs together, if the intermolecular attraction between the CNTs is increased, the efficiency of load transfer among the neighboring CNTs may also be improved, leading to an elevated tensile strength.
In this paper, a new and facile method, namely spraying while winding (SWW), was introduced for synthesizing CNT paper. It allows a decreasing of the inter-tube distances and thus increases attractions among the neighboring CNTs, leading to an improved strength of the CNT paper without sacrificing its electrical conductivity. Through this method, CNT paper with tunable orientation, size and thickness can be obtained in only one-step. Three different VACNT arrays were used to provide forest-drawn CNT sheet as the nanotube sources.

2. Experimental

2.1. Preparation of CNT paper

Three different VACNT Arrays, namely CNT-1, CNT-2 and CNT-3, were synthesized in a chemical vapor deposition system by different catalysts. CNT-1 and CNT-2 arrays were grown using CVD from catalyst of deposited thin iron films [21], while CNT-3 arrays were grown by one-step chloride-mediated CVD [22]. These vertically aligned CNTs have uniform height and can be pulled out as a layer of CNT sheet continuously. Fig. 1 demonstrates SWW approach for fabricating aligned CNT paper, where a CNT sheet was drawn out of a VACNT array and wound on a rotating mandrel covered by aluminum foil. During the processing, a solution with equal volumes of deionized water and ethanol was sprayed on the CNT sheet. The as-stacked sheets were densified due to the capillary force caused by the evaporation of the solvents [23]. To allow the solvents fully evaporated before covered by the subsequent wound CNT sheet, the CNT sheet drawing speed was kept at 18 mm/s according to our previous study [24]. By choosing an appropriate mandrel diameter, sheet width, and number of revolutions, highly orientated CNT papers with the desired size and thickness were produced by pealing them off the aluminum foil. In this study, the diameter of the mandrel was 4 cm and the CNT paper width was controlled around 5 mm to lower the CNT cost.

2.2. Microscopy analysis

Transmission electron microscopy (TEM) images of individual CNTs were collected in a TEM machine (Model JEOL 2010F) operation at 200 kV to measure the diameter and number of walls of CNTs. Scanning electron microscopy analysis (Model JEOL 6400F) was used to determine the arrangement of the CNTs in the CNT paper.

2.3. Determination of VACNT array quality

The quality of VACNT arrays was assessed using Renishaw Ramascope. The laser of 514 nm wavelength was focused on the sample through a Reinshaw microscope.

![Spray gun, Mandrel, CNT array, CNT sheet](image)

**Fig. 1.** Schematic view of the spraying while winding process for fabricating CNT paper. A CNT sheet is drawn out of a drawable VACNT array and continuously wound onto a rotating mandrel on which micrometer-sized droplets of DI water/ethanol are deposited.

3. Results and discussion

3.1. Structure of the CNTs

Fig. 2 shows the TEM images of the CNT-1, CNT-2 and CNT-3 nanotubes. These tubes differed from each other greatly in their diameter and number of walls as shown in Table 1. The CNT-1 tubes were mainly double- and triple-walled and about 8 nm in diameter. The CNT-2 tubes had mostly 6 walls and diameters ranging from 8 to 10 nm. The CNT-3 tubes were mainly wall-y-walled (about 50) and the outer diameter was also very large, around 45 nm. CNT-1, CNT-2 and CNT-3 were 200, 300 and 700 μm in lengths respectively.

![Raman spectra of CNT-1, CNT-2 and CNT-3](image)

**Fig. 3.** Raman spectra of CNT-1, CNT-2 and CNT-3. As indicated by the ratio \(I_D/I_G\) of the D and G band intensities of the Raman scattering spectrum which was 0.54 and 0.63 for the CNT-1 and CNT-2 arrays, more defects were found as the number of walls increased. It suggested that the thinner CNT-1 tubes contained fewer defects and thus were stronger. Using a different synthesizing system, CNT-3 tubes with around 50 walls showed the least defects with the \(I_D/I_G\) of 0.35 though it had large tube diameters.

3.2. Analysis of the SWW process for fabricating aligned CNT paper

The CNT-2 sheet (Fig. 4a), drawn from vertically aligned array, is composed of aligned CNTs by entangling and van de Waals interactions. The veil-like CNT sheet is very easy to be torn due to the loose structure and weak interaction between the adjacent nanotubes. After continuous winding and spraying the ethanol–water solution, CNT sheet can be tightly compacted. As shown in Fig. 4b, the as-produced CNT-2 paper has a denser structure than the CNT-2 sheet. It has been verified by our previous study that the contact angle between the ethanol–water droplet and the CNT sheet is substantially small than 90° [25]. Therefore, the liquid bridge [26] would pull the neighboring nanotube together when the liquid volume diminished due to evaporation (Fig. 5). The high surface energy of CNTs prevented the bundle from separating again. However, the neighboring nanotubes not only gathered into bundles but also left vacancies between them, resulting in the porosity of the CNT paper. Furthermore, the tubes were still highly aligned and only a few of them were crooked, which indicated the spraying processing did not disrupt the basic orientation of the nanotubes in the CNT sheet. The compacted structure and alignment of CNTs ensured greater intermolecular attraction forces, facilitating load transfer and sharing, potentially resulting in a stronger CNT paper without degrading electrical properties in the CNT oriented direction.

3.3. Comparison of the tensile properties of CNT papers

Tensile strength of CNT paper made of few-walled (2–3), several-walled (6), and many-walled (~50) nanotubes were compared
Due to the long CNTs and high orientation in the condensed structure, CNT papers made by SWW showed much better mechanical properties than other CNT papers fabricated using filtration process [17, 27, 28]. The strongest CNT paper made by CNT-1 achieved an average strength of 562.5 MPa and a modulus of 15.3 GPa. As only the outermost layer of a CNT carries the load before fracture, the ratio of the effective cross-section area of the outermost wall to the total cross-section area, $X_{\text{effective}}$, can be utilized to estimate how much area contributed to the load transfer (assuming the aligned MWCNTs are hexagonally closely packed) [20]. $X_{\text{effective}}$ is expressed as:

$$X_{\text{effective}} = \frac{2\pi d D}{\sqrt{3}(d + D)^2}$$

where $d$ is the spacing between graphite (002) planes, $D$ is the diameter of the CNT. As shown in Table 2, CNT-1 paper has the highest calculated $X_{\text{effective}}$ of 14%, which indicated largest load transfer among CNTs. Similar ratios of $X_{\text{effective}}$ from 11% to 14% were obtained for CNT-2 paper. However, the mean values of strength and modulus were only 75% and 67% of those of the CNT-1 paper, due to the more defects on the tube structure as well as much less effective outermost wall per unit volume. Another reason could be that thick CNTs might have less intermolecular attraction between neighboring nanotubes due to the increased bending stiffness which could hinder tight packing of the tubes. For CNT-3 paper, only 3% of the total cross-section area for each tube was effective concerning with the mechanical properties. Therefore, the tested strength and modulus were 117.7 MPa and 5.2 GPa, respectively. However, even this tensile strength was 42 MPa higher than that of the oriented CNT paper obtained by winding the CNT sheet and spraying ethanol afterwards, using CNTs with diameter in the same range (30–50 nm). Instead of spraying afterwards, SWW achieved better alignment and closer packing of the neighboring nanotubes in the CNT paper.

Notice that there were different ways of CNT papers to respond to the external strain based on the stress–strain curves in Fig. 6. The tensile stress of CNT-1 and CNT-2 papers increased almost linearly upon stretching with much larger slope or modulus, while the CNT-3 paper demonstrated a much lower slope or smaller modulus. For the former ones, both of their stress–strain curves showed relatively gentle slope at the beginning due to the realignment of the wavy tubes after starting to bear the load. This behavior is the same as the refinement of the CNT fiber during stretching [29]. As the strain increased over 1%, all the aligned tubes in the closely packed paper responded uniformly, resulting in a large modulus and sufficient strain at break. However, for CNT-3 paper, the situation changed for the diameter of nanotubes was several times large. The smaller effective cross-section area brought reduced strength and modulus. In addition, tube-tube interaction weakened as the contact area per unit volume between the CNTs decreased. Therefore, the nanotubes in CNT-3 paper slide away from each other as strain increased and fractured gradually.

### 3.4. Comparison of the electrical conductivity of CNT paper

The three different CNT papers are also good electrical conductors with conductivity of $3.6 \times 10^4$, $5.5 \times 10^4$ and $2.9 \times 10^4$ S/m,
correspondently to the paper fabricated from CNT-1, CNT-2 and CNT-3. The conductivity of CNT paper relies on the conductivity of the tubes and the CNT organization, such as orientation and compact density, in the paper. For example, the aligned and densely packed CNT paper made by ”domino pushing” has an electrical conductivity of $2 \times 10^4 \text{S/m}$, 25% higher than the randomly aligned paper from same batch of CNTs [19]. Similarly, CNT performs made by ”shear pressing” showed better electrical conductivity of $1.2 \times 10^4 \text{S/m}$ in the longitudinal direction than the electrical conductivity of $0.4 \times 10^4 \text{S/m}$ in the transverse direction [14]. In a CNT network, electric current was transferred through the main channel formed by the contact area, which can be improved magnificently by the alignment and density of CNT bundles. As a result, CNT papers obtained by SWW showed a great improvement on the conductivity over the CNT papers fabricated by conventional filtration method.

In this study, since CNTs were highly oriented in the structure, electron transported predominantly through the outermost wall. However, the CNT-1 paper did not possess better electrical conductivity than other two CNT papers, which is counter intuitive that it owned largest contact area between nanotubes and highest effective cross-section area due to the smallest dimension. For single tube with length over 200\mu m, the resistance along the tube is also as high as the contact resistance [30,31], therefore the overall resistance of the CNT paper depends on not only the junction resistance of CNTs but also the resistance of individual CNTs. On one hand, CNT-1 has the shortest length, which contributed in more contact resistance in the CNT paper. On the other hand, if the outermost wall of MWNT can be considered as single wall nanotube, the electrical conductivity of the nanotube would be metallic or semi-conduct. The possibility of metallic nanotube would increase with the increasing of the diameter. In other words, there could be a larger number of semi-conductive nanotubes in CNT-1 paper than CNT-2 and CNT-3 paper, resulting in a lower electrical conductivity.

### 4. Conclusions

CNT papers were fabricated with desired structure of highly orientated CNTs tightly packed together by a simple SWW method. In this method, continuous CNT sheet composed of aligned nanotubes were wound on a rotation mandrel as DI water/ethanol solution was sprayed. The capillary force during the solvent evaporation drew neighboring tubes closer together while maintaining the CNT alignment. As a result, high strength and good conductivity were obtained along the oriented direction. Using CNTs with diameters around 8 nm, the CNT paper achieved mean strength of

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
<th>Modulus (GPa)</th>
<th>Standard Deviation (GPa)</th>
<th>Strain (%)</th>
<th>Standard Deviation (%)</th>
<th>$X_{\text{effective}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-1 paper</td>
<td>562.5</td>
<td>59.4</td>
<td>15.3</td>
<td>1.1</td>
<td>4.7</td>
<td>0.5</td>
<td>14</td>
</tr>
<tr>
<td>CNT-2 paper</td>
<td>422.6</td>
<td>17.4</td>
<td>10.1</td>
<td>0.9</td>
<td>6.4</td>
<td>0.5</td>
<td>11–14</td>
</tr>
<tr>
<td>CNT-3 paper</td>
<td>117.7</td>
<td>21.1</td>
<td>5.2</td>
<td>2.0</td>
<td>24.5</td>
<td>1.9</td>
<td>3</td>
</tr>
</tbody>
</table>

### Table 2

Mechanical properties and $X_{\text{effective}}$ of the CNT-1, CNT-2 and CNT-3 paper.

![Fig. 4](a) SEM image of the surface of the as-drawn CNT-2 sheet. (b) SEM image of the surface of the as-produced CNT-2 paper.

![Fig. 5](Attractive force of liquid bridge pulled nanotube together upon evaporation when the contact angle of the liquid is $0^\circ < \theta < 90^\circ$ (after Rondeau et al. [26]).

![Fig. 6](Typical stress–strain curve of three types of CNT papers.)
562.5 MPa and mean modulus of 15.3 GPa. CNT paper fabricated with CNTs of 8–10 nm diameters showed the highest electrical conductivity of 5.5 × 10^4 S/m.

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