Electrical property enhancement of carbon nanotube fibers from post treatments

Peng Liu\textsuperscript{a}, Dennis C.M. Hu\textsuperscript{a}, Thang Q. Tran\textsuperscript{a}, Daniel Jewell\textsuperscript{b}, Hai M. Duong\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, EA-07-05, Singapore 117575, Singapore
\textsuperscript{b} Department of Materials Science and Metallurgy, University of Cambridge, United Kingdom

**HIGHLIGHTS**

- Highly conductive CNT fibers were fabricated using a floating catalyst method and a two-step post treatment technique.
- The electrical conductivity of the CNT fiber was significantly enhanced due to the stronger inter-CNT interactions.
- The maximum current density of the CNT fiber was up to 66000 A/cm\textsuperscript{2}, competitive to the conventional copper wires.

**ABSTRACT**

Utilizing the superior properties of individual carbon nanotubes (CNTs), the production of continuous CNT fibers has paved the way for novel CNT macroscale applications. However, it is still a great challenge to create highly electrically-conductive CNT fibers due to the poor transfer of electrical property from nanoscale individual CNTs to macroscale CNT fibers. Here, we report a fast and effective post treatment method consisting of mechanical condensation and acid treatment to enhance the electrical conductivity of the CNT fiber by a factor of 9. Such great enhancement is attributed to the surface modification effects during the post treatments, resulting in the lower contact resistance and stronger inter-CNT interactions. Moreover, the maximum current density of the acid-treated CNT fiber is up to 66000 A/cm\textsuperscript{2}, competitive to the conventional copper wires. The promising results in this study enable the CNT fibers novel materials for electrical wiring applications.

**ARTICLE INFO**

Article history:
Received 9 June 2016
Received in revised form 6 September 2016
Accepted 11 September 2016
Available online 12 September 2016

Keywords:
Carbon nanotube fiber
Acid treatment
Post treatment
Electrical conductivity
Maximum current density
Floating catalyst method

1. Introduction

Carbon nanotubes (CNTs), possessing excellent mechanical, electrical and thermal properties, are promising for a wide range of applications [1]. In the past two decades, researchers have tried to transfer the outstanding properties of individual CNTs to their macroscale assemblies. Among various CNT macroscale assemblies including CNT arrays [2], films [3], fibers [4–6] and aerogels [7], CNT fibers, comprising axially aligned and highly packed CNTs, would preserve better axial properties of individual CNTs and allow more versatility in industrial applications, such as high-performance composites [8] and electrical wires [9].
To date, significant progress of fabricating continuous CNT fibers has been done through the wet-spinning methods [4,10], array-spinning methods [11,12] or floating catalyst methods [5,8]. In general, wet-spinning method can produce high-performance CNT fibers but would require additional efforts to purify the fibers after fabrication [4,10]. Array-spinning method can produce strong and relatively clean CNT fibers [13,14]. Nevertheless, this method is not feasible for mass production of the CNT fibers due to the limited size of the CNT array and the difficulties of producing the spinnable CNT arrays [1]. Alternatively, continuous CNT fibers can be drawn directly from the aerogels formed in the process of the floating catalyst methods [5,8]. The floating catalyst method enables the large-scale fabrication of the aligned CNT fibers with outstanding mechanical and electrical properties [5,8,15].

Because of their high electrical conductivities, low densities and good mechanical properties, CNT fibers have the potential to replace conventional metals in many cabling applications. Individual CNTs show ultrahigh electrical conductivity up to $10^6$ S/cm [16]. However, this value dramatically drops by a few orders of magnitude to $\sim 10^2$–$10^4$ S/cm for most of the CNT fibers reported in the literature [5,17–24]. Such lower electrical conductivities can be ascribed to the difficulties in controlling the CNT fiber morphologies [5]. Hence, more detailed investigations on the synthesis processes and post treatments are of great importance in order to further enhance the electrical properties of the CNT fibers.

The electrical conductivity of CNT fiber is mainly related to the intrinsic electrical properties of CNTs, intertube spacing, contact resistance, CNT alignment, and impurities inside the CNT fiber [8]. It has been reported that the multi-properties of the CNTs can be improved by adjusting the CNT type and diameter [5,25] and controlling the amount of impurities and defects [25,26]. Ideally, the CNT fibers consisting of pure metallic single-walled nanotubes would demonstrate electrical conductivity as high as that of individual CNTs. However, it is still a great challenge to control CNT chirality on a large scale.

Compared to tailoring the intrinsic properties of CNTs, post treatments, using either mechanical or chemical approaches, are more feasible to enhance the electrical properties of the CNT fibers. Mechanical treatments such as twisting [12], stretching [27] and pressing [8,28] can effectively condense the CNT fibers, improve the CNT alignment and reduce the intertube spacing. However, CNTs are still interacting through intrinsically weak van der Waals forces, leading to the less significant improvements of the mechanical treatments [29]. On the other hand, chemical treatments, such as acid treatment or doping, can enhance the inter–CNT interactions by the surface modifications [30,31]. Song et al. [32] developed a two-step process consisting of annealing at high temperature and purifying by the concentrated hydrochloric acid over a duration of three days and achieved an electrical conductivity of 5900 S/cm. Zhao et al. [33] developed a series of steps over a duration of five days, including annealing at high temperature, purifying by the concentrated hydrogen peroxide and hydrochloric acid followed by soaking in the concentrated sulfuric acid, to achieve an electrical conductivity of 20,000 S/cm. Although great improvement has been achieved, the complicated and time-consuming processes involved in the previous methods make them difficult to be applied for large-scale fabrications and practical applications. Therefore, there is a clear motivation to develop a fast and effective method to improve the electrical properties of the CNT fibers.

In this work, we successfully developed a two-step post treatment method by combining mechanical condensation and acid treatment to enhance the electrical properties of the CNT fibers. The CNT fibers were continuously fabricated using the floating catalyst method and undergone the post treatments. The overall duration of this post treatment method was less than 2 h, significantly shorter than the previous works [32,33]. The combined post treatment method demonstrated great improvements in both the electrical conductivity and the maximum current density of the CNT fibers by factors of 9 and 10 respectively. The mechanisms of the electrical property enhancement are also discussed in this article.

2. Experimental

2.1. Materials

Ferrocene, thiophene, ethanol and concentrated nitric acid (HNO₃, 65 wt.%) were purchased from Sigma-Aldrich Company Ltd. Methane (CH₄), hydrogen (H₂), helium (He) and nitrogen (N₂) were purchased from Chem–Gas Pte Ltd. All the chemicals were used as received without further purification.

2.2. Fabrication of the CNT fibers

The CNT fibers were synthesized using the floating catalyst method [8,34]. A mixture of CH₄ (160 mL/min), H₂ (2500 mL/min), ferrocene (250 mL/min) and thiophene (20 mL/min) were injected into the tube furnace at 1200 °C. The continuously formed CNT aerogels were pulled out of the furnace and collected onto a rotating spindle with a rate of $\sim$2 km/h. Before the CNT fibers were collected onto the spindle, a mixture of ethanol and N₂ was sprayed onto the drawn out CNT fibers for the higher CNT packing.

2.3. Post treatments of the CNT fibers

A two-step post treatment method consisting of mechanical condensation [8] and acid treatment [34] was conducted on the as-spun CNT fibers.

2.3.1. Mechanical condensation

The CNT fiber was placed in between two sheets of A4 paper to prevent damages to the surface during the densification process [8]. Then, a stainless steel spatula with a flat end was used to compress the CNT fiber along the direction of the CNT fiber axis. The contact area between the flat edge of the spatula and the flat surface of the CNT fiber was estimated to be 3 mm² and the applied force was estimated to be 100 N [8].

2.3.2. Acid treatment

The mechanical-condensed CNT fibers were immersed into 65 wt.% HNO₃ at room temperature for 30 min. The acid-treated fibers were subsequently washed in de-ionised water and then dried in a fume hood at room temperature. In this study, we defined the CNT fibers without the post treatments, with the mechanical condensation and with both the mechanical condensation and the acid treatment as the as-spun, mechanical-condensed and acid-treated CNT fibers.

2.4. Characterizations

The surface morphologies and cross sectional areas of the as-spun, mechanical-condensed and acid-treated CNT fibers were investigated with a field emission scanning electron microscope (FE-SEM, Model S-4300, Hitachi).

The electrical resistances (R, Ω) of the as-spun, mechanical-condensed and acid-treated CNT fibers were measured by a two-probe method using a Fluke 73III multimeter. For better electrical contacts, the two ends of the CNT fibers were fixed on two glass slides using silver paste. The electrical conductivities (σ, S/cm) of the samples were then calculated according to: $\sigma = l/RA$, where $l$ and $A$ are the length and cross sectional area of the samples respectively.
3. Results and discussion

3.1. Morphologies of the as-spun, mechanical-condensed and acid-treated CNT fibers

As shown in Fig. 1a, the as-spun CNT fiber consists of the CNTs with fair alignment. The current previous studies reported that the CNTs inside the as-spun fibers were multi-walled nanotubes with diameter of ~15 nm [35]. The content of impurities (i.e., iron particles and amorphous carbon) in the as-spun fibers varies between 18 and 21 wt% [35]. Although the as-spun fibers were densified in situ by the sprayed ethanol during the synthesis process, we still observe a porous structure with large intertube spacing in Fig. 1a. Fig. 1b and c show the surface morphologies of the mechanical-condensed CNT fiber. A more compacted structure with better CNT alignment and smaller intertube spacing can be observed, compared to the as-spun fiber. This indicates that mechanical condensation is a more effective method than the liquid condensation method to achieve a sufficiently compacted CNT fiber structure. Fig. 1d and e show the surface morphologies of the acid-treated CNT fiber. It is revealed that the fiber structure is further condensed and the surface of the CNT fiber becomes smoother after the acid treatment.

3.2. Electrical conductivities of the as-spun, mechanical-condensed and acid-treated CNT fibers

3.2.1. Effects of the mechanical condensation on the electrical conductivity of the CNT fibers

The electrical resistances and conductivities of the as-spun, mechanical-condensed and acid-treated CNT fibers are summarized in Fig. 2. Through the mechanical condensation, the electrical conductivities increase by a factor of 4, from 2000 ± 404 S/cm to 8500 ± 859 S/cm, while the resistances slightly decrease from 450 ± 45 to 420 ± 20 Ω/cm. The significant enhancement in the electrical conductivity of the mechanical-condensed CNT fibers can be attributed to the minimized contact resistance between the CNTs in the highly compacted CNT structure [12]. The SEM observations clearly demonstrate that the intertube spacing reduced significantly in the mechanical-condensed CNT fiber (Fig. 1b) compared to the as-spun CNT fiber (Fig. 1a). The denser packing of CNTs leads to the smaller cross-sectional area of the mechanical-condensed fibers, which may be the main reason for the great enhancement of electrical conductivity. The increased CNT alignment can be another reason for the higher electrical conductivity.

As shown in Fig. 1a, the dangling ends and interweaving structure can be observed in the highly porous as-spun fibers. Such structural inhomoginities lead to the poor inter-CNT contacts. After the mechanical condensation, the CNTs become more aligned with less structural inhomoginities (Fig. 1b). The increased CNT alignment results in an enhanced intertube conducting areas which in turn give rise to the improved electrical conductivity of the CNT fibers [36].

3.2.2. Effects of the acid treatment on the electrical conductivity of the CNT fibers

In order to further enhance the electrical conductivity of the CNT fibers, a fast acid treatment was conducted on the mechanical-condensed CNT fibers. As shown in Fig. 2, the electrical conductivity of the acid-treated CNT fiber reaches as high as 18,000 ± 400 S/cm, 2 times higher than the mechanical-condensed fiber and 9 times higher than the as-spun fiber. In addition, the resistance of the acid-treated fiber considerably decreases up to 50%, compared to the as-spun and mechanical-condensed fibers, indicating the main reasons for the conductivity enhancement may be the surface modification during the acid-treatment other than the change of fiber dimension.

There are several possible reasons for the considerable enhancement of conductivity during the acid treatment. Concentrated nitric acid may induce several modifications to the CNT structure including purification (i.e., to eliminate amorphous carbon adhering to the CNTs) and functionalization of the CNTs [37]. Amorphous carbon and catalyst particles, causing the degradation in the electrical conductivity, were observed in our previous study on the CNT fibers [34]. A short acid treatment can effectively remove the amorphous carbon on the outer wall of CNTs, thus improving the inter-CNT contact [37].
In addition to the purification, various functional groups, such as hydroxyl, methyl, methylene and carbonyl, can be generated on the CNTs [31]. Due to the existence of dipole–dipole interaction and hydrogen bonding, the interaction between the acid-treated CNTs might be stronger than the van der Waals interaction between the pristine CNTs [31,34]. Therefore the intertube spacing may become smaller. This is supported by the further condensed fiber structure, as shown in Fig. 1d. Besides the less porous structure, larger CNT bundles with diameter of 150 nm are observed in the acid-treated fibers as shown in Fig. 1e, while the bundle diameter in the mechanical-condensed fibers is approximately 80 nm as shown in Fig. 1c. Since the contact resistance depends strongly on the contact angle and intertube spacing, the enhancement of conductivities can be attributed to the shorter intertube spacing, larger effective contact area and improving CNT–CNT contact conductance after the densification.

As shown in Table 1, the electrical conductivities of the CNT fibers in this work are much higher than those of many other CNT fibers fabricated by various methods, such as array-spun CNT fibers [19–22], wet-spun CNT fibers [10,17,18] and aerogel-spun CNT fibers [5,23,24]. In particular, the electrical conductivity of the acid-treated CNT fiber is comparable to those of the best performing CNT fibers reported in the literature [4,33].

### 3.3. Maximum current densities of the as-spun, mechanical-condensed and acid-treated CNT fibers

The maximum currents and maximum current densities of the as-spun, mechanical-condensed and acid-treated CNT fibers are summarized in Table 2. The acid-treated CNT fibers demonstrate the highest maximum current and maximum current density. This may due to the lower resistance of the acid-treated samples generating less heat, thus resulting in the higher maximum current at burning. As shown in Table 2, the maximum currents and maximum current densities of the CNT fibers in this work are comparable to the best performing CNT fibers reported in the literature [33]. Moreover, our CNT fibers possess maximum current densities competitive to those of copper wires and much higher than aluminium and steel wires [15].

The superior electrical conductivity and ultra-high maximum current density of the CNT fibers in this work show their potential application as electrical wires. As shown in Fig. 3a and b, an LED bulb was connected to a Keithley 2420 source meter by the CNT fibers. In this circuit, a portion of the copper wires was replaced with the CNT fibers. The LED light was able to light up and its brightness can be varied by changing the input current. The CNT fiber functioned well for the whole testing period.

In addition, the CNT fiber is flexible and is able to be knotted, as shown in Fig. 3c. The impacts of a knot on the fiber resistances and maximum currents are summarized in Table 3. The changes from the knot are around 25–30% for the resistance and 1–2 mA for the maximum current, indicating that no significant resistance is introduced by the knot. Hence, the CNT fiber can be regarded as a type of conducting wire where slight deformation of the CNT fibers would not cause drastic change of the resistance [38]. This result also suggests the possibility of fabricating longer CNT fibers through connecting many shorter ones in the practical applications.

### 4. Conclusions

Using a two-step post treatment approach, the electrical properties of the CNT fibers were enhanced significantly by a factor of 9, from 2000 S/cm to 18,000 S/cm. The great enhancement in the electrical conductivity is attributed to the densification and purification effects of the post treatments, hence the shorter intertube spacing, better CNT alignment and reducing contact resistance in the CNT fibers can be achieved. The acid-treated CNT fibers demonstrated the maximum current density as high as 66,000 A/cm², comparable to those of the best performing CNT fibers and the conventional copper wires. Due to their superior electrical properties and flexibility, the CNT fibers show great potential to replace the conventional metal wires for the electrical wiring applications in the future.

---

**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample treatment</th>
<th>CNT type</th>
<th>Electrical conductivity (S/cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>as-spun CNT fiber</td>
<td>MWNT</td>
<td>150</td>
<td>[17]</td>
</tr>
<tr>
<td>2</td>
<td>doped with 102% H₂SO₄</td>
<td>SWNT</td>
<td>5000</td>
<td>[18]</td>
</tr>
<tr>
<td>3</td>
<td>spun with PVA</td>
<td>SWNT</td>
<td>10</td>
<td>[10]</td>
</tr>
<tr>
<td>4</td>
<td>doped with HSO₃Cl</td>
<td>SWNT</td>
<td>29,000</td>
<td>[4]</td>
</tr>
<tr>
<td>5</td>
<td>doped with HSO₃Cl + I₂</td>
<td>SWNT</td>
<td>50,000</td>
<td>[4]</td>
</tr>
</tbody>
</table>

---

**Table 2**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample treatment</th>
<th>Maximum current (mA)</th>
<th>Maximum current density (A/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>as-spun CNT fiber</td>
<td>18.8 ± 0.6</td>
<td>5500</td>
<td>This work</td>
</tr>
<tr>
<td>2</td>
<td>mechanical-condensed CNT fiber</td>
<td>19.4 ± 1.8</td>
<td>43,000</td>
<td>[33]</td>
</tr>
<tr>
<td>3</td>
<td>acid-treated CNT fiber</td>
<td>23.1 ± 3.0</td>
<td>66,000</td>
<td>[33]</td>
</tr>
<tr>
<td>4</td>
<td>oxidized &amp; I₂ doped CNT fiber</td>
<td>22.5</td>
<td>10⁻³ – 10⁻⁴</td>
<td>[33]</td>
</tr>
<tr>
<td>5</td>
<td>copper wire</td>
<td>21.8</td>
<td>10⁻³ – 10⁻⁴</td>
<td>[33]</td>
</tr>
<tr>
<td>6</td>
<td>aluminium wire</td>
<td>–</td>
<td>10,500</td>
<td>[15]</td>
</tr>
<tr>
<td>7</td>
<td>steel wire</td>
<td>–</td>
<td>5800</td>
<td>[15]</td>
</tr>
</tbody>
</table>

---

**Table 3**

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample treatment</th>
<th>Knotted</th>
<th>Resistance (Ω/cm)</th>
<th>Maximum Current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>mechanical-condensed CNT fiber</td>
<td>No</td>
<td>490</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>mechanical-condensed CNT fiber</td>
<td>Yes</td>
<td>520</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>acid-treated CNT fiber</td>
<td>No</td>
<td>223</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>acid-treated CNT fiber</td>
<td>Yes</td>
<td>198</td>
<td>18</td>
</tr>
</tbody>
</table>
Acknowledgment

The authors would like to thank Temasek Laboratory@NUS Singapore (R-394-001-077-232) for the financial support for this project.

References


Fig. 3. (a) CNT fiber as a segment of conductive media connected to a DC source and loaded with an LED bulb. (b) Schematic illustration of the circuit. (c) An SEM image of a knot tied onto the CNT fiber.


