Multi-property enhancement of aligned carbon nanotube thin films from floating catalyst method

Peng Liu a, Yu Feng Tan a, Dennis C.M. Hu a, Daniel Jewell b, Hai M. Duong a,⁎

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

HIGHLIGHTS

• Strong and highly conductive carbon nanotube thin films are successfully fabricated by the floating catalyst method.
• The combined mechanical and chemical treatments significantly enhance the multi-properties of the carbon nanotubes films.
• The mechanical condensation on the carbon nanotube films eliminates the intertube spacing and reduces the nanotube waviness.
• The purification and densification effects of the acid treatment make the films more compacted and less defective.

GRAPHICAL ABSTRACT

ABSTRACT

The carbon nanotube (CNT) thin film synthesized by the floating catalyst method has attracted increasing attention because of the easy fabrication process and promising mass production at low cost. However, the limited morphology-controlled structure and the loose CNT arrangement make CNT films show relatively low mechanical and electrical properties. In this work, highly dense CNT films with controllable density have been successfully fabricated by a fast two-step post treatment technique combining mechanical condensation and acid treatment. Multiple fracture mechanisms have been identified and analyzed to explain the mechanical performance of these CNT films, including the load transfer efficiency between CNTs, alignment and waviness of CNT films, as well as the effects of CNT qualities. Benefited from the stronger intertube interaction and better CNT quality, the combined post treatment method is found to have dramatically enhanced the mechanical and electrical properties of the CNT films, with tensile strength up to 243 ± 16 MPa (by 101%), modulus up to 2.5 ± 0.1 GPa (by 32%) and electrical conductivity up to 4990 ± 636 S/cm (by 254%) compared to the as-prepared ones. This work proposes a route to fabricate high-quality CNT films on a large scale as promising multifunctional engineering materials.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) possess a unique combination of high strength, electrical and thermal conductivities, and outstanding physical properties [1–7]. Due to their superior properties, CNTs show a huge
array of potential applications, such as engineering fibers, electronic devices like actuators and supercapacitors, and advanced composites [8–12]. Extending these superior properties towards a macroscopic CNT film is vital for real life applications, and a highly dense aligned CNT structure helps to achieve these expectations.

To date, the methods of synthesizing CNT films can be classified into indirect preparation and direct growth methods. The indirect preparation typically consists of two steps: fabricating the CNTs and combining them into one entire macroscopic sheet. Some indirect methods involve wet approaches like vacuum deposition, spin coating and spray coating [16]. However, the CNT films fabricated with these methods usually have random orientations and weak van der Waals inttube interaction, resulting in low mechanical properties [17]. Other indirect approaches to produce CNT films are based on vertically aligned CNT arrays like domino-pushing, shear pressing and dry-spinning from vertically aligned CNT arrays [18–20]. Typically, CNT films fabricated from aligned CNT arrays have good mechanical, electrical and thermal properties [21–23]. Nonetheless, these methods still face limitations of low volume production of CNT arrays.

Moreover, CNT films can be directly and continuously collected at the end of a furnace by floating catalyst chemical vapor deposition (FCCVD) method [24–26]. The advantages of this method are cost-effective, can be called up for mass production and large-scale CNT films [27–29]. However, the FCCVD-spun CNT films are highly porous, giving rise to higher tensile strain but lower tensile strength and modulus than the expected from the superior mechanical performance of individual CNTs [6,17].

Efforts of improving the CNT mechanical performances include controlling the CNT length, number of CNT walls, CNT diameter [30,31], CNT alignments [32] and intertube load transfer [33,34]. The intertube load transfer between the CNTs could be improved by enhancing their coherent cross-links using irradiation [34], van der Waals interaction by densification [35], and cross-link bonds by polymerization [36]. The FCCVD-spun CNT macroscopic assemblies have porous structures which allow them to be further densified to more closely packed and better aligned structures [18], Tran et al. [37] reported an increase in stiffness and strength of CNT ribbons by 18 and 10 times, 79 GPa and 2.8 GPa respectively after mechanical densification. Additionally, surface modification of the CNTs has shown its effectiveness in creating the interfacial bonding among the CNTs [38]. Concentrated acid treatment has been reported to enhance mechanical strength and electrical conductivity of the CNT macroscopic assemblies by the effective surface modifications on the CNTs [39–42].

Herein, a combination of the post treatment methods is conducted on the FCCVD-spun CNT thin films to achieve a multi-property enhancement in this work. Impacts of the post treatments on the morphology, mechanical and electrical properties of the CNT thin films have been investigated in details. Due to the increased intertube interaction, the combined post treatment approach demonstrates great improvements on tensile strength, Young’s modulus and electrical conductivity of the CNT films.

2. Experimental section

2.1. Materials

Methane (CH₄), helium (He) and hydrogen (H₂) were purchased from Chem–Gas Pte Ltd. Ferrocene, thiophene, ethanol and nitric acid (HNO₃, 67 wt.%) were purchased from Sigma-Aldrich Company Ltd. All the chemicals above were used as received.

2.2. Fabrication of CNT films

The CNT films were synthesized using the FCCVD method [8]. Under a reducing H₂ environment (1500 ml/min), CH₄ (160 ml/min), ferrocene (250 ml/min) and thiophene (20 ml/min), acting as the carbon source, catalyst and reaction promoter respectively, were injected into the furnace at 1200 °C. The CNT aerogels, continuously formed in the heated furnace, were pulled out and collected on a roller to form the CNT film. The collection area was controlled to be a width of 2 cm on the roller, giving a CNT film with a size of 25 cm × 2 cm. CNT film with collecting time of 5, 10, 17.5 and 30 min were obtained in this work.

2.3. Post treatments

2.3.1. Mechanical condensation

In the mechanical condensation method [37], the as-prepared CNT films were firstly straightened and fixed in between two sheets of A4 paper by the following procedures: one end of the CNT film was first fixed on the paper by plastic tape; second, the film was slightly straightened until it closely attached to the paper and the other end of the film was fixed by plastic tape; and then the other sheet of paper was covered on the film. These steps helped to ensure that the CNT film would not get damaged during the mechanical densification process but at the same time allowed the force to be applied directly on the CNT film. A stainless steel spatula with a flat end was used to compress the A4 paper and CNT film from one end of the film and slid across, along the direction of the CNT axis. The applied force was approximately 100 N, 45° above the flat surface [37]. This densification process was repeated 10 times for each sample.

2.3.2. Acid treatment

The mechanical-condensed CNT films were immersed into HNO₃ for 30 min at room temperature. Subsequently, the samples were washed by de-ionized water and dried in a fume hood at room temperature.

In this article, we define the CNT films without post treatments, with mechanical condensation and with mechanical condensation followed by acid treatment as: as-prepared, mechanical-condensed and acid-treated CNT film respectively.

2.4. Characterizations

The morphology of the CNT films was investigated using a field emission scanning electron microscope (FE-SEM, Model S–4300, Hitachi). The mass of the CNT films (m) were measured by a high-precision Sartorius microbalance. The density (ρ) of the film was then calculated by ρ = m/lwt, where l, w and t were the length, width and thickness of the sample.

Tensile tests of the CNT films were conducted on a tensile tester (XS(08)XT-3, Shanghai Xusai Co.), using a load cell of 15 N with precision of 0.01 cN. The CNT films were cut into slices with 2 mm in width, and fixed in between two pieces of cardboard paper. The samples were tested using a gauge length of 10 mm and an elongation rate of 1.2 mm/min [43].

The electrical resistances (R) of the CNT films were measured using an Agilent U1241B multimeter. The two ends of the CNT films were fixed onto two separate glass slides, using silver paste to ensure good electrical contact. The electrical conductivity (σ) of the film was then calculated by σ = l/Rwt.

All the electrical and mechanical properties of the CNT films were measured in the direction parallel to the CNT alignment. Results for the mechanical and electrical tests were calculated based on the average of at least 3 samples.

3. Results and discussion

3.1. Morphology and density of the CNT films

The properties of the as-prepared, mechanical-condensed and acid-treated CNT films are summarized in Table 1. Fig. 1a shows a photograph of the as-prepared CNT film with the collecting time of 30 min. As shown in Fig. 1b, the as-prepared CNT film, consisting of aligned
CNTs and CNT bundles, is observed to have a highly porous structure which is believed to account for their low densities (0.30–1.39 g/cm³, see Table 1). Transmission electron microscopy (TEM) conducted in our previous studies [9,39] revealed that the CNTs in the films are multi-walled nanotubes with 15–20 walls and their diameters are approximately 15 nm.

After mechanical condensation, the CNT film (Fig. 1c) is observed to have more compacted structure with decreased intertube spacing, less entangled CNTs and better CNT alignment. Comparisons between the as-prepared and mechanical-condensed CNT films of all collecting times from Table 1 have revealed that the thickness of the films have shown consistent decrease after mechanical condensation, leading to the increased densities of the mechanical-condensed CNT films. Due to the applied mechanical force through densification, we believe that the porous structure of the as-prepared CNT film gives room for the bundles to compact together, resulting in more CNT bundles per unit area and therefore an increase in density.

Fig. 1d shows the morphology of the acid-treated CNT film suggesting a further densified structure with an enlargement in CNT bundles. However, the calculated density of the acid-treat CNT films (30 min collecting time, marked in asterisk * in Table 1), is found to be slightly higher than the theoretical value of CNTs (2.1–2.2 g/cm³). We believe that the presence of impurities in the CNT film accounts for this phenomenon. Thermo gravimetric analysis (TGA) and energy-dispersive X-ray spectroscopy (EDX) conducted on the CNT film in the past studies [9,37,39] revealed these CNT films consist of 18–21% impurities, such as iron catalysts and amorphous carbon.

3.2. Mechanical properties of the CNT films

Fig. 2 shows the typical stress-strain curves of the as-prepared, mechanical-condensed and acid-treated CNT films. The deformation behavior of the films demonstrates different stages of elastic, plastic and damage-fracture [44]. As tensile loading is applied from zero, the stress-strain curves typically exhibit elastic deformation and show a steeper slope at lower strains (1–3%), followed by a gradual decrease in gradient at higher strains (3% onwards). As the CNT network is entangled [45], the steeper gradient found at lower strains is attributed to the realignment of CNT bundles, and thus requiring a greater force to overcome them. As tensile load increases, the transition from elastic behavior to plastic deformation can be observed from 3% strain onwards; we believe that this is mainly caused by the slippage among CNTs. Further increase of loading and accumulation of slippage finally ends with failure, suggesting ductility of the CNT films. The various post treatments are believed to increase local contact forces and load bearing areas of the CNT films, resulting in improved mechanical properties. Therefore, we observe an increase of up to 118% in modulus and 140% in tensile strength comparing between the as-prepared CNT film and the acid-treated specimen.

As shown in Fig. 3a and b, both the tensile strength and modulus increase with the increase of collecting time which is corresponding to the increasing film density. After mechanical condensation, the CNT films exhibit an increase of up to 80% in tensile strength and 78% in modulus: the mechanical-condensed CNT films of 5, 10, 17.5 and 30 min collecting time show higher tensile strength of 87 ± 8, 132 ± 16, 169 ± 27 and 227 ± 3 MPa from 65 ± 12, 107 ± 14, 115 ± 29 and 121 ± 8 MPa, and higher moduli of 1.2 ± 0.1, 1.3 ± 0.4, 1.7 ± 0.5, 2.0 ± 0.2 GPa from 0.7 ± 0.1, 0.8 ± 0.2, 1.0 ± 0.2 and 1.9 ± 0.1 GPa respectively. The acid-treated CNT films show an even further improvement in mechanical properties with tensile strengths of up to 243 ± 16 MPa and moduli of up to 2.5 ± 0.1 GPa respectively. -3 times more in strength than graphene oxide paper [46], and ~3 times more than anisotropic CNT papers [47]. The largest improvement in tensile strength can be observed for the CNT film of 5 min collecting time. As this sample has the lowest density and therefore more interspatial pores, we believe that the improvement may be due to the acid being able to effectively permeate the highly porous structure, giving more room for mechanical improvement.

The experimental fracture morphologies of the as-prepared (Fig. 4a and b), mechanical-condensed (Fig. 4d and e) and acid-treated (Fig. 4g and h) films reveal differences in their fracture mechanisms, as illustrated in Fig. 4c–i. The interface plays a significant role in the stress transfer and the consequent improvements in the stiffness and strength [48]. The uniformity of the fracture surfaces indicates the degree of the CNT slippage and the intertube load transfer. For the as-prepared CNT film, uncoordinated deformation of the individual layers (Fig. 4a) and the fluffy fracture morphology (Fig. 4b) with long-distance slippage and wavy pullout end of nanotubes (Fig. 4c) indicates the easy sliding of the CNTs over each other and the weak intertube interaction in the highly porous structure of the as-prepared films [37]. These results are consistent with the large strain to break and the large plastic regions of the as-prepared CNT films.

In contrast, the mechanical-condensed film shows a fairly straight fracture surface with shorter CNT pullout (Fig. 4d). In the mechanical condensation, the close stacking of the CNT bundles and the reduced intertube spacing results in the improved CNT alignment (Fig. 4e), giving rise to the stronger intertube interaction thus minimizing the intertube slippage [17]. These contribute to the higher load bearing capability of the mechanical-condensed CNT films.

A more uniform and compacted fracture surface with shorter nanotube pullout (Fig. 4g) and larger CNT bundles (Fig. 4h) is observed in the acid-treated film. The enlargement of CNT bundles may be ascribed to

<table>
<thead>
<tr>
<th>Collecting time (min)</th>
<th>Mechanical condensation</th>
<th>Acid treatment</th>
<th>Thickness (μm)</th>
<th>Density (g/cm³)</th>
<th>Electrical conductivity (S/cm)</th>
<th>Tensile strength (MPa)</th>
<th>Young's modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared CNT film</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>No</td>
<td>No</td>
<td>8.0 ± 4.5</td>
<td>0.30</td>
<td>491 ± 90</td>
<td>65 ± 12</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>No</td>
<td>No</td>
<td>5.5 ± 0.3</td>
<td>0.69</td>
<td>865 ± 156</td>
<td>107 ± 14</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>17.5</td>
<td>No</td>
<td>No</td>
<td>8.2 ± 0.4</td>
<td>0.88</td>
<td>913 ± 163</td>
<td>115 ± 29</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>No</td>
<td>No</td>
<td>7.9 ± 1.0</td>
<td>1.39</td>
<td>1410 ± 110</td>
<td>121 ± 8</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>Mechanical-condensed CNT film</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>No</td>
<td>4.5 ± 0.4</td>
<td>0.49</td>
<td>663 ± 124</td>
<td>87 ± 8</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>Yes</td>
<td>No</td>
<td>4.2 ± 0.2</td>
<td>1.00</td>
<td>1010 ± 132</td>
<td>132 ± 16</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td>17.5</td>
<td>Yes</td>
<td>No</td>
<td>4.9 ± 0.4</td>
<td>1.50</td>
<td>1440 ± 122</td>
<td>169 ± 27</td>
<td>1.7 ± 0.5</td>
</tr>
<tr>
<td>30</td>
<td>Yes</td>
<td>No</td>
<td>5.6 ± 0.6</td>
<td>2.16</td>
<td>2150 ± 338</td>
<td>227 ± 3</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Acid-treated CNT film</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>Yes</td>
<td>7.5 ± 0.3</td>
<td>0.47</td>
<td>951 ± 66</td>
<td>142 ± 24</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>10</td>
<td>Yes</td>
<td>Yes</td>
<td>3.5 ± 0.2</td>
<td>1.29</td>
<td>2050 ± 140</td>
<td>156 ± 4</td>
<td>1.9 ± 0.3</td>
</tr>
<tr>
<td>17.5</td>
<td>Yes</td>
<td>Yes</td>
<td>4.5 ± 0.2</td>
<td>2.22</td>
<td>3000 ± 238</td>
<td>183 ± 5</td>
<td>2.4 ± 0.5</td>
</tr>
<tr>
<td>30</td>
<td>Yes</td>
<td>Yes</td>
<td>4.3 ± 0.2</td>
<td>2.34</td>
<td>4990 ± 636</td>
<td>243 ± 16</td>
<td>2.5 ± 0.1</td>
</tr>
</tbody>
</table>
the functional groups (such as hydroxyl, methyl, methylene and carbonyl) generated on the CNTs during the acid-treatment [40] resulting in the dipole-dipole interaction or hydrogen bonding. Such interaction between acid-treated CNTs might be stronger than the van der Waals interaction between the as-prepared CNTs [37,40], contributing to the further densified CNT structure. The enhanced interactions between CNT bundles and local contact forces can improve the load transfer under applied tensile stress, which is consistent to the observed enhanced mechanical properties. Furthermore, we believe that the concentrated HNO₃ plays a role in the purification of the CNT films. The existence of amorphous and reactive carbon on the as-prepared CNT films may serve as “defect” which leads to an uniformed local force distribution in the entire film and limits the intertube contact, thus depressing the mechanical properties of the specimens. These amorphous sites could be oxidized during acidification, and removed by the subsequent aqueous washing [38,49], resulting in the remarkable mechanical improvement. Therefore, we suggest that the mechanical condensation and acid treatment respectively play different roles in the nanotube rearrangement. The combination of the two types of post treatment approaches results in a higher degree of alignment and denser CNT packing, significantly enhancing the mechanical properties of the CNT films.

3.3. Electrical properties of the CNT films

The electrical properties of the CNT films are shown in Fig. 5a. The as-prepared CNT films show an increase in electrical conductivity from 491 to 1410 S/cm while the film density increases from 0.30 g/cm³ to 1.39 g/cm³. As discussed above, the presence of interspatial

![Fig. 1.](image1.png)

(a) An as-prepared CNT film with the collecting time of 30 min. SEM images of (b) the as-prepared, (b) the mechanical-condensed, and (c) the acid-treated CNT film with the collecting time of 30 min.

![Fig. 2.](image2.png)

Typical stress-strain curves of the as-prepared, mechanical-condensed and acid-treated CNT films.

![Fig. 3.](image3.png)

Effects of the mechanical condensation and acid treatment on the (a) tensile strength and (b) modulus of the CNT films.
pores between the CNT bundles leads to the lower electrical conductivity.

Similarly, the CNT films of various collecting times (5, 10, 17.5, 30 min) that have undergone the mechanical condensation all show an increase in electrical conductivity, from 491 ± 90, 865 ± 156, 913 ± 163 and 1410 ± 110 S/cm, to 663 ± 124, 1010 ± 132, 1440 ± 122 and 2150 ± 338 S/cm, while their densities increase from 0.30, 0.69, 0.88 and 1.39 g/cm³, to 0.49, 1.00, 1.50 and 2.16 g/cm³ respectively. These promising results show a 16% to 57% increase in electrical conductivity after condensation. The highest conductivity of 2150 ± 338 S/cm, is about 5 times higher than that of anisotropic CNT sheets [47]. The conduction of CNT macroscale assemblies is mainly controlled by an electron hopping mechanism [42]. As discussed above, the mechanical condensation effectively reduces the intertube spacing, thus resulting in an enhanced hopping and a significant decrease in the contact resistance [50]. Moreover, the applied compressive force may have re-oriented the nanotubes, leading to more contacts between nanotubes [51].

The acid-treated CNT films demonstrate a general increase in electrical conductivity by at least a factor of 2. The 30 min sample has the most significant enhancement with the electrical conductivity of 4990 ± 636 S/cm, much larger than 960 S/cm of SOCl₂-treated buckypaper [52] and ~2000 S/cm of SOCl₂-treated CNT film [53]. This enhancement can be attributed to two factors where the acid treatment first purifies the CNTs [54] and possibly introduces some functional groups into the CNTs [55]. This enhancement can be attributed to two factors where the acid treatment first purifies the CNTs [54] and possibly introduces some functional groups into the CNTs [55]. Fig. 5b compares the Raman spectra of the as-prepared and acid-treated specimens. The higher ratio of the intensity of G peak to the intensity of D peak (I_G/I_D) indicates the less defective structure of the acid-treated film, suggesting the purification effect of the acid treatment. As the presence of impurities (amorphous carbon, highly defective CNTs and catalysts) are known to impede electrical conduction [56], purification of the film through the use of acid treatment is believed to have resulted in the removal of some impurities, thereby improving conductivity. Another factor that contributed to the increase can be the addition of functional groups onto the CNTs which may generate hydrogen bonding or dipole-dipole interaction [39]. These stronger interactions between nanotubes can result in further densification of the CNT bundles [40], as shown in Fig. 4h. As mentioned previously, densification of CNT films reduces contact resistance between individual CNTs resulting in better electrical conductivity. Furthermore, it has been reported that the functional groups might improve the conductivity by serving as efficient electron pathways [57]. However, a sufficient functionalization of CNTs usually leads to a decreased I_G/I_D indicating a more defective CNT structure [40,42]. Unlike these studies, the increased I_G/I_D in this study suggests the degree of the functionalization may be very slight during the 30 min treatment. Hence, the main effects of the acid treatment in this work are suggested to be the purification and densification of the CNT films.

The CNT films in this work exhibit both high tensile strength and high electrical conductivity, making them promising candidates as engineering materials for various applications such as advanced multifunctional composites [58–61]. As shown in Table 2, the electrical and mechanical properties of the CNT films are much higher than those of many other CNT films fabricated by different methods reported in the literature [47,62–65]. However, the tensile strength is still lower than some ultra-strong CNT films [23], probably attributed to the CNT diameter. Considering that the outermost walls of CNTs play a dominate role in load transfer [6], smaller-diameter CNTs are superior because of the larger contact area between nanotubes, compared to the CNTs with larger diameter [23]. Moreover, the tensile strength of CNT films is mainly derived from interactions between CNTs, such as van der Waals force, nanotube entanglement or crosslinking between nanotubes. It has been reported that cross-linking CNTs by polymerization [59], functionalization [58] or irradiation [65] can significantly improve the intertube interactions, thus leading to the enhanced mechanical performances of the CNT-based films. Therefore, it is of great importance in our future work to design CNT films consisting of fewer-walled CNTs with stronger intertube interaction for further improvement in mechanical properties.
increase in mechanical and electrical performances with increased CNT film density. The as-prepared CNT film manifests a highly porous structure which results in an ununiformed fracture surface with a large slippage during the tensile tests. After the mechanical condensation and acid treatment, the tensile strength and electrical conductivity reach up to $243 \pm 16$ MPa and $4990 \pm 636$ S/cm, with a $101$% and $254$% improvement respectively, compared to the as-prepared one. The analysis indicates that mechanical condensation tends to eliminate the gaps between CNT bundles and reduce the waviness of nanotube, which can greatly increase the intertube interactions. The purification and densification effects of acid treatment make the film more compacted and less defective, resulting in the further property enhancement.

Acknowledgements

The authors would like to thank Temasek Laboratory @ NUS-Singapore (R-394-001-077-232) for their financial support in this project. The authors would also like to acknowledge Mr. Thang Quyet Tran and Dr. Zeng Fan for their guidance in this project.

References


[34] A. Kashemninkov, F. Banhart, Engineering of nanostructured carbon materials with electron or ion beams, Nat. Mater. 6 (10) (2007) 723–733.


