Carbon-Nanotube-Based Electrical Conductors: Fabrication, Optimization, and Applications

Songlin Zhang, Nam Nguyen, Branden Leonhardt, Claire Jolowsky, Ayou Hao, Jin Gyu Park, and Richard Liang*

1. Introduction

Rapid developments and new technologies in different fields across our daily life have created an urgent demand for more electrical energy and have drawn a lot of attention among researchers to find more efficient ways for its generation and transmission. This has arisen the demand for new conductive materials that show significantly better performance than conventional conductive materials. However, great technical challenges still exist in transferring the superior properties of individual CNTs to highly conductive bulk CNT assemblies, such as continuous wires, cables, and sheets. This paper gives an overview of the state-of-the-art advances in CNT-based conductors in terms of fabrication methods, characterization, conduction mechanisms, and applications. In addition, future research directions and possible attempts to improve performance are analyzed. The opportunities and challenges for related nonmetal competitive conductors are also discussed.

The lack of progress to obtain commercially available large-scale production of continuous carbon nanotube (CNT) fibers has provided the motivation for researchers to develop high-performance bulk CNT assemblies that could more effectively transfer the superb mechanical, electrical, and other excellent properties of individual CNTs. These wire-like bulk assemblies of CNTs have demonstrated the potential for being used as electrical conductors to replace conventional conductive materials, such as copper and aluminum. CNT conductors are extremely lightweight, corrosive-resistant, and mechanically strong while being potentially cost-effective when compared to other conventional conductive materials. However, great technical challenges still exist in transferring the superior properties of individual CNTs to highly conductive bulk CNT assemblies, such as continuous wires, cables, and sheets. This paper gives an overview of the state-of-the-art advances in CNT-based conductors in terms of fabrication methods, characterization, conduction mechanisms, and applications. In addition, future research directions and possible attempts to improve performance are analyzed. The opportunities and challenges for related nonmetal competitive conductors are also discussed.

1. Introduction

Rapid developments and new technologies in different fields across our daily life have created an urgent demand for more electrical energy and have drawn a lot of attention among researchers to find more efficient ways for its generation and transmission. This has arisen the demand for new conductive materials that show significantly better performance than conventional metal materials, such as copper, and has stimulated a strong interest in research to develop cost-effective, lightweight, and environmentally friendly conductive cables or wires as a replacement for copper. From this view, carbon-based nanomaterial is a potential candidate. Carbon related nanomaterials including fullerenes, carbon nanotubes (CNTs), and graphene are promising due to their exceptional conductive and electronic transport properties, which may accelerate the practical and potential applications for various kinds of novel engineering areas spanning from electronics, energy storage, and advanced materials to nanotechnology and biotechnology. Among the family of carbon nanomaterials, CNTs have been a particularly attractive material since its discovery in 1991 by Iijima,[1] due to their nanoscale 1D shape, excellent mechanical properties, tunable electrical properties either metallic or semiconducting, high current carrying capacity, and many other exciting properties. These properties have highlighted the potential of CNTs use in a plethora of applications, including electrically conductive fillers in polymer composites, flexible and transparent conductive films, microelectronics (transistors, interconnectors, heat dissipaters), and lightweight conducting wires and cables.[2] Figure 1 points out the forecast presented by Endo et al.[3] on the present, near future, and long term applications of CNTs in various fields. An interesting potential application of CNTs is the long-term electrical conductors, which are able to transmit power from plants to plants or households, as well as be used in electronic devices.

Compared to conventional copper cables or wires, CNT based cables have several advantages including 1) a lower density of 1.3 g cm⁻³ for single-walled carbon nanotubes (SWCNTs)[4] and 2.1 g cm⁻³ for multiwalled carbon nanotubes (MWCNTs),[5] both of which are much lower than that of copper, 8.96 g cm⁻³;[6] 2) environmental stability, which can stand with severe conditions including high pressure, large temperature changes, etc.; 3) excellent mechanical performance with a Young’s modulus and strength in the ranges of 1.0 TPa and 50 GPa, respectively;[7] 4) ultrahigh electrical conductivity as high as 10⁸ S m⁻¹ for SWCNTs, which is higher than that of copper (≈10⁷ S m⁻¹).[8] Furthermore, the limited amount of conventional conductive metal resources in nature and their soaring market price greatly increased the need for a desirable alternative solution that are abundant in nature, low-cost, and...
can compete with the conventional conductors. Thus, from the perspective of conductive performance and resource capacity, CNTs are “the material of future.”[9]

Because of these outstanding advantages, including both mechanical and electrical properties of individual CNTs, researchers show strong impetus to develop high-performance macroscopic CNT assemblies. Assemblies here usually refer to fiber (or yarns, or wires) and films (or sheets, or buckypaper). In the following discussion, we will not differentiate fibers, yarns, or wires, neither films, sheets, or buckypaper. This promises more attractive real-world engineering applications as electrical conductors. However, this is a challenging task. At the nanoscale level, an individual nanotube can be viewed as a single graphene sheet that has been rolled into a seamless nanotube with or without fullerene caps to form a SWCNT or multiple rolled up graphene sheets for MWCNTs.[96] Depending on the chirality (which is defined by chiral vector C (n,m), where n and m are the geometry parameters of graphene[9a]), CNTs can be semiconducting or metallic in nature.[10] Additionally, the lengths and diameters of CNTs have great influence on the electrical performance.[11] Coupling with the atomic structures, such as the number of walls and atomic defects and doping,[5,11e,h] these intrinsic factors determine the electronic structure and geometry of CNTs, and play critical roles in intrinsic-structure-dependent properties including mechanical, electrical, and other properties of CNTs.[12,a] However, for macroscopic fibers and films, excluding the intrinsic parameters of CNTs, many other factors related with the microstructures and macrostructures of CNT assemblies (so-called extrinsic factors), such as alignment, packing, and contacts,[11a,13] significantly influence the electrical and mechanical performances of CNT assemblage. Figure 2 illustrates these two intrinsic and extrinsic factors and their interactions.

Intrinsic factors, such as the length, diameter, chirality, and atomic structures, are challenging to control using current available synthesis methods; therefore, synthesizing nanotubes with designed diameter, length, chirality, and without defects is difficult. In fact, researchers have devoted a significant effort to achieving controlled synthesis of CNTs by lengthening, or using pure single-wall nanotubes, or with armchair chirality only (metallic conduction).[11b,14] In practice, macroscopic CNT fibers, which consist of tens of thousands of nanotubes with uncontrollable distribution of chirality, diameters, lengths with many atomic defects, show limited electrical conductivity. This limited electrical conductivity is due to the lack of control of the intrinsic factors of each nanotube and the extrinsic factors, like misalignment and many contacts among CNT assemblies during manufacturing. All these uncontrolled effects from intrinsic and extrinsic factors severely deteriorate the electrical performance of macroscopic CNT assemblies including fibers and films, resulting in a much lower electrical conductivity as compared with that of the perfect individual CNT with metallic conduction.[15] Figure 3 schematically shows the parameters at different scales, which have significant influences on the electrical conductivity of macroscopic assemblage.

The lack of in-depth understanding of achieving better control on the aforementioned factors and the relationship between high electrical conductivity and the nanoscale and microscale structures are barriers and require further exploration. While
the research on synthesis of perfect CNT growth with controlled intrinsic parameters, such as specific diameter, length, chirality, and no-defects, is ongoing, more efforts on the control of extrinsic parameters, which involve various post-treatments, are needed for further improvement of electrical conductivity to bring the application of CNT conductors into reality.

Several reviews are related to fabrications, as well as electrical and mechanical properties of CNT assemblies, with most focusing on the applications of CNTs as structural materials, electrochemical electrodes, or sensors.\textsuperscript{[8,16]} Although two publications briefly review the application of CNT conductors by Jarosz et al.\textsuperscript{[9b]} and Lekawa-Raus et al.,\textsuperscript{[9a]} a comprehensive review on the post-treatment methods of improving electrical conductivity of CNT conductors and structure–property relationship is still lacking. The recent rapid advances of CNT fibers and films with ultrahigh electrical conductivity motivate us to create this review report. After the brief introduction in Section 1, we address the major achievements of CNT conductor developing history in Section 2. The main fabrication methods of CNT fibers and films and their mechanical, electrical, and thermal properties are highlighted in Sections 3 and 4, respectively, with a focus on the importance of post-treatment methods to improve electrical conductivity. Section 5 summarizes various post-treatment methods and discusses opportunities and challenges. The major applications of CNT conductors are summarized in Section 6. Section 7 provides a brief conclusion and future research direction discussion.

2. The Development of CNT Conductors

Transferring the excellent properties of individual CNTs to macroscopic CNT assemblies is attractive yet challenging. Macroscopic CNT fibers made from axially aligned and densely packed nanotubes can reportedly exceed the specific modulus and strength of commercial carbon fiber and polymeric fibers\textsuperscript{[17]} and the specific electrical conductivity of copper.\textsuperscript{[18]} However, great challenges must be overcome. For example, Zhao et al.\textsuperscript{[18]} successfully fabricated iodine doped carbon nanotube cables after a lengthy
washing process using various acids, showing a specific conductivity (conductivity divided by density) of $2.03 \times 10^4$ S m$^{-2}$ kg$^{-1}$ (Figure 4), which exceeded that of copper ($6.67 \times 10^3$ S m$^{-2}$ kg$^{-1}$).

Unfortunately, only small diameter (<10 µm) CNT cables possessed such conductivity. They found that the larger the diameter of the CNT cables, the lower the conductivity. Such large differences in electrical conductivity between CNT cables of various diameters were ascribed to the extrinsic factors of structure defects such as voids, pores, and misalignment, which were inevitably introduced into the larger cables during the fabrication process, and induced high contact resistance between neighboring nanotubes, as shown in Figures 2 and 3. Therefore, the extrinsic factors of the microstructure and macrostructure of these macroscopic CNT assemblies strongly influence their mechanical and electrical conduction performance. For example, Wang et al.\[19\] found that an aligned and densely packed CNT ribbon several hundreds of nanometers (≈500 nm) thick has low contact resistance, possessing a very high electrical conductivity of up to $\approx 1.82–2.24 \times 10^6$ S m$^{-1}$. Therefore, better control on these microstructures related extrinsic factors is expected to achieve high mechanical and electrical properties.

Generally, a more compact and aligned structure of the fibers with smaller diameters or films with less thickness will have less contact resistance between neighboring CNTs, resulting in a higher conductivity.\[11d,20\] Tables 1 and 2 summarize the most promising conductive results from literatures for CNT fibers and films, respectively. Usually these good numbers are based on measurements from small sample sizes. However, for potential engineering applications, transferring the exceedingly high electrical conductivity and mechanical properties of individual CNTs or small sample sizes to macroscopic CNT assemblies, including fibers and films, requires a great effort to achieve better control over the extrinsic properties of CNT assemblies. Taking the tensile strength of a SWCNT as high as 50 GPa\[7\] as an example, the tensile strength of macroscopic CNT fibers typically reaches around 2 GPa.\[21\] Recently, Xu et al.\[13c\] reported a CNT film (small ribbon) possessing an extremely high tensile strength.
### Table 1. Electrical conductivity of CNT fiber with different dimensions.

<table>
<thead>
<tr>
<th>Type of CNTs</th>
<th>Length [cm]</th>
<th>Diameter [µm]</th>
<th>Cross-sectional area [µm²]</th>
<th>Electrical properties of CNT macroassemblies</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grown by CVD, then oxidation, soaking (30% H₂O₂, 37% HCl, 98% H₂SO₄) and DI water washing</td>
<td>DWCNTs</td>
<td>–</td>
<td>5.5</td>
<td>95</td>
<td>20</td>
</tr>
<tr>
<td>Iodine doping (200 °C, 12 h) for above sample</td>
<td>DWCNTs</td>
<td>–</td>
<td>5.5</td>
<td>95</td>
<td>67</td>
</tr>
<tr>
<td>Dry spinning from CNT array, densified by PDA then pyrolysis (1050 °C, 2 h)</td>
<td>–</td>
<td>–</td>
<td>7.3</td>
<td>176.5</td>
<td>4.836e±0.223</td>
</tr>
<tr>
<td>Wet spinning from superacid, doped with HSO₃Cl</td>
<td>SWCNTs</td>
<td>No limit</td>
<td>8–10</td>
<td>201–314</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>Above sample additionally doped with I₂</td>
<td>SWCNTs</td>
<td>No limit</td>
<td>8–10</td>
<td>201–314</td>
<td>50 ± 5</td>
</tr>
<tr>
<td>Wet spinning from superacid, doped with H₂SO₄-HSO₃Cl</td>
<td>SWCNTs</td>
<td>No limit</td>
<td>13</td>
<td>531</td>
<td>8.3</td>
</tr>
<tr>
<td>CNT film (grown by CVD), drawing through a die and rolling</td>
<td>–</td>
<td>–</td>
<td>45–100</td>
<td>6359–31 400</td>
<td>9–10</td>
</tr>
<tr>
<td>Grown by CVD</td>
<td>SWCNTs</td>
<td>Few of cm</td>
<td>50</td>
<td>7850</td>
<td>1.43e</td>
</tr>
<tr>
<td>Wet spinning from superacid, doped by H₂SO₄</td>
<td>SWCNTs</td>
<td>No limit</td>
<td>52.7</td>
<td>8721</td>
<td>5.0</td>
</tr>
<tr>
<td>CNT net from CVD and twisted, soaked in acetone and H₂O₂ (34.5%)</td>
<td>DWCNTs</td>
<td>–</td>
<td>95</td>
<td>28 339</td>
<td>3.61e</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values that are calculated from the data that authors provided; <sup>b</sup>π = 3.14.

### Table 2. Electrical conductivity of thin CNT film with different dimensions.

<table>
<thead>
<tr>
<th>Method and treatment</th>
<th>Type of CNTs</th>
<th>Length [cm]</th>
<th>Thickness [µm]</th>
<th>Cross-sectional area [µm²]</th>
<th>Electrical properties of CNT macroassemblies</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet spinning from superacid with postprocessing</td>
<td>SWCNTs</td>
<td>4–5</td>
<td>–</td>
<td>1200–1500</td>
<td>41–50</td>
<td>2.2 e±106</td>
</tr>
<tr>
<td>Vacuum assisted filtration, then doping (KAuBr₄)</td>
<td>SWCNTs</td>
<td>–</td>
<td>20</td>
<td>–</td>
<td>4.3</td>
<td>–</td>
</tr>
<tr>
<td>Synthesized by aerogel technique</td>
<td>SWCNTs</td>
<td>–</td>
<td>0.1</td>
<td>–</td>
<td>1.43e</td>
<td>–</td>
</tr>
<tr>
<td>CNT stocking from CVD, shrinking (by water/ethanol) and winding</td>
<td>–</td>
<td>No limit</td>
<td>5–9</td>
<td>160 × (5–9)</td>
<td>1.27</td>
<td>–</td>
</tr>
<tr>
<td>Above sample additionally rolling mechanically</td>
<td>–</td>
<td>No limit</td>
<td>0.5</td>
<td>220 × 0.5</td>
<td>18.2–22.4</td>
<td>1400–1723</td>
</tr>
<tr>
<td>Spinning from CNT array</td>
<td>MWCNTs</td>
<td>–</td>
<td>3</td>
<td>–</td>
<td>1.0</td>
<td>119</td>
</tr>
<tr>
<td>Above sample additionally microcombing</td>
<td>MWCNTs</td>
<td>–</td>
<td>2</td>
<td>–</td>
<td>1.8</td>
<td>173</td>
</tr>
<tr>
<td>Vacuum assisted filtration, then aligning by stretching</td>
<td>MWCNTs</td>
<td>–</td>
<td>10–20</td>
<td>–</td>
<td>2.4</td>
<td>–</td>
</tr>
<tr>
<td>Above sample additionally soaking (HNO₃) and cross-link by polymer</td>
<td>MWCNTs</td>
<td>–</td>
<td>10–20</td>
<td>–</td>
<td>6.2</td>
<td>–</td>
</tr>
<tr>
<td>Vacuum assisted filtration then washing surfactants</td>
<td>SWCNTs</td>
<td>–</td>
<td>11</td>
<td>–</td>
<td>0.17</td>
<td>–</td>
</tr>
<tr>
<td>Domino pushing CNT array</td>
<td>MWCNTs</td>
<td>–</td>
<td>26</td>
<td>–</td>
<td>0.2</td>
<td>34e</td>
</tr>
<tr>
<td>Filtration from CNTs dispersion, doped with HNO₃</td>
<td>SWCNTs</td>
<td>–</td>
<td>60</td>
<td>–</td>
<td>0.3</td>
<td>–</td>
</tr>
<tr>
<td>Mechanical stretching and iodine doping, coated by PEDOT:PSS</td>
<td>MWCNTs</td>
<td>No limit</td>
<td>28–35</td>
<td>199 500–245 000</td>
<td>10–13</td>
<td>–</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values were calculated from the data that authors provided; <sup>b</sup>π = 3.14.
of around 9.6 GPa after various post-treatments including controlled winding and mechanical rolling processes. Although such high mechanical performance of CNT sheets can be approached in research labs, the thickness of this film is only in the nanoscale range of around 120 nm, which severely impedes the potential engineering applications. In terms of high electrical conductivity, the same situation occurs in which the high electrical performance of CNT assemblies is limited to very small sample sizes. For example, Zhao et al. observed an ultrahigh conductivity of $6.7 \times 10^6$ S m$^{-1}$ for CNT cable with a diameter $\approx 5$ µm after purification and iodine doping. This value was the highest reported electrical conductivity found in the literature, although it is still one magnitude lower than the theoretical conductivity of perfect individual CNTs. Behabtu et al. developed a wet spinning method to fabricate CNT fibers with high electrical conductivity of up to $4.5 \times 10^6$ S m$^{-1}$, but a small diameter size of $<10$ µm.

Nevertheless, the past two decades have seen significant progress on improving the electrical conductivity of macroscopic CNT fibers or films by various methods, which are briefly summarized in Figure 5. Since the high electrical conductivity of

![Figure 5](https://www.advelectronmat.de/)

**Figure 5.** a) Timeline of the development history of CNT electrical conductors. This timeline summarizes the following main discoveries or reports: Thess et al. (Reproduced with permission. Copyright 1996. AAAS.), Zhu et al. (Reproduced with permission. Copyright 2002, AAAS.), Ericson et al. (Reproduced with permission. Copyright 2004, AAAS.), Zhang et al. (Reproduced with permission. Copyright 2004, AAAS.), Dettlaff-Weglikowska et al. (Reproduced with permission. Copyright 2005, American Chemical Society.), Ma et al. (Reproduced with permission. Copyright 2004, American Chemical Society.), Wang et al. (Reproduced with permission. Copyright 2008, IOP Publishing Ltd.), Alvarenga et al. (Reproduced with permission. Copyright 2010, AIP Publishing LLC.), Zhao et al. (Reproduced with permission. Copyright 2011, Nature Publishing Group.), Behabtu et al. (Reproduced with permission. Copyright 2013, AAAS.), Wang et al. (Reproduced with permission. Copyright 2014, Nature Publishing Group.), Janas et al. (Reproduced with permission. Copyright 2014, Elsevier.), Bucossi et al. (Reproduced with permission. Copyright 2015, American Chemical Society.), Tran et al. (Reproduced with permission. Copyright 2016, Elsevier.), Han et al. (Reproduced with permission. Copyright 2017, Elsevier.), Zhang et al. (Reproduced with permission. Copyright 2017, Elsevier.). b) Ashby plots of electrical conductivity versus density of conductive polymers including polyaniline (PANI), polypyrrole (PPY), polystyrene (PS) (black diamonds), C-conductors including carbon fiber, graphite, and CNTs (green square), metal conductors including copper, aluminum, silver, gold, steel, magnesium, and nickel (blue triangle), ideal lightweight C-conductors (red circle). c) Specific electrical conductivity versus strength Ashby plot, showing different regions for metals and C-conductors. Metal conductors fall in medium strength, high conductivity region; C-conductors define a high strength and medium-to-high conductivity. Ideal C-conductors possess high strength and high conductivity.
a single-rope of CNTs was experimentally measured to be in the range of $10^6$ S m$^{-1}$ in 1996 by Thess et al. $^{[20b]}$. Great effort has been devoted to the fabrication of CNT fibers or films with large dimensions,$^{[13b,26,27,37]}$ high electrical conductivity,$^{[18,22,34,38]}$ and the capability of large-scale production.$^{[13b,19,22,29,39]}$ In 2002, Zhu et al.$^{[46]}$ reported the direct collection of centimeter-long strands of aligned SWCNTs by an optimized floating catalyst chemical vapor deposition (FCCVD) method. This method was also adopted to prepare CNT film by Ma et al.$^{[37]}$ in 2007, achieving similar result in the range of $10^5$ S m$^{-1}$. In 2004, even longer CNT fiber was fabricated by Zhang et al.$^{[27]}$ by a simple method of spinning from vertically aligned carbon nanotube (VACNT) arrays, achieving a high CNT alignment degree with the fibers. Due to the size limitation of VACNT arrays, this spinning method was later replaced by the further optimized FCCVD method, which can continuously produce CNT fibers from the deposition zone as long as the carbon source is fed. The very recent progress and results can be found in the reports by Wang et al.$^{[19]}$, Tran et al.$^{[36]}$, Han et al.$^{[39]}$, and Zhang et al.$^{[13b]}$, and are listed in Table 3.

Electrical performance has also been greatly improved by chemical doping and optimizing microstructures and macrostructures. In 2004, the wet spinning method was reported to make continuous CNT fibers with high conductivity of $5 \times 10^3$ S m$^{-1}$ by Ericson et al.$^{[38a]}$ obtaining a good CNT alignment from the liquid phase alignment. Further improvements in conductivity were reported by Behabtu et al.$^{[35]}$ in 2013 by spinning CNT fibers from chlorosulfonic acid (CSA, HSO$_3$Cl) stabilized liquid crystalline phase of CNTs, reaching the range of $10^5$ S m$^{-1}$. Similar results were also observed by Bucossi et al.$^{[29]}$. Chemical doping including SOCl$_2$ by Dettlaff-Weglikowska et al.$^{[40]}$, iodine by Zhao et al.$^{[18]}$, and Janas et al.$^{[38d]}$ could improve the conductivity to the range of $10^5$ S m$^{-1}$. Additionally, control on microstructures and macrostructures of fibers, such as CNT alignment by Wang et al.$^{[34]}$, Zhang et al.$^{[13b]}$, dense packing structures by Alavarenga et al.$^{[38d]}$ and Tran et al.$^{[36]}$ could also improve the conductivity to the range of $10^5$ S m$^{-1}$. Figure 5b,c compares various carbon conductors (C-conductor, including carbon fiber, graphite, and CNT, data are from the literature) to conventional metal conductors$^{[6]}$ and conductive polymers$^{[41]}$ offering advantages of low density, high electrical conductivity, high specific electrical conductivity, and high tensile strength. Ideal CNT conductors should combine the high specific electrical conductivity and excellent mechanical performance of carbon fibers compared to metal conductors (copper, silver, and aluminum)$^{[22]}$.

By further comparing the conduction mechanism of individual CNTs and CNT fibers or films, different electron transport behaviors can be expected at the nanoscale and macroscale levels. Although ballistic transport was observed on single metallic CNT$^{[50]}$, the high content of impurities including catalyst and amorphous carbon on the surface of CNTs may further interrupt the electron transport by intruding random scattering, thus increasing the contact resistance between neighboring CNTs$^{[51]}$. Additionally, improving the alignment of CNTs, decreasing the voids, and increasing the packing density of CNT assemblies may increase the contacts area of neighboring nanotubes, thus resulting in a low contact resistance.$^{[13c]}$ Therefore, research on controlling extrinsic factors must be thoroughly investigated prior to experimental work on the controlled synthesis of perfect nanotubes with tailored intrinsic factors including diameter, length, chirality, and without defects. These extrinsic factors include nanoscale and microscale alignment of CNTs, dense packing structures, and contacts between neighboring nanotubes. Controlling these extrinsic factors could be an effective solution to achieve a near-theoretical electrical conductivity of macroscopic CNT fibers for potential engineering applications.$^{[9,10]}$ Before being utilized as alternatives to conventional metal conductors, several benchmarks and challenges for the CNT conductor development must be addressed in research and engineering fields, including 1) preparing macroscopic CNT fibers and films that retain the excellent conductivity of individual nanotubes, 2) controlling the negative size-effects on the mechanical and electrical properties of macroscopic CNT assemblies, 3) developing large-scale production processes with competitive cost and high efficiency, and 4) achieving green manufacturing with less side-products or no environmental issues.

### 3. Carbon Nanotube Assemblies for the Use of Electrical Conductors

To date, the available highly conductive CNT assemblies are always short in length or small in area compared to copper wires and tapes. Instead of such small samples, a promising large-scale production process of highly conductive CNT fibers or films is needed to accelerate the utilization of these lightweight electrical conductors. Several different manufacturing processes have already been developed to make continuous macroscopic CNT fibers and films, which mainly fall into two categories: dry and wet methods. For the dry method, the most developed manufacturing processes are spinning from CNT array (or forest or carpet)$^{[17,21,27,52]}$ and spinning from CNT aerogel in a reaction zone using FCCVD technique.$^{[26,53]}$ So far, the reliable drawing speeds of fibers are $\approx 30$ and $\approx 180$ m h$^{-1}$ for the array-based and FCCVD approaches, respectively.$^{[54]}$ Alternatively, wet spinning is another effective technique to prepare large quantity of CNT fibers.$^{[22]}$ By modifying the vacuum filtration system, a continuous manufacturing process was developed at High-Performance Materials Institute (HPMI, Florida State University) that can produce tens-of-meters long CNT sheets either in 6 in. width or 12 in. width depending on the apparatus used in manufacturing process.$^{[55]}$ The fabrication of both CNT fibers and films will be briefly discussed in the following section, and electrical performance related property will also be reviewed. For more details of CNT fiber and film manufacturing, several specific reviews are available by Di et al.$^{[116]}$, Janas et al.$^{[16b]}$ and Kong et al.$^{[56]}$. Meanwhile, in the following sections, we mainly focus on CNT fibers as electrical conductors. CNT films will be discussed if needed.

#### 3.1. Carbon Nanotube Fibers

The fabrication methods of CNT fibers can be mainly classified into two categories—wet (liquid) spinning and dry (solid) spinning.$^{[9a,57]}$ Other methods, including electrospinning,$^{[56]}$ are probably of little importance due to either the low electrical
Table 3. The high electrical conductivities of CNT fibers and films achieved by various post-treatment methods and other characterizations.

<table>
<thead>
<tr>
<th>Fabrication process</th>
<th>Comments</th>
<th>CNT characteristics</th>
<th>Fiber characteristics</th>
<th>Electrical properties</th>
<th>Tensile strength</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Type</td>
<td>Diameter [nm]</td>
<td>Length [µm]</td>
<td>Density [g cm⁻³]</td>
<td>σ [×10⁶ S m⁻¹]</td>
</tr>
<tr>
<td>CNT in superacid (HSO₃Cl) solution</td>
<td>As-spun, aligned</td>
<td>SWCNT</td>
<td>–</td>
<td>5</td>
<td>9</td>
<td>1.3</td>
</tr>
<tr>
<td>Above fiber</td>
<td>Iodine</td>
<td>SWCNT</td>
<td>–</td>
<td>5</td>
<td>9</td>
<td>1.4</td>
</tr>
<tr>
<td>CNT in superacid of H₂SO₄ and HSO₃Cl</td>
<td>As-spun, aligned</td>
<td>SWCNT</td>
<td>1.95</td>
<td>500</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CNT in superacid (H₂SO₄)</td>
<td>Doped</td>
<td>SWCNT</td>
<td>–</td>
<td>–</td>
<td>52.7</td>
<td>1.11</td>
</tr>
<tr>
<td>CNT in superacid (HSO₃Cl)</td>
<td>Stretched</td>
<td>SWCNT</td>
<td>–</td>
<td>5</td>
<td>1400⁷</td>
<td>–</td>
</tr>
<tr>
<td>Spun from FCCVD</td>
<td>Aligned</td>
<td>SWCNT</td>
<td>1.1</td>
<td>–</td>
<td>50</td>
<td>–</td>
</tr>
<tr>
<td>Spun from CNT array, shrunk by ethanol, then combed</td>
<td>Aligned</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3⁶</td>
<td>1.04</td>
</tr>
<tr>
<td>Spun from FCCVD</td>
<td>Aligned, dense-packed</td>
<td>SWCNT</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.3</td>
</tr>
<tr>
<td>Spun from CNT array and combed</td>
<td>Aligned</td>
<td>MWCNT</td>
<td>4–8</td>
<td>–</td>
<td>–</td>
<td>0.96</td>
</tr>
<tr>
<td>Grown by FCCVD, soaked in H₂O₂ and HCl</td>
<td>Radical pressing</td>
<td>DWCNT</td>
<td>2.1⁸</td>
<td>–</td>
<td>45–100</td>
<td>0.4–0.9</td>
</tr>
<tr>
<td>Spun from FCCVD, sprayed ethanol</td>
<td>As-spun aligned</td>
<td>MWCNT</td>
<td>15</td>
<td>–</td>
<td>13.5</td>
<td>–</td>
</tr>
<tr>
<td>Above fiber</td>
<td>Spatula pressing</td>
<td>MWCNT</td>
<td>15</td>
<td>–</td>
<td>22 × 0.65</td>
<td>–</td>
</tr>
<tr>
<td>CNT stocking from FCCVD, soaked in water, then winded</td>
<td>As-spun aligned</td>
<td>DWCNT</td>
<td>4.5⁹</td>
<td>–</td>
<td>160 × 7³⁹</td>
<td>–</td>
</tr>
<tr>
<td>Above fiber</td>
<td>Pressing</td>
<td>DWCNT</td>
<td>4.5⁹</td>
<td>–</td>
<td>220 × 0.5³</td>
<td>–</td>
</tr>
<tr>
<td>FCCVD→CNT film</td>
<td>Roll press 3000 N</td>
<td>MWCNT</td>
<td>6–17</td>
<td>–</td>
<td>14.8</td>
<td>1.38</td>
</tr>
<tr>
<td>FCCVD→CNT film</td>
<td>Spatula 100 N</td>
<td>MWCNT</td>
<td>15</td>
<td>–</td>
<td>5.6</td>
<td>2.16</td>
</tr>
<tr>
<td>CVD→overlap strands</td>
<td>Roll pressed at 450 kN</td>
<td>SWCNT</td>
<td>1–2</td>
<td>20</td>
<td>20</td>
<td>–</td>
</tr>
<tr>
<td>CVD spun on mandrel</td>
<td>Stretched while submerged in acetone</td>
<td>MWCNT</td>
<td>3–5</td>
<td>200</td>
<td>–</td>
<td>1.21–1.35</td>
</tr>
<tr>
<td>FCCVD→CNT fibers</td>
<td>4 dies, plate press 3.7 GPa</td>
<td>SWCNT</td>
<td>1.6</td>
<td>11.6</td>
<td>8</td>
<td>1.66</td>
</tr>
<tr>
<td>Cu–CNT composite by two-step deposition</td>
<td>Fully densified</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>5.2</td>
</tr>
<tr>
<td>Silver coating around CNT fiber surface</td>
<td>Conformal coating</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.08</td>
</tr>
<tr>
<td>Spun from VACNT array, dopamine infiltrated</td>
<td>Pyrolysis</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7.3</td>
</tr>
<tr>
<td>CNT sheets aligned by stretch</td>
<td>Aligned</td>
<td>MWCNT</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Above sheets, cross-linked</td>
<td>PCDO</td>
<td>MWCNT</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Grown by FCCVD, then soaking (30% H₂O₂, 37% HCl, 98% H₂SO₄) and washing</td>
<td>As-spun, aligned</td>
<td>DWCNT</td>
<td>–</td>
<td>–</td>
<td>5.5⁹</td>
<td>0.28</td>
</tr>
<tr>
<td>Above fiber</td>
<td>Iodine</td>
<td>DWCNT</td>
<td>–</td>
<td>–</td>
<td>5.5⁹</td>
<td>0.33</td>
</tr>
<tr>
<td>Spun from FCCVD, soaked in acetone, H₂O₂</td>
<td>Twisted, doped</td>
<td>DWCNT</td>
<td>–</td>
<td>–</td>
<td>95</td>
<td>1.29</td>
</tr>
<tr>
<td>Vacuum filtration of CNT suspension, then doping</td>
<td>KAuBr₄</td>
<td>SWCNT</td>
<td>–</td>
<td>–</td>
<td>20⁶</td>
<td>–</td>
</tr>
<tr>
<td>Aluminum</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.7</td>
</tr>
<tr>
<td>Copper</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>8.93</td>
</tr>
<tr>
<td>Silver</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>10.49</td>
</tr>
</tbody>
</table>

¹Values that are calculated from the data that authors provided; ²Rectangular shape of cross-sectional area; ³Cross-sectional area (µm²); ⁴Thickness of CNT film.
performance of the as-prepared CNT fibers, the complexity of manufacturing processes, or higher cost.

Based on the dopes used when spinning CNT fibers, two basic wet spinning methods were investigated: spinning 1) from stable CNT solutions using surfactant as dispersant,[39] and 2) from liquid crystalline suspensions of CNTs using superacid as a solvent.[22,29,38a] Vigolo et al.[59a] first reported CNT fibers spun from sodium dodecyl sulfate stabilized solutions using coagulation spinning approach. Because the polymer solution (polyvinyl alcohol (PVA) as the coagulation bath) was more viscous than the nanotube dispersion, flow-induced alignment of the nanotubes was expected, which is important for the improvement of electrical conductivity (see Section 5.1 for more details about the effects of CNT alignment on electrical conductivity). However, the polymer (PVA) in the coagulant bath, which exists in the final CNT fiber, is detrimental to the electrical transport due to the insulating nature of polymer. Additionally, other chemicals, such as water,[24,38a] alcohol,[60] and acid,[59b,60] could be used as the coagulant bath to replace the insulating polymer.

The other popular wet spinning method was first reported by Ericson et al. in 2004 using the liquid crystalline phase of CNT suspension.[38b] Instead of using surfactant as a dispersant, stable CNT suspension was prepared using superacid as the solvent (i.e., fuming sulfuric acid). CSA was also reported as a solvent for the preparation of liquid crystalline phase of CNT suspension.[22] Although these superacid solvents may remain in the spun CNT fiber as residual impurities, the electron transport performance can be enhanced through p-type doping of the superacid solvents, which is advantageous over using surfactant stabilized CNT solutions. And the reported conductivity can be up to $2.9 \times 10^6 \text{ S m}^{-1}$.[22] Another advantage is that alignment can be introduced either by the shearing force during spinning or retained from the aligned CNT domains of liquid crystalline suspension after spinning.[24,61] The coagulant bath composition was also investigated, which showed great influence on the surface morphology, diameter, and alignment of CNT fibers.[29] However, the main shortcoming of liquid crystalline phase spinning was also due to using superacid, which may cause issues after prolonged contact of the superacid with manufacturing equipment.

Alternatively, dry spinning from CNT forest or aerogel eliminated the difficulty in preparing stable CNT suspensions. Jiang et al.[52] first reported the 30 cm long CNT fiber in 2002, which was directly spun from a CNT array 100 μm in height. They found that the continuous fibers can only be drawn out from super-aligned CNT arrays. This has motivated research to improve either the spinnability of CNT arrays, which is related to their morphology,[62] or the electrical and mechanical properties by enhancing the interconnections between neighboring CNTs, which involves various in situ or ex situ treatments.[27,38b,44,61]

3.1.1. Compact Structure by Twisting

Twist densification has been widely investigated for CNT fiber fabrications.[64] Zhang et al.[27] first used a modified fabrication spinning process from CNT array by twisting during spinning to form a closely packed CNT fiber, achieving a high tensile strength between 150 and 300 MPa, and a high electrical conductivity of $\approx 3 \times 10^4 \text{ S m}^{-1}$. Recently, Shang et al.[44] reported a combination method, where CNT fibers were first twisted and then compressed. They found that the twisting and compressions are complementary steps in controlling the fiber structure and improving mechanical (2.5–3.0 GPa) and electrical ($\approx 1.2 \times 10^6 \text{ S m}^{-1}$) properties. The enhanced conductivity of CNT yarns is known to be attributed to the decreased yarn porosity. However, overtwisting may result in inner structural damages within the fibers. Additionally, the improvements of properties may be compromised due to the removal of twist when fibers are not tethered.[64]

3.1.2. Liquid Densification

Densely packed CNT fibers can be obtained by introducing volatile liquid solutions, such as acetone or alcohol, during spinning. This could induce shrinking effects on CNT fibers when they vaporize due to the capillary force, creating densely packed fibers. Consequently, the as-spun CNT fibers showed improved electrical or mechanical properties depending on the liquid solution used.

3.1.3. Polymer Infiltration

Tensile strength of CNT fibers can be significantly improved by polymer infiltration due to an enhanced load transfer between neighboring nanotubes. PVA is the most investigated polymer,[63a,63b] and could enhance the mechanical strength of CNT/PVA composite fibers to almost 2 GPa.[63c] However, Zhang et al.[27] found that although higher mechanical strength of 850 MPa can be obtained for CNT fibers by infiltration with PVA, the insulation nature of PVA (nonconductive polymer) decreased the conductivity of fiber by about 30%. Other polymers including polyimide,[66] BMI, and biomaterials, were explored to either improve mechanical or electrical properties or both. Recently, Ryu et al.[23] proposed a modified fabrication process to achieve mechanically strong and electrically conductive CNT fiber using a biopolymer polydopamine (PDA). Interestingly, the insulating and amorphous polymeric structure of PDA could be thermally converted to a conductive graphene-like adhesive structure, which served as a conductive bridge and connection among nanotubes for load transfer and charge transport. The resulting fiber exhibited both ultrahigh strength (=4 GPa) and electrical conductivity (=5.0 × 10^5 S m^-1).

3.1.4. Mechanical Densification

A simple mechanical densification can also stimulate strong interactions among nanotubes, which improves fiber performance. For example, by drawing a CNT fiber through a series of dies with decreasing diameters, the inner pores and void spaces were eliminated, which was verified by the increased bulk density up to 1.8 g cm^-3.[38b] Additionally, by using potassium tetrabromoaurate (KAuBr4) as a liquid lubricant for drawing, an electrical conductivity of $1.3 \times 10^6 \text{ S m}^{-1}$ was achieved. Tensile
strength could also be significantly improved after mechanical densification up to ≈9.6 GPa, which was well above those for all other man-made fibers.\(^{[134]}\)

Since the first long CNT strand spun from aerogel with good alignment using FCCVD technique by Zhu et al.\(^{[38]}\) in 2002, great improvements have been made to transfer the excellent properties of individual CNTs to macroscopic CNT fibers. To date, ultra-high tensile strengths of up to 8.8\(^{[67]}\) and 9.6 GPa\(^{[134]}\) have been reported using FCCVD technique, which are well above those for fibers spinning from arrays or liquid solutions. Additionally, incorporating various post-treatments previously mentioned, including twisting, chemical doping, and mechanical densification, can increase electrical conductivity up to \(6.7 \times 10^6\) S m\(^{-1}\)\(^{[19,38c,68]}\) and easily approach the range of \(10^6\) S m\(^{-1}\)\(^{[13c,19,38c,44,63d,65,76]}\). The drawbacks in these measurements are always based on a very small and short fiber specimen. Table 3 lists the mechanical properties of fibers, which are highly conductive through various post-treatments reported in literature. More details about mechanical properties of CNT fibers can be found in the reviews by Lu et al.\(^{[8]}\) A great challenge in using CNT fibers as conductors is simultaneously achieving high electrical conductivity and high mechanical strength. For example, after polymer infiltration treatment, the tensile strength of a CNT fiber showed an increase of more than 1.2 times from \(\approx 2.81\) to \(\approx 3.6\) GPa, while a sharp decrease of electrical conductivity was observed from \(\approx 1.2 \times 10^6\) to \(\approx 4.9 \times 10^5\) S m\(^{-1}\)\(^{[38c]}\). Further research is needed to discover a better way to balance the trade-offs between high electrical conductivity and high mechanical property.

### 3.2. Carbon Nanotube Films

Processes for making free-standing CNT films have been widely reported, including vacuum filtration,\(^{[69]}\) liquid casting,\(^{[70]}\) and droplet-drying.\(^{[71]}\) Similarly, the liquid crystalline phase of both CNT and graphene suspension was used to produce both fibers and films.\(^{[72]}\) Among the suspension processes, vacuum filtration is a simple and versatile method suitable for nanoscale fibrous materials. By adjusting the amount of suspension used for filtration, CNT films with a controlled thickness can be obtained. Recently, CNT film with good alignment was also reported by He et al.\(^{[71]}\) using a super-slow filtration rate of 1–2 mL h\(^{-1}\). Additionally, various post-treatments are available to further improve the mechanical and electrical conductivity of as-prepared films. Overall, the big issue of current filtration method is the low production rate, although large filtration systems can be used. One good example is to develop a continuous filtration system, which paves the way for large scale production and potential engineering applications.\(^{[55a]}\)

Like the dry spinning method to prepare fibers, CNT films can also be produced by drawing sheets directly from CNT arrays\(^{[45,74]}\) or aerogel\(^{[33a,75]}\) through a layer-by-layer deposition. The production rate of drawing from arrays may be only limited by the dimensions of CNT arrays. For example, a forest of 1 cm long and 245 \(\mu\)m high yielded a 3 m long free-standing MWCNT sheet.\(^{[56]}\) However, using FCCVD technique, CNT films collected directly from aerogel can be continuously obtained, which have been commercialized by several companies, including Nanocomp. Inc.\(^{[53a]}\)

### 4. Properties of CNT Assemblies

#### 4.1. Mechanical Properties

Although difficulties exist in transferring the excellent mechanical properties of individual CNTs to macroscopic fibers, the past few years have seen great improvements in transferring both tensile strength (up to 9 GPa\(^{[13c,38c,67]}\)) and stiffness (up to 250 GPa\(^{[38c]}\)). This caliber of mechanical performance is better than the conventional metals used in electrical conductor engineering fields today. Such high mechanical performance is usually realized in CNT fibers by various post-treatments including mechanical densification and polymer infiltration.\(^{[13c,19,38c,44,63d,65,76]}\) The drawbacks in these measurements are always based on a very small and short fiber specimen. Table 3 lists the mechanical properties of fibers, which are highly conductive through various post-treatments reported in literature. More details about mechanical properties of CNT fibers can be found in the reviews by Lu et al.\(^{[8]}\) A great challenge in using CNT fibers as conductors is simultaneously achieving high electrical conductivity and high mechanical strength. For example, after polymer infiltration treatment, the tensile strength of a CNT fiber showed an increase of more than 1.2 times from \(\approx 2.81\) to \(\approx 3.6\) GPa, while a sharp decrease of electrical conductivity was observed from \(\approx 1.2 \times 10^6\) to \(\approx 4.9 \times 10^5\) S m\(^{-1}\)\(^{[38c]}\). Further research is needed to discover a better way to balance the trade-offs between high electrical conductivity and high mechanical property.

#### 4.2. Thermal Properties

High thermal conductivity is necessary to achieve good performance of thermal dissipation when CNT conductors are subject to high current density. Theoretically, CNT fibers and films have great potential applications in thermal management,\(^{[77]}\) flexible heating,\(^{[78]}\) or batteries.\(^{[79]}\) The thermal conductivity of CNT fibers at room temperature was reported with a value of (60 ± 20) W m\(^{-1}\) K\(^{-1}\).\(^{[80]}\) This value is far lower from the predicted theoretical value of up to 3000 W m\(^{-1}\) K\(^{-1}\).\(^{[81]}\) Possible reasons are attributed to the interfacial thermal resistance, defects in the individual nanotubes, and macroscopic structural imperfection.\(^{[82]}\)

However, by optimizing the macroscopic structure to achieve good CNT alignment and dense packing, the as-spun CNT fiber using liquid crystalline spinning method has a thermal conductivity of up to 380 W m\(^{-1}\) K\(^{-1}\). This value was even doubled (635 W m\(^{-1}\) K\(^{-1}\)) after iodine doping.\(^{[22]}\) Additionally, thermal conductivity of CNT films showed an in-plane thermal conductivity of 110 W m\(^{-1}\) K\(^{-1}\). Researchers condensed CNT films into fibers combining with mechanical stretching, resulting in a significant improvement of thermal conductivity (770 ± 10 W m\(^{-1}\) K\(^{-1}\)).\(^{[81]}\) They claimed this value is the highest thermal conductivity reported for CNT bulk materials to date. However, more research on the thermal dissipation of CNT fiber and film under high current density is still needed.

#### 4.3. Electrical Properties

Currently, the electrical conductivity of as-prepared CNT fibers reported in literature has a very broad range from 10 to \(6.7 \times 10^6\) S m\(^{-1}\).\(^{[18,59a]}\) Even the most conductive fibers are still inferior compared to metal conductors of up to \(10^5\) S m\(^{-1}\). Tremendous efforts have been initiated to synthesize uniform nanotubes of macroscopic assemblies, which possess high electrical conductivity. This uniformity includes diameters, length, chirality, and number of walls. However, using current CVD techniques to achieve controlled synthesis of nanotubes is challenging.\(^{[81]}\) In practical situations, diffusive conductions were observed for CNT assemblies. This is probably arising from factors such as atomic structure defects of individual nanotubes, imperfect microstructure and macrostructure of CNT
assemblies, including misalignment, impurities, voids, and pores.\cite{84} Several conduction mechanisms are proposed to obtain a fundamental understanding of the electrical transport properties of macroscopic CNT assemblies,\cite{15,85} Hopping, in general, can be described as the inelastic tunneling transfer of an electron between two localized electronic states centered at different locations. The most important type of hopping conduction is variable-range hopping (VRH). This model describes the low temperature conduction behavior in any strongly disordered system with localized states (CNT assemblies could belong to this disordered system). Mott first pointed out at low temperature, the most frequent hopping would not be to the nearest neighbor.\cite{86} Hence, electrons hop from one initial site to another with energy hop as low as possible. This VRH model gives the relation between conductivity $\sigma_{\text{CNT}}$ and temperature $T$, which is described by the following equation as\cite{83}

$$\sigma_{\text{CNT}}(T) = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/(1+d)} \right]$$

where $\sigma_0$ is a constant, $T_0$ is related to the energy barrier for electron hopping through nanotube junctions, and $d$ is the effective dimensionality ($D$) of the system. One example where the VRH model is applicable is in the electrical conduction behavior of a CNT fiber, which was reported to follow a 3D VRH model by Li et al.\cite{15} Figure 6a shows the temperature dependence of resistivity $\rho$ and conductivity $\sigma$ in a low temperature range, which can be well fitted using the 3D VRH model (Figure 6b).

As shown in Figure 6b, with a dimensionality fact $d=3$, this 3D hopping conduction characteristic is most likely due to the imperfect intertube structures (high contact resistance) of CNTs and other structure defects in assemblies. Thus, electrons may hop from one localized site to another, or possibly from one CNT to another, as long as hopping energy is as low as possible.\cite{83} The main contact resistance (energy barrier) at the intertube connections within CNTs assemblies significantly decreases the electron transport efficiency, resulting in a low conductivity. Foroughi et al.\cite{83} found that by adding graphene sheets into CNT fiber, the graphene/CNT hybrid fiber showed higher conductivity than the pristine CNT fiber, and also followed the 3D-VRH behavior, as shown in Figure 6c. The calculated hopping distance (another parameter in VRH model) of graphene/CNT hybrid fiber showed a much smaller value of 0.25 nm than that of pristine CNT fiber of 1.28 nm, which explained its higher conductivity and indicated that graphene decreased the contact resistance.

Kaiser et al.\cite{85} pointed out the conduction similarity between SWCNTs and conducting polymers, as the temperature reaches low range,\cite{85} which can be explained by the heterogeneous model.\cite{85a} To simplify, resistivity of CNT assemblies primarily comes from two parts: the resistance of individual CNTs and the contact resistance between neighboring CNTs as previously discussed. The resistance of tunneling these contact barriers comes from the intertube gaps where carriers transfer from one nanotube to another within the same bundle or the nearby one. In CNT networks, barriers for carrier transporting are misalignments, twists (waviness), intertube contacts, or other defects along the CNTs. Taking into account barrier resistance given by fluctuation-assisted tunneling through thin barriers between metallic regions\cite{88} and the metallic resistance arising from backscattering by phonons along CNT longitudinal direction,\cite{89} an expression for the resistivity, described by the heterogeneous model,\cite{85a} is given by

$$\rho(T) = \frac{1}{\sigma(T)} = A \exp\left( - \frac{T_{\text{mb}}}{T} \right) + B \exp\left( \frac{T_b}{T - T_b} \right)$$

where $A$ and $B$ represent the geometrical factors particularly depending on the alignment of nanotubes. Typical barrier energies are related with the value of $k_B T_b$ (where $k_B$ is Boltzmann’s constant), and the resistivity of quantum tunneling through the barrier in the low temperature limit is indicated by the value of factor $T_b/k_B$. To achieve high conductivity, barrier energy should be as small as possible, which requires to eliminate all sources that may cause barriers for electron transport, such as contact resistance from misalignment, voids, and impurities.

Controlling the intrinsic properties of nanotubes (diameters, length, chirality, and number of walls) is challenging; however, 

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*Figure 6. a) Temperature dependence of the resistivity ($\rho$) and conductivity ($\sigma$) of a spun CNT fiber. b) Fitting of the conductivity data of spun CNT fibers with variable range hopping (VRH) conduction mechanisms. (a), (b) Reproduced with permission.\cite{15} Copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA. c) Temperature dependence of dc conductivity of the CNT yarn and CNT/graphene yarn. The arrow shows the crossover temperature $T^*$ between two regions. Solid lines are fits to 3D-VRH model (Reproduced with permission.\cite{87} Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA.).*
based on the conduction mechanism previously discussed, minimizing contact resistance among neighboring nanotubes can sufficiently improve the electrical conductivity of CNT fibers and films. Due to the complexities of synthesizing uniform CNTs, the low electrical performance of as-prepared fibers indicates that more research may focus on simple and effective post-treatment methods (see Section 5). For example, Zhao et al.\textsuperscript{[18]} found that the effects of iodine doping on the conductivity of CNT fibers are significantly effective, improving from $2.0 \times 10^6$ to $6.7 \times 10^6 \text{ S m}^{-1}$. Zhang et al.\textsuperscript{[18]} reported the effectiveness of CNT alignment on the conductivity of CNT tapes up to $2.5 \times 10^5 \text{ S m}^{-1}$. Mechanical pressing was also investigated by Wang et al.\textsuperscript{[19]} to enhance conductivity of a CNT ribbon by one order of magnitude from $1.27 \times 10^5$ to $2.1 \times 10^5 \text{ S m}^{-1}$. However, the combination of high conductivity, efficiency, and environmental sustainability with the capability of large-scale production is still challenging. Currently, it would seem that the high conductivity is furnished from the smaller size of the sample. Additionally, either toxic acid, harmful gas, or extended post-treatment times are utilized to approach the high electrical performance. Therefore, an efficient and environmentally friendly way to manufacture highly conductive macroscopic CNT assemblies requires further research.

5. Improving the Electrical Conductivity of CNT Conductors

Recent investigations have focused primarily on post-treatment methods in order to achieve CNT conductors with significantly improved electrical conductivity. Some of these methods aim to improve the physical aspects of the CNT conductors, such as nanotube alignment\textsuperscript{[13a,19,38c]} and increased nanotube packing density.\textsuperscript{[13e,19,38c]} Others concentrate on chemical alterations including chemical doping and cross-linking.\textsuperscript{[91]} Furthermore, hybrids of CNT and graphene are also reported to be highly electrical conductive.\textsuperscript{[92]} Interestingly, all the aforementioned post-treatment methods could be explained by two working mechanisms: either minimizing the contact resistance between individual CNTs or bundles or increasing carrier concentration/mobility of CNT assemblies. Contact resistance is reported to dominate the resistivity of macroscopic CNT assemblies.\textsuperscript{[13a,15,19,22]} This chapter covers the most important methods used to improve the electrical conductivity of CNT conductors including: 1) aligning the CNTs or bundles in one direction (Section 5.1),\textsuperscript{[13a,38c,93]} 2) decreasing the tube–tube contact resistance (Section 5.2),\textsuperscript{[13c,19,25]} 3) increasing the concentration of charge carriers and enhancing their mobility within CNT assemblies by chemical bonding and doping (Section 5.3),\textsuperscript{[18,22,31,40]} 4) balancing the synergistic effects of CNT and graphene (Section 5.4).\textsuperscript{[92a,34]}

5.1. Introducing Alignment

The alignment of nanoscale or microscale fibril components in macroscopic materials is preferred when attempting to achieve a high performance for both electrically and physically. For instance, unidirectional carbon fiber reinforced composites possess a much higher tensile strength in the fiber aligned direction.\textsuperscript{[99]} When it comes to CNT composites, a good dispersion of CNTs (no aggregation) in a polymer matrix with a preferential alignment direction can result in several times higher mechanical properties than that of its counterpart with aggregation and random CNT distribution.\textsuperscript{[13a,93,96]} Similarly, inducing nanotube alignment in fibers and films to achieve high electrical performance of CNT conductors is also important.\textsuperscript{[113b,19,22,25,38c]}

5.1.1. Electrical and Magnetic Field Induced Alignment

Several scientific reports on the alignment of CNTs induced by an electric field, a magnetic field, or the combination of both, have been published.\textsuperscript{[13,97]} When an electric field was applied, one basic effect regarding to the alignment of CNTs was observed: electrophoresis.\textsuperscript{[98]} Under the electric field, dipole moments are induced to nanotubes, causing a rotational force which aligns the nanotubes in the electric field direction (Figure 7a).\textsuperscript{[97d]} Afterward, an electrostatic interaction between the ends of oppositely charged CNTs is generated (as dipoles shown in Figure 7b), and an electrophoretic force is induced by the presence of the charged surfaces.\textsuperscript{[98a]} Driven by the oppositely charged ends, the CNTs also gradually move closer, forming a network of tubes connected head-to-head, aggregating in chain-like structures (Figure 7c).\textsuperscript{[97d]} The CNT network is stretched across the space between the two electrodes to provide a conductive pathway through the sample, which further facilitates their alignment.\textsuperscript{[98a]} An indirect indicator of improved alignment involved monitoring the electrical current changes over time (Figure 7d). The trend showed a significant increase in current when electric field was applied. After the initial steep increase, the current reached a plateau indicating that the conductive CNT pathway was established.\textsuperscript{[97d]} Shekhar et al.\textsuperscript{[98a]} found that the alignment assembly was mainly controlled by four parameters at fixed electrode distance: the applied external voltage $V_{pp}$ (namely the electric field), sinusoidal frequency ($f$), the concentration of the CNT solution, and electrophoresis time. Under optimized conditions, highly dense and aligned CNT networks can be obtained. To take an example, by varying the concentration of the CNT solution while keeping the other parameters fixed, the aligned CNT assembly was achieved at different densities, as shown in Figure 7e–j.\textsuperscript{[98b]}

CNT alignment can also be obtained by applying a magnetic field due to their paramagnetic property of CNTs in the direction of their long axes, as shown in various theoretical calculations.\textsuperscript{[99]} Recently, metal particles were shown to help the alignment of CNTs when going through magnetic field.\textsuperscript{[100]} Thus, CNTs are susceptible to strong anisotropic magnetic fields and can be freely rotated and aligned in liquid a suspension. Smalley and co-workers produced macroscopic SWCNT films with good alignment by filtering the CNT suspension under a 25T magnetic field. Additionally, the simultaneous application of electric and magnetic fields could improve the alignment degree of CNT in composites.\textsuperscript{[97c]} Although the electrical properties may be improved by these two methods, the disadvantages may outweigh the benefit. Small sample size, low CNT concentration in polymer matrix, or the significantly high
energy demand of generating high magnetic fields (e.g., 25 T) render both the electric and the magnetic alignment method impractical and noneconomic.

5.1.2. Alignment from Liquid Crystalline Phase Spinning

The concept of high-aspect-ratio rigid-rod polymers was also reported to be applicable for CNTs. This analogy between polymers and CNTs will allow us to take advantage of coagulation spinning and the use of the liquid-crystalline phase, which are widely used in polymers spinning processes, to obtain nanotube alignment within CNT fibers. Song et al. first reported the liquid crystallinity of a MWNT suspension, which directed tremendous efforts toward developing wet spun CNT fibers and films. Zhang et al. reported a coagulation spinning method successfully fabricating well-aligned CNT fibers due to the combination of shear forces during spinning and the use of the liquid-crystalline phase of CNT suspension. The CNT fibers showed highly anisotropic electrical properties with an electrical conductivity of 800 S m\(^{-1}\) along the fiber axis at room temperature, which is about 100 times higher than perpendicular to the fiber axis. This measurement indicates that a high alignment degree endorses the substantial improvement in electrical conductivity along the fiber axis.

A great improvement in the electrical conductivity of CNT fibers was reported by Pasquali and co-workers in 2013, using chlorosulfonic acid as a solvent to achieve spinnable liquid crystalline dopes of CNTs. The as-spun fibers were collected onto a winding drum with a linear velocity that was higher than the dope speed at the spinneret exit so as to align CNTs by continuously stretching and tensioning the filament. The high alignment degree of nanotube bundles within the CNT fiber was revealed by high resolution SEM (HRSEM), as shown in Figure 8f. Those highly aligned CNT fibers displayed a high room temperature electrical conductivity of around \((2.9 \pm 0.3) \times 10^6\) S m\(^{-1}\), as shown in Figure 21d. The iodine doping further increased the conductivity to \((5 \pm 0.5) \times 10^6\) S m\(^{-1}\) (see Section 5.3 for more details concerning chemical doping). These values were reported to be stable over a year in laboratory conditions.

An explanation of the nature of a CNT liquid crystalline suspension of CNT can be found in the review by Zhang et al. Generally, to form a liquid crystalline phase at room temperature, a stable and highly concentrated CNT suspension is needed—already a challenge due to the strong van der Waals attraction between CNTs. Therefore, a strong solvent with the ability to disperse CNTs into individually floating nanotubes is necessary. Several different strategies have been developed to successfully form a CNT liquid crystalline suspension including the negative or positive charging of CNT surfaces, polymer wrapping, drop drying, drop drying, and shear flow. Among them, the combination of the first two methods has been the optimal technique, displaying the highest production capability and electrical conductivity as compared to polymer wrapping (insulation issue) and drop drying (low yield). Acid oxidation (negative charging of the CNT surface) and protonation (positive charging) proved to be the reasons of screening out the strong van der Waals attractions between CNTs, allowing a liquid crystalline phase to form. Specifically, acid oxidation introduces carboxylic, carbonyl, and hydroxyl groups, improving the dispersibility and stability of the CNTs in a polar solvent. For acid protonation, it has been suggested that CNTs can behave as weak bases and get protonated by superacids. As a result, the delocalization of positive charge over the entire CNT occurs. Such protonation yields the formation of ordered acid layers on the CNT surfaces and thus the dissolution of CNTs, as shown in Figure 8g,h, is one possible mechanism that generates the
repulsive interaction between CNTs. As a result, typical solvents are not good for CNT dispersion; therefore, only extremely dilute solutions of CNTs are thermodynamically stable and show no liquid crystalline phase at room temperature. However, superacids (highly concentrated acid such as $100+\text{wt}\%\ \text{H}_2\text{SO}_4$ or $\text{HSO}_3\text{Cl}$) was reported to disperse CNTs at a concentration of 2–6 wt%, forming a spinnable liquid crystalline dope, as shown in Figure 8e. The alignment characteristics in the liquid crystal domain were retained in the final macroscopic fiber (Figure 8f) directly using wet spinning process (shear flow). Stronger acids yield larger liquid-crystalline domains, resulting a higher alignment within the macroscopic CNT fibers. Additionally, the spinning process and coagulation bath composition also affect the final fiber morphology.

After carefully examining the data from literature shown in Table 3, we determined CNT fibers from liquid crystalline phase spinning coupled with chemical doping should achieve the best electrical performance to date. Naturally, this method would seem to prevail over other methods due to the high electrical conductivity, potential scalable production capability, and stable performance. Note that CNT fibers spun from a liquid crystalline suspension (i.e., $\text{HSO}_3\text{Cl}$ as solvent) showed the highest electrical conductivity of $\approx 2.9 \times 10^6 \text{ S m}^{-1}$. This value is one magnitude higher than other spun fibers without the use of a liquid crystalline phase. Recently, Bucossi et al. optimized a liquid crystalline phase spinning process by adjusting the coagulation bath composition, which produced CNT fibers with the highest reported room temperature electrical conductivities to date of up to $(4.1–5.0) \times 10^6 \text{ S m}^{-1}$. Although other methods, such as mechanical pressing, could achieve conductivities of $\approx 2.0 \times 10^6 \text{ S m}^{-1}$, the effectiveness of conductivity improvement and production scalability are inferior as compared to superacid induced liquid crystalline phase spinning. Neglecting any atomic control of individual CNTs, including the number of walls, diameter, length, and chirality, the major reasons that liquid crystalline phase spun CNT fibers are highly conductive may be explained by: 1) ultrahighly aligned nanotubes/bundles within the as-spun CNT fibers, 2) compact structure/high packing density of the CNT fiber from liquid crystalline phase spinning technique, 3) crystalline-like structure with fewer impurities (less defects of amorphous carbon, or catalyst, etc.), and 4) ultrahigh carrier concentration benefiting from the superacid as a dopant.

For example, Figure 8f shows an HRSEM image of well aligned CNT fibrils/bundles spun from a liquid crystalline suspension.

Figure 8. Nanotube alignment within CNT fibers from liquid crystalline phase spinning. a) The schematic of the experimental setup for the liquid-crystalline spinning process of well-aligned nanotube fibers. b) Optical images of the fiber with and without crossed polars; under crossed polars, the fiber is strong nematic-like birefringent. c) SEM image of the as-spun fiber from a 3 wt% CNT suspension in glycol. d) High-magnification image of the fiber surface shows that the individual nanotubes are well aligned along the fiber longitudinal axis. (a)–(d) Reproduced with permission. Copyright 2008, Wiley-VCH Verlag GmbH & Co. KGaA. e) Light micrograph of a birefringent fiber spinning suspension (3 wt% CNT in chlorosulfonic acid). f) High-magnification SEM showing the typical morphology of as-spun CNT fiber composed of $\approx 100 \text{nm}$ thick fibrils aligned along the fiber axis. (e),(f) Reproduced with permission. Copyright 2013, AAAS. g,h) A model illustrating the swelling of SWCNT bundles in sulfuric acid. g) A cartoon of SWCNTs in van der Waals (VdW) contact within a neat fiber, and h) the same SWCNT fiber after re-exposure to sulfuric acid. (g),(h) Reproduced with permission. Copyright 2004, AAAS. i,j) SEM images showing fiber’s cross-section with no micrometer-sized voids and only few hundred-nanometer-sized voids. k) single-fibril TEM micrograph and electron diffraction (inset) showing near-crystalline packing within a fibril. (i)–(k) Reproduced with permission. Copyright 2013, AAAS.
phase in HSO$_3$Cl (typical dimension of 10–100 nm in diameter and >50 µm in length). The high alignment was quantitatively confirmed by a Herring orientation factor of 0.986. From the cross-sectional image shown in Figure 8i, only occasional ≈100 nm voids were observed. The volume density of fiber (1.3 g cm$^{-3}$) is ≈90% of the theoretical close-packed density of 1.5 g cm$^{-3}$. Additionally, the CNT fibrils/bundles exhibited near-crystalline packing, as shown in Figure 8k. The doping effect of the superacid (HSO$_3$Cl) further improved the conductivity approximately fivefold to tenfold due to the increased intra-CNT conductivity of the semiconducting CNTs higher carrier concentration, and also the increased disorder that helps relax the momentum conservation required for inter-CNT transport.[22] These advantages seem to prevail over the conductivity loss due to enhanced electron-impurity scattering. Therefore, a more environmentally friendly method would be desired.

5.1.3. Aligned CNT Fibers from Dry Spinning CNT Array and Aerogel

The dry spinning method used to fabricate CNT fibers can be categorized into two different types: a one-step method (directly spinning from CNT aerogel) and a two-step method (mostly growing vertically aligned CNT (VACNT) array on a substrate first, and then spinning from the array).

Spinning from VACNT Array (Two-Step Method): Spinning a CNT fiber from a VACNT array grown on a substrate is like drawing a thread from a silk cocoon. In 2002, Jiang et al.[52] pioneered the VACNT spinning process by continuously drawing aligned CNT arrays into self-assembled yarns of up to 30 cm in length with remarkable mechanical, electrical, and thermal properties. Further modifications to improve their properties were made in the form of various post-treatments. Some of these include introducing twists into the fibers during the spinning process,[15,27,107] mechanical stretching, pressing, and microcombing to improve alignment and packing density within the fibers.[13a,32,42] Depending on the collection method, either CNT fibers or films can be made from a VACNT array.[54,74c,108] Figure 9a shows a typical spinning method.[74c]

The CNT arrays are grown on the silicon substrate with a catalyst layer deposited on top before the CVD process. By varying the size of the silicone substrate and the CVD process parameters (growth zone temperature, carbon source flow rate, and deposition time etc.), a large CNT array can be grown, which can produce a large quantity of CNT fibers and films, as shown in Figure 9b,c.[54,74c] So far, a production rate of 30 m h$^{-1}$ can be achieved.[54]

The details behind the continuous spinning of aligned fibers and films from a VACNT array can be found in other reports.[62a,107b,108,109] To put it simply, when the first bundle is pulled away from the CNT array and substrate, the process will pull out adjacent ones. Once dislodged from the array, they connect to each other in a repeated end-to-end configuration, which engenders a continuous fiber or film with good alignment (Figure 9d–f).[109] The schematic drawing shown in the Figure 9f inset graphically displays this process.[109] In this model, the

Figure 9. CNT fibers and films spun from a vertical array. a) A CNT film spun from a VACNT array on a 4 in. silicon wafer was continuously wound on a rotating spindle and collected. b) Flexible CNT film strip. (a), (b) Reproduced with permission.[74c] Copyright 2012, American Chemical Society. c) The production of hundreds of meters-long fibers spun from CNT arrays (Reproduced with permission.[54] Copyright 2016, Wiley-VCH Verlag GmbH & Co. KGaA.). d) Electron microscopy images of VACNT array grown on silicon wafer (low magnification). e) Cross-sectional view of the CNT forest’s edge showing CNT self-assembly to form a sheet. f) High magnification image showing the alignment of the CNTs in the forest side-wall. (d)–(f) Reproduced with permission.[108] Copyright 2010, Elsevier. (f) (Inset) The scheme drawing model of VACNT array spinning process of pulling out a forest tree from the forest (Reproduced with permission,[109] Copyright 2011, American Chemical Society.).
original forest was assumed to consist of vertically oriented forest trees, known as large bundles, which were interconnected by smaller bundles or individual nanotubes, called connects. Therefore, the first bundle (forest tree) is peeled off (unzipped) from the bottom of the forest, while the next bundle will be pulled off from the top (Figure 9f, inset). Then, all bundles are connected to each other and aligned in the pulled direction. Simultaneously, this pulling process is repeated so that continuous fibers and films with good alignment can be obtained.

Unfortunately, not all CNT arrays are suitable for spinning, as described by spinnability. The spinnability is strongly dependent on the morphology of arrays, including the height of arrays, density, and substrate. As a result, many groups have worked to adjust and control the morphology of VACNT arrays through modified CVD methods. These projects investigated the roles of catalysts, the surface chemistry of substrates, gas flow rates, reaction temperatures, times, etc. More details can be found in the review by Huynh and Hawkins. The quality and spinnability of VACNT arrays are important factors affecting alignment during the direct spinning process and therefore, the mechanical and electrical performance of as-spun CNT fibers and films. Other post-treatments, such as stretching, pressing, and chemical doping, are required to further improve the electrical and mechanical properties of as-spun fibers and films. Nevertheless, due to the size limitation of the CVD furnace and substrate, only batch production is available. This presents issues for various applications in the future where large quantities are required.

Spinning Directly from CNT Aerogel (One-Step Method): In 2002, Zhu et al. first reported a 20 cm long well aligned SWCNT strand, which was directly spun from the CNT aerogel synthesized by the catalytic pyrolysis of n-hexane with an enhanced vertical FCCVD technique. The as-spun CNT fiber was characterized to possess good strength ($\approx 1.2$ GPa) and electrical conductivity ($1.4 \times 10^5$ S m$^{-1}$).

To date, great improvements in both the electrical and mechanical properties of fibers and films produced via aerogel spinning were reported by several research groups, including Zhao et al., Wang et al., Tran et al., and Zhang et al. Figure 10a schematically shows direct aerogel spinning. The grown CNTs entangle to form an aerogel consisting of thousands of individual nanotubes. Once the aerogel is drawn out from the furnace, the van der Waals forces between the CNTs hold them together forming monolithic entities of fibers or films. The alignment was induced by varying the winder collection speed or using a series of collection winders with different speeds. This winding process can introduce the effects of mechanical stretching. Usually, on-line condensation is introduced, such as acetone, ethanol, or PVA spray, to densify the loose CNT network. Typi- cally, a large quantity of less aligned CNT films can be readily produced (Figure 10b,c). Therefore, post-treatments such as mechanical stretching, pressing, and chemical doping are applicable to these products to further improve their electrical conductivity. The mass production capability of the aerogel spinning process is exceptionally higher than that of the CNT array batch method. The reliable drawing speed of the aerogel spinning method hovers around 180 m h$^{-1}$. Naturally, this technology has already been commercialized by several companies including Nanocomp. Inc. (Figure 10b–d).

5.1.4. Mechanical Stretching Induced Alignment

Although CNT fibers and films spun from CNT aerogel using FCCVD technique resulted in good alignment, this in-line
alignment method is not efficient due to low stretching ratio and the degree of alignment is not sufficient to approach the excellent properties of individual CNTs. During the polymer fiber extrusion process, mechanical stretching was applied to straighten the polymer chain and increase the crystalline area, improving the mechanical properties. Similarly, it was also found to be efficient enough as a postalignment method to achieve ultrahigh degree of alignment degree of CNTs with controllability. Many research groups have used this mechanical stretching method to align the CNT bundles. Liang and co-workers reported a direct mechanical stretching method, as shown in Figure 11a, where randomly oriented CNTs will become aligned under the stretching force due to their entanglement and large aspect ratio. The electrical conductivity was improved from $4.2 \times 10^4$ to $6.0 \times 10^4 \text{ S m}^{-1}$ at a 40% stretching ratio (Figure 11b), due to the better alignment, denser packing, and better contacts between neighboring nanotubes. Before the mechanical stretching process, the randomly oriented CNT films were wetted by a liquid solvent or polymer, which assisted the movement of entangled nanotubes.

Figure 11. Mechanical stretching method to align CNTs. a) Direct mechanical stretching to align nanotubes in the as-received random CNT film. b) Effects of stretching ratio on electrical conductivity of aligned CNT film parallel to the alignment (stretching) direction. (a),(b) Reproduced with permission. Copyright 2009, Wiley-VCH Verlag GmbH & Co. KGaA. c) Schematic illustration of multistep stretching–pressing method. Reproduced with permission. Copyright 2015, Nature Publishing Group. d) The polarized Raman spectra of $G_\parallel$ and $G_\perp$ bands for the as prepared CNT sheet, e) processed after stretching and pressing, and f) after second stretching and pressing. (d–f) Reproduced with permission. Copyright 2014, Royal Society of Chemistry.
CNT bundles by acting as a lubricant under stretching.\cite{93,115} Liu et al.\cite{76b} and Han et al.\cite{96} reported a multistep stretching and pressing method (Figure 11c), resulting in highly dense CNT sheets, which showed a considerably high volumetric density of 0.98 g cm\(^{-3}\) after two stretching–pressing processes. The degree of alignment was characterized by the intensity ratio of G-band peaks (\(I_{G//}/I_{G\perp}\)) from polarized Raman spectroscopy, as shown in Figure 11d–f. The ratio increased from \(\approx 1.1\) for the as-prepared CNT sheet, to \(\approx 8.8\) for the stretching–pressing process sheet, indicating an extremely high degree of nanotubes alignment.

The benefit of CNT alignment is the improved electrical conductivity. With a VRH model, one can explain a portion of alignment induced high conductivity on the basis of simple geometrical considerations. Initially, one must assume that the intrinsic resistance of a nanotube should be much lower than the tube–tube contact resistances. Considering there are fewer tube–tube contacts for a given length of an aligned sample in the alignment direction as compared with the random sample in any specified direction, the resistance should be lower. This translates to the difference in hopping rate between the alignment direction of the aligned sample and any other specified direction in the random sample.\cite{116} As shown in Figure 12a, the ability of electrons to hop at the interfaces/ends between neighboring CNTs is crucial in determining the electrical resistance of the fiber. Fewer interfaces/ends and shorter distances at the interfaces help to reduce the electron loss during the hopping process,\cite{117} resulting in a high conductivity, which is why the aligned and densely packed structure within fibers and films matters in determining the electrical conductivity. The effect of alignment on the electrical and thermal conductivity was also observed experimentally by Chen et al. (Figure 12b–d).\cite{116b}

Understanding the dynamic structure–property relationship between the electrical conductivity and the structure of CNT network during mechanical stretching would be beneficial. However, correlating the structural changes to the performance improvements, such as electrical conductivity and mechanical strength, would be challenging considering the directly observed parameters of structural evolution including bundle size and alignment degree change are not direct indicators of electrical or mechanical performance. Basic indicators, such as load transfer and electron transport efficiency (or band structure change), are more directly related to mechanical and electrical properties, respectively. Once the relationships between structural parameters, such as bundle size and alignment, and basic indicators of properties, including electrical and mechanical performance, become more obvious and acceptable, a precise mathematical model may be derived.

Figure 13 schematically shows the structural evolution of the CNT network under stretching and the corresponding imaging electron microscopy (SEM)/transmission electron microscopy (TEM) images.\cite{37} Although the stretching induced structural change model was conducted\cite{116b} and the relationships between stretching ratio and electrical conductivity were also reported by Cheng et al.,\cite{118} the specific mechanism to account for the electrical conductivity improvement after high mechanical stretching is still absent. The in situ structure–property relationship characterization during stretching (i.e., interfacial shear stress (IFSS) change or, contact resistance change when bundles are merging together) is urgent and still challenging.
5.2. Minimizing Intertube Contact Resistance

Due to the weak interaction between CNT bundles, the mechanical and electrical properties of macroscopic CNT assemblies are significantly lower than those of their individual components. Several methods have been attempted to improve the packing density of CNT bundles within fibers, consequently increasing their interbundle and intertube interactions.[19,23,38c] The ideal packing structure of crystalline-like CNTs or dog-bone like collapsed CNTs is needed to achieve high electrical, thermal, and mechanical performance.[118] To date, obtaining such an ideal structure within a macroscopic CNT fiber is challenging. An alternate form of nanoscale welding was also enlisted to build the conduction pathway between the neighboring CNTs.[48,119] Through all these various processes, the post-treated CNT fibers and films could have fewer interspace (voids) between neighboring CNTs, more conductive pathways, and strong intertube interactions, resulting in a high contact friction (high mechanical strength) and low contact resistance (high electrical conductivity).

5.2.1. Mechanical Pressing and Rolling

The nature of the porous structure of macroscopic CNT fibers and films deteriorates their properties and is a critical issue which impedes their practical applications as electrical conductors or other engineering materials. For example, the electrical resistivity of a pure single crystal of copper, where nearly no grain boundary is present internally, is 2–10% lower than that of polycrystalline copper. According to Matthiessen’s rule,[120] due to the presence of impurities, defects, and grain boundaries in polycrystalline copper, additional resistivity could result from those defects scattering.[120] Similarly, the presence of voids, disorders, impurities, and loose packing structure also contributes to the loss in electrical conductivity, which poses a challenge.

Some groups have attempted to approach the ideal electrical transport value of individual CNTs by aligning the nanotubes along the fiber axis direction and densely packing them.[22] As shown in Figure 14a,b, achieving a crystal-like structure of CNT bundles/ropes with a conductivity in the range of \( \approx 10^6 \) S m\(^{-1} \) is possible.[20a,b] However, the “crystallite” size is limited to the nanoscale range. Another dense packing structure called flattened “dog-bone” like CNTs[121] or collapsed CNTs[115] could possibly exhibit better performance (Figure 14c,d). Indeed, the stacked-collapsed nanotube structure is shown to inherit the ultrahigh thermal conductivities of individual nanotubes,[118] which may also transfer the ultrahigh electrical and mechanical properties. Theoretical and simulation studies showed that high pressure strengthens the interactions between fullerene and carbon nanotubes, even after pressure was released.[122] Because
of the structure change induced by mechanical pressing, the bandgap was greatly reduced from semiconducting to metallic conduction, which indicates a major improvement in electrical conductivity.\cite{123}

Researchers have employed mechanical pressing and a rolling process to increase the packing density and alignment of CNT assemblies.\cite{119a,19} These densification processes are simple but highly effective to achieve a densely packed structure. As previously discussed, a continuous CNT fiber could be spun from an aerogel using the FCCVD technique, as shown in Figure 15a.\cite{38c} Even after an on-line liquid densification process is applied, the porous structure of CNT fibers can still be obviously observed (Figure 15c).\cite{38c} These pores lower the mechanical performance of the fiber by limiting the load transfer and reduce the electrical performance by increasing defects and contact resistance. Tran et al.\cite{38c} reported a mechanical densification process, as shown in Figure 15b, that used a stainless-steel spatula with a flat edge to slide across and densify the CNT fiber at a specific angle and force. After pressing with the spatula, it became a ribbon-like fiber (Figure 15d) with much smaller pores than without pressing, as shown in Figure 15c,e. The effects on electrical conductivity improvement are significant (Figure 15f), and the conductivity of the ribbon-like CNT fiber approached an impressive value of \(1.2 \times 10^6 \text{ S m}^{-1}\).

For large quantity production, developing a continuous process is important. By using a rolling and pressing method, Wang et al.\cite{19} reported a densified CNT ribbon with increased contact area (packing density). Interestingly, the rolling and pressing process is a common technique in the textile industry when fabricating fiber or fibril network. Similar to the spatula pressing method, the CNT fibers became densified after passing through the rolling and pressing system, as shown in Figure 15g. Since the fibers had a much larger aspect ratio in their cross-section, the fibers could be oriented on the roller so that it always compressed in its thickness direction (Figure 15h,i).\cite{19}

The rolled sample possessed significantly increased density, varying from 1.3 to 1.8 g cm\(^{-3}\) and demonstrated high electrical conductivity around \((1.82-2.27) \times 10^6 \text{ S m}^{-1}\). Additionally, an extremely high mechanical performance was obtained from a ultrahighly densified thin CNT ribbon (hundreds of nanometers in thickness) after repeated rolling and pressing, as shown in Figure 15j, with an average tensile strength of 9.6 GPa.\cite{13c}

Individual CNT alignment and packing structure are critical nanoscale factors that influence the electrical conductivity of their macroscopic CNT fibers. Specifically, the ideal case is all of the nanotubes are crystalline-packed (Figure 14), and all of the bundles are well aligned in one direction with strong surface interactions and long-range-order. However, achieving such an ideal long-range-order structure within macroscopic fibers using currently available methods such as dry fabrication (i.e., spinning from VACNT array or aerogel) or wet fabrication (i.e., liquid crystalline phase spinning) is difficult. Therefore, the challenge in transferring the excellent properties of individual CNTs to macroscopic CNT fibers and films is to extend the well-aligned and densely packed CNT crystalline size from the nanoscale and microscale range to the macroscale range, ultimately eliminating any possible misalignment, disorder and crystal defects (voids).

5.2.2. Nanowelding and Coating

Incorporating highly conductive metals into CNT assemblies in the form of coatings or nanowelding is another method being studied. These efforts attempt to improve the electrical conductivity by providing efficient conducting pathways between neighboring nanotubes.\cite{48,119a} These conductive metal nanoparticles act as an adhesive between neighboring CNTs, filling the voids and decreasing the contact resistance.\cite{47,124} The deposition of Au or Cu layer onto a CNT fiber can realize a metal-like conductivity of \((2-3) \times 10^7 \text{ S m}^{-1}\).\cite{124a} Most reports from the literature apply metal layer on the surface of a CNT fiber through electrodeposition. In this case, the thickness of the metal coating is important because the density of the resulting CNT–metal composite fiber will increase when a thicker coating is deposited. This is inferior to the intrinsic advantage of the low density of CNT conductors. Xu et al.\cite{48} reported a modified
method to fabricate CNT–Cu fibers where the fiber spinning, CNT anodization, and metal deposition were continuously integrated. Figure 16a,b shows the surface change for uncoated and coated CNT–Cu composite fibers. The anodization process assisted the strong interfacial bonding between Cu and CNT. Additionally, by varying the deposition time, the thickness of the coating layer could be precisely controlled. The final Cu–CNT composite fiber (Figure 16c) with a Cu thickness of 1 µm, showed a high conductivity of $1.81 \times 10^7$ S m$^{-1}$. Pt and Pd have also been used as coating layers to enhance electrical properties.\[124a\] Typically, the thicker the coating layer, the higher the electrical conductivity. However, a plateau in the conductivity (upper limit) was found when the thickness reached a specific range, as shown in Figure 16d.\[124a\] Though this continuous production method engenders CNT materials with high conductivities, most of the metal is attributed to surface deposition. This indicates less penetration, which is necessary for filling the voids and pores of the fiber. In fact, only a small amount of metal is actually needed to fill the voids and bridge the electrons between neighboring CNTs. Therefore, most metal coated CNT fibers may exhibit high conductivities due to their external metal layers instead of their inner CNT fibers.

Infiltration processing with a metal nanoparticle suspension (i.e., silver paste) was shown to use less metal particles while simultaneously increasing the electrical performance of the CNT fiber.\[124b\] Silver paste not only formed a “tube” layer around the CNT fiber, but also penetrated within, improving the electrical performance of the composite fiber (Figure 16d).\[124b\] To further strengthen the interfacial connectivity between neighboring CNTs, Ganguli et al.\[119a\] deposited in situ Au nanoparticles on a vertical CNT array before the fiber spinning process. After a continuous yarn was spun from the Au decorated CNT array, heat treatment was applied to metalize the CNT yarn, resulting in a 40% increase in electrical conductivity. The gold particles can be found throughout the cross-sectional diameter of the yarn in Figure 16f,g. These particles can coalesce and induce the intertube joining, forming a CNT-CNT junction, as shown in Figure 16h.\[119a\] Zhao et al.\[125\]
used vibration-assisted infiltration of nanocompounds of Pt and Au into CNT fiber, resulting in a great improvement in conductivity from $5.84 \times 10^4$ to $1.25 \times 10^5$ and $2.39 \times 10^5$ S m$^{-1}$ at a loading of 1.0 and 3.5 at% for Pt and Au, respectively.

Ideally, a dual continuous phase of CNT and metal with minimum metal incorporation is desired to achieve optimum CNT conductors with high electrical conductivity. However, conventional electro or electroless deposition methods can only deposit most metals on the surface of the CNT fiber. The incorporation of nanometals into CNT fibers is still challenging. Recently, Subramaniam et al.\textsuperscript{[47]} reported a new two-step electroplating approach. The raw CNT material was spun from a VACNT array and then densified by the Cu ion liquid, producing a well-aligned and densely packed structure. First Cu seeding within the CNT ribbon was nucleated by the continuous growth of copper around the Cu ions in an organic Cu electrolyte solution, then followed by an inorganic Cu electrolyte deposition until all the mesopores were filled. Homogeneous copper seeding within the hydrophobic CNT is critical in obtaining a high Cu filling throughout, not merely on the surface. The CNT–Cu composite prepared by this new two-step method showed an ultrahigh electrical conductivity up to $4.7 \times 10^7$ S m$^{-1}$ and an extraordinary current-carrying capacity of $6 \times 10^8$ A cm$^{-2}$, which is 100 times greater than copper. Nevertheless, the high-volume fraction of copper (45 vol%) resulted in a large increase in density of CNT–Cu composite (5.2 g cm$^{-3}$) as compared with pure CNT fibers (1.3–1.5 g cm$^{-3}$). Therefore, future research may investigate a critical volume percent which may optimize conductivity while minimizing the amount of metal used.

Although CNT/metal composites may possess copper-like electrical conductivities and even higher current carrying capacities, nonmetal conductors are still preferred for next
generation electronics and power transmission, especially for deep space exploration. All carbon-based conductors, such as CNT/C composite fibers, are expected to become competitive candidates in the near future. They have been widely investigated due to the novel interface structure between CNTs and the graphene-like carbon matrix. This interface can simultaneously enhance the load transfer and electron transport from one tube to another. To this end, graphene-like structures (few layers) have been introduced to fill voids within CNT fibers. For one, this produces a CNT/C composite with a dual-continuous phase and thereby a good interfacial structure. Second, it decreases contact resistance and increases load transfer between neighboring nanotubes. Just as in C/C composite manufacturing, either polymer infiltration pyrolysis (PIP) or chemical vapor infiltration (CVI) are commonly used to “grow” a graphene-like carbon matrix for CNT reinforced composites. For the PIP method, ideally all of the polymer is completely converted to graphene-like structures: bulk free CNT/C composite fibers and films (Figure 17b1,b2). This is contrary to conventional composites, which have lots of amorphous and semi-crystalline carbon (Figure 17a1,a2). The graphene-like structures can also be introduced by the CVI method, as explained by the CNT templated growth mechanism.

However, most researches only focus on the structure evolution mechanism of pyrolytic carbon during the PIP or CVI methods. For example, Lin et. al. reported an epitaxial growth mechanism with graphitic periphery around aligned CNT core, resulting in an “annual ring” cross-section structure (Figure 17c). Zhu and co-workers reported an aligned CNT/C production process that applied polyacrylonitrile (PAN) solution layer-by-layer, while the CNTs were being collected from an array. This was followed by a graphitization process. They claimed that the aligned CNT structure accelerated the ordering of the PAN matrix during the pyrolysis, resulting in a graphitic structure on the interface region between the CNT and PAN matrix. Apart from the CNT alignment, other effects of the CNT morphology including diameter and number of walls on the mechanical and electrical properties were also discussed. Nevertheless, neither mechanical nor electrical properties were significantly improved, as seen from the data in published literature. The process requires further study. The continuous graphene-like structure is critical to realize a full load transfer for mechanical application and efficient electron transport for electrical application.

5.3. Chemical Bonding and Doping

Covalent bonding on the side wall of a CNT is technically viewed as a defect on the intrinsic properties of individual carbon nanotubes. However, covalent functionalization can improve the mechanical properties of CNT/polymer composites due to the improved interfacial interactions. Unfortunately, this covalent bonding is usually detrimental to the electrical properties because of atomic structure damage and the insulating nature of most chemicals (i.e., polymers) used. Therefore, simultaneously improving the mechanical and electrical properties through covalent bonding remains a challenge. However, by carefully designing the bonding, both high mechanical and electrical properties can be obtained. Park et al. developed a simple and effective post-treatment method for improving the mechanical and electrical properties of CNT fibers by using aryl radical coupling reactions of poly(p-iodostyrene) (PIS), as shown in Figure 18a. After polymer infiltration and thermal treatment, the cross-linked CNT fiber exhibited 160% and 53% improvement in tensile strength and electrical conductivity, respectively (Figure 18b). The high mechanical properties can be attributed to the effective load transfer arising from the strong interfacial
chemical bonding by cross-linking, while the enhanced electrical conductivity can be mainly interpreted as an iodine doping effect from poly(p-iodostyrene).

Instead of creating disruptive chemical bonding, \( \pi-\pi \) conjugated structuring is another mild method that can create strong interactions between neighboring nanotubes.\(^\text{[23,91b,128c,135]}\) Consequently, the electrical conductivity of CNT fibers can be improved by increasing the intertube carrier transport efficiency through this \( \pi-\pi \) conjugated structure. Ryu et al.\(^\text{[23]}\) demonstrated that poly-dopamine (PDA) infiltration followed by pyrolysis (i.e., the insulation-to-conduction transformation) increased both CNT fiber (py-PDA-CNT) mechanical strength and electrical conductivity (Figure 18c–e). The PDA acted as an adhesive (noncovalent bonding from \( \pi-\pi \) interaction) to strengthen the connection among neighboring CNTs even after pyrolysis treatment. However, the insulation-to-conduction transformation of PDA through thermal treatment created a conductive multilayer graphene-like structure that built an electron transport pathway between the neighboring nanotubes, resulting in highly efficient carrier transport between CNTs. Compared to other CNT fibers, as shown in Figure 18f, the py-PDA-CNT fiber showed a high electrical conductivity of around \( 5.0 \times 10^5 \) S m\(^{-1} \). Another noncovalent bonding interaction with a \( \pi-\pi \) conjugated structure can be realized by choosing chemicals with a benzene-like structure.\(^\text{[91b,132b,134b]}\) Chen\(^\text{[91b]}\) achieved noncovalent functionalization of a SWCNT film by reacting two pyrene-based chemicals.

**Figure 18.** Covalent and noncovalent bonding to strengthen the interaction between CNT bundles. a) Schematic depict for synthesis of PIS-cross-linked CNTF by aryl radical coupling reaction, and b) electrical conductivity of raw CNTF and modified CNTF. (a),(b) Reproduced with permission.\(^\text{[134e]}\) Copyright 2016, Elsevier. c) Schematic and TEM images of a CNT fiber (the red line represents the thickness of a single CNT), d) a PDA-CNT fiber, and e) a py-PDA-CNT fiber (the blue line represents a py-PDA film). f) Electrical conductivity of a CNT fiber, PDA-CNT fiber, py-PDA-CNT fiber, and CNT fiber after pyrolysis. (c)–(f) Reproduced with permission.\(^\text{[23]}\) Copyright 2015, Wiley-VCH Verlag GmbH & Co. KGaA. g) Schematic illustration of the SWCNT cross-linking procedure with two pyrenyl derivatives, and h) mechanical properties of pristine and cross-linked SWCNT films. (g,h) Reproduced with permission.\(^\text{[91b]}\) Copyright 2013, Royal Society of Chemistry.
as shown in Figure 18g. The π–π stacking interactions between the CNT and benzene based chemicals served as cross-linkers and conductive bridges to connect neighboring CNTs together, thus strengthening interfacial interaction and decreasing the contact resistance.[23,49,91b,134c,135a] Not surprisingly, this process simultaneously increased the mechanical properties (Figure 18h) and the electrical conductivity (≈9.1 × 10^6 S m⁻¹).[91b]

Research on CNT chemical doping modifications is ongoing and important for improving electrical conductivity by increasing carrier concentration and mobility.[13a,18,22,31,40,136] Among the various chemical doping methods, one popular modification is the intercalation of n-type or p-type dopants for shifting the Fermi level, thereby, changing the conduction type and the major carrier types. Oxidant chemicals, including I₂, SOCl₂, HNO₃, and H₂O₂, are the most commonly used p-type dopants for the post-treatments of CNT assemblies due to their strong electron withdrawal abilities. As a result, they increase carrier concentration and mobility, resulting in high electrical conductivity.[18,22,28,40,136] Zhao et al.[18] reported an iodine doped CNT fiber with a super high electrical conductivity of 6.7 × 10^6 S m⁻¹. After doping, the iodine acted as an acceptor to form I⁻ and I₅⁺ polycation chains on the intercalated sites within CNT bundles. As a result, more holes were created in the CNTs. With a concomitant high density of mobile holes, this resulted in an improved mobility and consequently a high electrical conductivity.[36] One critical issue of chemical doping is the limited performance stability due to the high reactivity of oxidant chemicals with O₂ and H₂O in open air.[13b,136a] However, this can be suppressed by a polymer coating.[13b,136a]

Based on carrier concentration (n) and mobility (µ), the electrical conductivity (σ) is defined by $\sigma = ne\mu$. Zhang et al.[13b] found that after iodine doping, the hole concentrations of random and aligned CNT sheets were 2.90 × 10¹⁵ and 2.67 × 10¹⁹ cm⁻³, which were one order of magnitude higher than that of their undoped counterparts, 1.65 × 10¹⁸ and 1.62 × 10¹⁸ cm⁻³, respectively. These results indicate that the higher the percentage of dopants, the better the electrical performance of CNT sheets. However, the weight loading of a chemical dopant has a limit during doping process.[31,137] Since the interstitial sites within a CNT bundle are too difficult for dopants to penetrate, most dopants are absorbed onto the exterior and groove sites, which are limited due to the presence of CNT bundles instead of individual CNTs within a fiber or film.[138] Since direct theoretical and experimental works on the doping limit are absent, another example of molecular adsorption limit in CNTs was reported.[138] Recently, Mansour et al.[139] reported two doping modalities to improve the electrical conductivity of few-layer graphene: bulk intercalation and surface doping. Due to the limited surface area, the encapsulation of dopant between the graphene sheets is potentially an alternative route to higher doping level (high carrier concentration) and stability (out of air contact). This may theoretically and experimentally shed a light on the future research of CNT doping.

5.4. CNT/Graphene Hybrid Assemblies

Both CNT and graphene, due to their excellent mechanical, electrical, and thermal properties, show great potential applications in industry. Unfortunately, neither CNT nor graphene based macroscopic fibers and films maintain the excellent properties of their individual nanoscale components. For CNT fibers, due to the porous structure nature,[139] researchers found that inserting graphene sheets into the CNT network may increase the electrical and mechanical properties by bridging the gaps between neighboring nanotubes.[34,140] Different methods to hybridize CNT and graphene were attempted including in situ methods, such as CVD synthesis of CNT/graphene simultaneously[94b] and partially unzipping MWCNT[140g,140h] or ex situ methods, such as solution reaction through noncovalent and covalent bonding.[94c,d,140a]

Although both CNTs and graphene can be synthesized by the CVD method, the different synthesis mechanisms and conditions, including gas flow rates, reaction temperatures, time, and catalysts, greatly hamper the attempt and development of a covalently bonded combination of these two materials using this technique.[94b,140b] Recently Zhu et al.[94d] disclosed a method to prepare high-quality graphene with few-walled (one- to three-walled) CNT carpets seamlessly connected via covalent bonds shown in Figure 19a–c. A reconstructed scanning TEM (STEM) was successfully characterized showing the overlayered structure of graphene and CNT (Figure 19d,e). However, the complicated synthesis and small sample sizes make this in situ method inadequate to produce large quantities of CNT/graphene conductors. Instead of controlling the complicated synthesis conditions of CNT/graphene hybrid materials, Liu et al.[140g] proposed a relatively simple method to obtain the hybridization through partially unzipping MWCNTs (Figure 19f). This unique formation prevented the aggregation of graphene and promoted the formation of a 3D hybrid with a cross-linked nanostructure. The TEM images in Figure 19g–j show the unzipped edge of graphene sheet and the remaining MWCNT[140h]. Although this hybridization of CNT and graphene with covalent bonding can be fabricated by the in situ method, the electrical or mechanical performances of the CNT/graphene assemblies were rarely reported.

Instead of building covalent bonds, strong interactions between CNTs and graphene can be readily realized through the static force attraction of noncovalent bonding[87,94c] or mechanical interlocking.[94d] By introducing cationic functional groups to graphene sheets and anionic functional groups to MWCNTs (Figure 20a), Vinayan et al.[94c] developed a highly conductive hybrid nanocomposite of CNT/graphene. Apart from the improvement in electrical conductivity, excellent mechanical performance could be obtained due to the synergetic effects of CNT/graphene. Wang et al.[94d] found that by inserting graphene oxide sheets with a specific lateral size into the voids of a CNT fiber (Figure 20b–e), the interlocking effects of graphene oxide can inhibit the sliding of CNT bundles, resulting in a better load transfer. Graphene oxide was sized to match the voids in the CNT fiber. Foroughi et al.[97] recently adopted an in situ spraying technique that incorporated graphene solution within a synthesized CNT fiber during spin collection. Additionally, self-assembly strategy was also applied to construct CNT/graphene hybrids.[140d] However, just as in the fabrication of a dual-continuous phase of CNT/C composite fibers and films, a similar dilemma is confronted to prepare fully densified hybrids of CNT/graphene with good interface, which makes achieving high electrical conductivity still urgent and challenging.
5.5. Sub-Summary

As previously discussed, a plethora of methods were employed to improve the electrical conductivity of CNT fibers and films to approach the level of the individual nanotube; however, this still remains a challenge. All of the methods discussed showed the effectiveness of optimizing the structure of macroscopic CNT assemblies, resulting in an increased conductivity. The combination of microstructure optimization and doping to reduce contact resistance usually resulted in

Figure 19. In situ hybridization of CNT and graphene. a–e) Seamless junction between CNT and graphene: a) graphene grown on copper substrate by CVD, b) catalysts of iron and alumina on the surface of graphene by e-beam evaporation, c) hybrids of CNT/graphene with CNT directly grown from graphene surface, d) simulated STEM image of CNT/graphene junction area, and e) same area with an overlayed structural sketch from simulated STEM image (scale bar in (d) and (e), 0.2 nm). (a)–(e) Reproduced with permission. Copyright 2012, Nature Publishing Group. f) Schematic illustration showing the preparation steps for graphene/CNT hybrids from unzipping MWCNT. Reproduced with permission. Copyright 2013, Elsevier. g) Low magnification TEM image of a reduced graphene nanoribbon bundle obtained by unzipping MWNTs. h–j) HRTEM images of the same narrow graphene ribbons (white arrows indicate different edge terminations. (g)–(j) Reproduced with permission. Copyright 2014, Royal Society of Chemistry.

Figure 20. a) Scheme outlining the synthesis procedure adopted for synthesizing the graphene–MWNT nanocomposite. Reproduced with permission. Copyright 2012, Royal Society of Chemistry. b) Low magnification SEM image of a pristine CNT fiber surface (top view). c) Schematic 3D model of pristine MWCNT bundles intertwined with each other. d) AFM image of a single GO particle on a SiO2 surface. e) Schematic 3D model of GO infiltrated MWCNT bundles. (b)–(e) Reproduced with permission. Copyright 2016, Elsevier.
improved performance, as shown in Table 4. To date, the best CNT fiber electrical performance is garnered by either the combination of aerogel spinning and chemical doping,[13b] or the combination of liquid crystalline suspension spinning and chemical doping.[22] Additionally, the combination of VACNT array spinning and metal nanowelding has been effectively demonstrated to improve the conductivity of a CNT fiber to the same range of copper.[47] After mechanical pressing, the demonstration to improve the conductivity of a CNT fiber to array spinning and metal nanowelding has been effectively compared pure copper. Further success of a highly conductive fiber spun from a CNT aerogel showed a conductivity of up to $10^6$ S m$^{-1}$.

### Table 4. The pros and cons of various methods reported in literature to improve electrical conductivity of CNTs.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Pros</th>
<th>Cons</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity improvement</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNT alignment</td>
<td>• Good alignment</td>
<td>• Low efficiency</td>
<td>[33, 97c–e]</td>
</tr>
<tr>
<td>Electrical/magnetic field assisted</td>
<td>• Better control</td>
<td>• High cost</td>
<td></td>
</tr>
<tr>
<td>Liquid crystal suspension spinning</td>
<td>• High alignment degree</td>
<td>• Toxic solvent</td>
<td>[22, 29, 38a, 61]</td>
</tr>
<tr>
<td>VACNT array spinning</td>
<td>• Ultra high alignment degree</td>
<td>• Batch-to-batch variation</td>
<td>[15, 27, 52, 62b, 74c]</td>
</tr>
<tr>
<td>Continuous CNT aerogel spinning</td>
<td>• High production rate</td>
<td>• CNT array quality control</td>
<td>[18, 19, 26, 53c]</td>
</tr>
<tr>
<td>Mechanical stretching</td>
<td>• High production rate</td>
<td>• High impurity content</td>
<td>[13a, b, 76b, 115]</td>
</tr>
<tr>
<td>Contact resistance</td>
<td>• Feasible and green process</td>
<td>• Medium alignment degree</td>
<td></td>
</tr>
<tr>
<td>Mechanical densification</td>
<td>• Scalable production</td>
<td>• Sample size limitation</td>
<td></td>
</tr>
<tr>
<td>Nanowelding/coating</td>
<td>• High alignment degree</td>
<td>• Increased bulk density</td>
<td>[47, 48, 124b, d]</td>
</tr>
<tr>
<td>Chemical bonding/doping</td>
<td>• Continuous process</td>
<td>• Most particle on surface, less inside</td>
<td></td>
</tr>
<tr>
<td>Cross-linking</td>
<td>• Highly effective</td>
<td>• Medium production rate</td>
<td></td>
</tr>
<tr>
<td>Chemical doping</td>
<td>• Highly effective</td>
<td></td>
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</tr>
<tr>
<td>CNT/graphene hybrid</td>
<td>• Continuous process</td>
<td></td>
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<tr>
<td>Ex situ hybridization</td>
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6. Development of CNT Conductors for Engineering Applications

6.1. Lightweight Wires and Cables

Coaxial cables are significantly indispensable in modern technology and have a wide range of applications varying from navigation to telecommunication. The basic structure of coaxial cable is explained in Figure 22a, b, including a center conductor (CC) and an outer conductor (OC) separated by an insulating layer (dielectric).[141] Metals are generally used today as OCs due to their high conductivity, which helps decrease signal loss through the transmission line. However, the high density and limited fatigue resistance impede the current metal OCs in broad applications, particularly in aerospace applications where weight reduction directly affects launch cost and fuel efficiency. Mirri et al.[141] replaced the metal OC with a seamless CNT OC by a simple dip coating method. The cable made with a CNT OC meets military attenuation specifications at 1 GHz and has exceptional durability, comparable to commercial cables. These cables made out of CNT-only OC have an OC mass 97% lighter than conventional metal braids, and an overall cable weight reduction of around 50%.[141] Additionally, CNT sheets can be directly used as OC by wrapping them around CC.[142] Conductive CNT wires can also be directly used as current carrying cables in an electrical transformer or motor, as shown...
Figure 21. Some important examples of the significant improvement of electrical conductivity of macroscopic CNT assemblies enhanced by the combination of various post-treatments for the past few years. 

- **2017**
  - Spinning from FCCVD
  - Mechanical stretching induced alignment
  - Iodine doping
  - 12,000 S/cm

- **2016**
  - Spinning from FCCVD
  - Mechanical pressing
  - 12,000 S/cm

- **2014**
  - Spinning from FCCVD
  - Liquid densification
  - Roller pressing
  - 20,000 S/cm

- **2013**
  - Spinning from CNT liquid crystal solution
  - Chlorosulfonic acid doping
  - 50,000 S/cm

- **2011**
  - Spinning from FCCVD
  - Liquid densification
  - Strong acid doping
  - 67,000 S/cm

a) Zhang et al. (Reproduced with permission. Copyright 2017, Elsevier.).
b) Tran et al. (Reproduced with permission. Copyright 2016, Elsevier.).
c) Wang et al. (Reproduced with permission. Copyright 2014, Nature Publishing Group.).
d) Behabtu et al. (Reproduced with permission. Copyright 2013, AAAS.).
e) Zhao et al. (Reproduced with permission. Copyright 2011, Nature Publishing Group.).
in Figure 22c–h. Figure 22 shows a simple electrical transformer with a winding configuration connected to an operating device. The open circuit and current load tests demonstrated that transformers assembled with CNT wirings agree with the classical theory of electrical transformers. However, the CNT wires exhibited a higher resistance than conventional copper wires and reducing the high resistance of the CNT windings, which is being addressed in the ongoing research. Recently, a highly conductive CNT wire was fabricated by drawing through a diamond wire-drawing die. Due to the radial mechanical pressing effect, the resulting CNT fibers were well aligned and densely packed surfaces. Though a porous internal structure was still observed, the reduction of intertube distance was significant, resulting in a high stable electrical conductivity of around $1.6 \times 10^6 \text{ S m}^{-1}$ when exposed in air (Figure 22g). When this CNT wire replaced conventional copper wire in a motor prototype (Figure 22f), the CNT motor worked well at an applied voltage of $\approx 6 \text{ V}$. The unusual magnetic flux density behavior (a quadratic function to applied current) of the CNT motor was different from the linear relationship of a copper motor (Figure 22h). Further research is necessary to reveal the science behind the abnormal electromagnetic response.

Current carrying capacity is also important if and when CNT wires are used as power transmission cables. This is especially the case for high voltage transmission lines exhibiting high current from one power plant to another. Due to their high thermal conductivity (up to $3500 \text{ W m}^{-1} \text{ K}^{-1}$), CNT fibers and films possess excellent thermal dissipation, enabling their cable forms to maintain their high current carrying capacity in open air. Park et al. found that high electrical conductivity is required to achieve high current carrying capacity of the CNT film; however, limited heat dissipation through the CNT film can halt the further improvement of its current carrying capability. Therefore, achieving high electrical conductivity and fast thermal dissipation are the keys to attaining a higher current density of CNT cables. Wang et al. claimed that a densely packed structure of nanotubes with good alignment is beneficial to improving electrical conductivity, as well as crucial for instilling a large failure current density. A CNT/copper composite fiber with an extremely high current density of up to $6 \times 10^8 \text{ A cm}^{-2}$ was reported by Subramaniam et al. However, pure nonmetal CNT conductors are still absent.

Nevertheless, carbon nanotube wires demonstrate the potential to replace copper wires for the next generation.
electrical wiring applications offering high electrical conductivity, lower weight, and high mechanical properties. For power transmission systems and spacecraft, a balance between weight and conductive performance of current carrying cables should be thoroughly considered. Moreover, the specific mechanical strength of CNT fibers is already higher than that of steel, and significantly higher than that of copper. All these characteristics make CNT wires a promising candidate to replace metal conductors, especially copper, in the near future.

To be used as a conductive wire, an insulation layer must be developed to wrap around the CNT wire to avoid short circuiting. Generally, these insulating materials include PVA or silicone-based paste or a rubber like hydrogenated nitrile butadiene rubber. The typical requirements for the insulation layer include 1) prevention of mechanical tearing, 2) flexibility, 3) low weight, and 4) electrical insulation. An ideal insulation layer is coated on just the surface, as shown in Figure 23, with minimum penetration depth into the CNT wire. Infiltration could result in a negative effect on the conductivity. Forming a continuous and thin insulation layer that does not compromise the electrical conductivity of the CNT wire is a major technical challenge for further application of CNT conductors. Additional details on the engineering aspects of CNT cables as current carrying materials can be found in the reviews by Jarosz et al., Lekawa-Raus et al., and Lee and Ramakrishna.

6.2. Flexible and Stretchable Conductors

Superelastic conducting fibers with improved properties and functionalities are required for a wide range of applications spanning from aircraft fuselages to human bodies to create a network of sensors, processor, energy stores, or artificial muscles. The special requirement for flexible and stretchable conductors is the need for stability of their electrical performance under mechanical deformation. Basic mechanical deformations include cyclic bending at various angles and stretching at different strain ranges. Generally, the structural stability of CNT fibers and films engender their flexibility with a minimal resistance change during small angle bending tests. Depending on the application, a structure-tuned CNT fiber could also show relatively large resistance change if needed.

For stretchable conductors, typically a stretchable substrate (i.e., polydimethylsiloxane (PMMS) or rubber) was used as a support to respond to the stretching deformation, while CNT assemblies with special structure were used as a conductive component to compensate the resistance change during various kind of deformations. As shown in Figure 24a–d, Liu et al. developed a novel manufacturing method to obtain a super elastic CNT conductor. While the rubber fiber was under super stretching, different numbers of CNT layers were wrapped around the fiber (Figure 24a). Once the wrapping was finished and the rubber fiber was released, hierarchically buckled sheath (CNT)–core (rubber) fibers were obtained (Figure 24b–d). This kind of special buckled sheath–core structure demonstrated high stretchability with reasonable resistivity change $\frac{R_f}{R_0}$ versus strain. This was especially true at high strain values.

Flexible CNT films with high electrical conductivity would be good candidates to compete with the copper foils currently used. Zhang et al. reported a CNT film treated with a combination of mechanical stretching and iodine doping, which demonstrated a conductivity of CNT sheets up to $10^6 \text{ S m}^{-1}$, only one magnitude lower than that of copper. Additionally, the flexibility was not reduced by the chemical doping and mechanical stretching process. Furthermore, the high electrical conductivity was nearly size-independent, slightly jumping around $1.2 \times 10^6 \text{ S m}^{-1}$ within a wide range of width (Figure 25a). They also reported the use of a protective coating of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) to induce long-term stability in electrical performance. Correspondingly, only slight conductivity changes were observed during the test period (Figure 25b). Such CNT tapes with excellent electrical stability and size-independent properties indicate a great potential for use in wearable devices where flexible conductors are required.

6.3. Limitations

Currently, conductive CNT sheets have been successfully demonstrated in application of coaxial cable for signal transmission. Several reports of CNT winding coils replacing copper in transformers and motors were shown. Nonetheless, great challenges must still be addressed. The limitations of using conductive CNT fibers and films as engineering materials may include:
(1) Limited electrical conductivity (compared to the conductivity of copper);
(2) Large quality and property variations along fiber or sheet length, compared metal products;
(3) Limited lengths and sizes for engineering tests and product prototype development; and
(4) Higher cost.

Extensive and ongoing efforts are striving to improve the electrical conductivity of CNT based conductive fibers and films. Many are exploring a variety of techniques, including optimized synthesis methods, microstructural controls (i.e., alignment and packing), and chemical doping. Quality control of freshly synthesized CNT fibers and films can be guaranteed by the optimization of the CVD process and various post-treatment methods. Furthermore, the commercially available FCCVD process could address the cost issue by scaling up the production capability. Overall, the issues which delay the replacement of copper by CNTs are being actively studied in both academia and industries. New technique breakthroughs of CNT conductors could be expected in near future.

7. Summary and Outlook

Here, recent advances regarding CNT-based nonmetal conductors have been comprehensively reviewed with an emphasis on potential use as lightweight, flexible, and environmental resistance alternative conductors compared to metal. The main theme addressed the electrical conduction performance, fabrication methods, and potential applications. Although single CNTs with specific chirality and shorter lengths demonstrated high electrical conductivity, a significant issue currently lies in transferring those excellent properties from the nanoscale to the macroscale of CNT assemblies (i.e., fibers and films). Nevertheless, the advantages of CNT conductors over traditional metal conductors are obvious, including low density, better environmental stability, excellent mechanical...
performance, and ultrahigh electrical conductivity. CNT conductors delivered the best compromise in terms of specific conductivity and strength. Despite the great success of improving CNT assemblies to achieve high conductivity, several challenges still exist that impede large-scale production and engineering applications. Those challenges include: 1) achieving high conductivity of the individual CNT at macroscale, 2) developing cost-effective manufacturing methods, 3) establishing long-term stability of highly conductive performance, and 4) developing scale-up production capabilities with good quality control. These issues require further study before CNT conductors can be transferred into real-world engineering application.

Several potential strategies could be further developed to achieve the ultimate goal of using CNT as the next generation nonmetal electrical conductors to potentially replace traditional metals for many applications. First, understanding and optimizing the contact resistance between neighboring nanotubes is required to harness the overall high resistance of CNT assemblies. Different contact enhancers can be explored, such as nanocarbons (e.g., graphene and pyrolyzed polydopamine), conductive polymers (e.g., PEDOT:PSS) and nanometal particles or films. One principle when dealing with these contact enhancers is to incorporate just enough enhancers to achieve the minimum contact resistance. Second, better control over the alignment of CNTs could greatly enhance the electrical, mechanical, and thermal properties of fibers and films because of the enhanced contacts and the concomitant better interconnections between neighboring nanotubes. Thus, a dense packing structure of aligned nanotubes is desired and promises to be very effective when coupled with other contact enhancers, chemical and physical post-treatments. Finally, a continuous manufacturing method that embraces aspects mentioned above is critical for the realization of CNT conductors for commercial applications.

Despite the several challenges, the high specific electrical conductivity of CNT fibers has already been reported to be much higher that of copper, demonstrating the excellent potential of CNTs to replace traditional metal conductors. Inspired by these successes, CNT fibers and films with scale-up size can be potentially fabricated with high electrical conductivity through a better control of alignment, dense packing structure, and low contact resistance, which represents the major methods toward approaching the theoretical conductivity of individual CNTs. We believe that the development of further improved high conductivity of CNT conductors will promote the real-world applications as alternatives to metal conductors.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

alignment, carbon nanotubes, CNTs, contact resistance, doping, improving conductivity

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