Continuous Carbon Nanotube-Based Fibers and Films for Applications Requiring Enhanced Heat Dissipation

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Supporting Information

ABSTRACT: The production of continuous carbon nanotube (CNT) fibers and films has paved the way to leverage the superior properties of individual carbon nanotubes for novel macroscale applications such as electronic cables and multifunctional composites. In this manuscript, we synthesize fibers and films from CNT aerogels that are continuously grown by floating catalyst chemical vapor deposition (FCCVD) and measure thermal conductivity and natural convective heat transfer coefficient from the fiber and film. To probe the mechanisms of heat transfer, we develop a new, robust, steady-state thermal characterization technique that enables measurement of the intrinsic fiber thermal conductivity and the convective heat transfer coefficient from the fiber to the surrounding air. The thermal conductivity of the as-prepared fiber ranges from 4.7 ± 0.3 to 28.0 ± 2.4 W m⁻¹ K⁻¹ and depends on fiber volume fraction and diameter. A simple nitric acid treatment increases the thermal conductivity by as much as a factor of ∼3 for the fibers and ∼6.7 for the thin films. These acid-treated CNT materials demonstrate specific thermal conductivities significantly higher than common metals with the same absolute thermal conductivity, which means they are comparatively lightweight, thermally conductive fibers and films. Beyond thermal conductivity, the acid treatment enhances electrical conductivity by a factor of ∼2.3. Further, the measured convective heat transfer coefficients range from 25 to 200 W m⁻² K⁻¹ for all fibers, which is higher than expected for macroscale materials and demonstrates the impact of the nanoscale CNT features on convective heat losses from the fibers. The measured thermal and electrical performance demonstrates the promise for using these fibers and films in macroscale applications requiring effective heat dissipation.

KEYWORDS: carbon nanotubes, thermal conductivity, convective heat transfer, CNT macroscale assemblies, acid treatment

1. INTRODUCTION

Individual carbon nanotube (CNTs) demonstrate excellent mechanical (Young’s modulus up to 1 TPa),¹ electrical (up to 10⁶ S cm⁻¹),² and thermal (up to 3500 W m⁻¹ K⁻¹)³ properties. Many applications could benefit from CNT-based materials, including high-strength and conductive nanocomposites, electrochemical devices, sensors, and probes.⁴⁻⁶ However, practical applications require the extension of the superior properties of individual CNTs up to the macroscale. This remains a challenge due to the difficulty in synthesizing homogeneous and uniform quality CNT-based structures that fully exploit the excellent axial properties of individual CNTs.

Manufacturing CNTs into continuous, macroscale fibers is a significant step toward integrating them into practical applications. CNT fibers, produced by either wet-spinning from CNT/acid or polymer solutions,⁷,⁸ dry-spinning from...
vertically aligned CNT arrays, or direct-spinning from CNT aerogels formed in floating catalyst chemical vapor deposition (FCCVD) are promising as novel lightweight, high-strength, and highly conductive materials. Compared with commercial carbon and polymer fibers, CNT fibers demonstrate higher modulus and strength, better electrical and thermal conductivities, and more flexibility. The effects of fabrication processes and different post-treatment methods on the morphology, mechanical, and electrical properties have been systematically studied for several years. But there are only a few reported experimental studies on the thermal properties of CNT fibers, and the large difference in reported thermal conductivities between these similar fibers indicates a significant dependence on quality and processing technique.

CNT fibers can be assembled directly from CNT aerogels in FCCVD leveraging the ability to produce CNT fibers in large scale efficiently with controllable CNT structures and outstanding mechanical and electrical properties. This is in contrast to the wet-spinning and array-spinning methods where individual CNTs are first produced as powders or arrays and require a separate postprocess of spinning to create the fibers. Although the thermal conductivity of the CNT fibers directly spun from FCCVD-synthesized CNT aerogels has not yet been reported in detail, they are expected to have high thermal conductivity. Despite years of research, the reported effective thermal conductivities of CNT fibers are still much lower than those of individual CNTs. High defect concentration and high thermal contact resistance between CNTs in macroscale assemblies are commonly cited reasons for the low performance of CNT-based networks. Chemical modifications to the CNTs, such as acid treatments, have been demonstrated to improve CNT quality and manage the interfacial interactions. For instance, soaking CNT fibers in nitric acid increases their electrical conductivity. But little thermal transport data exists for such modifications, and the effect of acid treatment on the thermal conductivity of CNT macroscale assemblies has not yet been experimentally investigated.

In this work, we measure the thermal conductivity and heat transfer coefficient by natural convection of CNT fibers and thin films fabricated from CNT aerogels, which are grown by FCCVD. We develop a steady-state Joule heating infrared thermal metrology technique to study the thermal conductivity and convective heat transfer for the CNT-based fibers. This technique leverages infrared microscopy as a noncontact, nondestructive, fast thermal characterization tool to measure the two-dimensional temperature maps in the CNT fibers and films self-heated by Joule heating. As opposed to conventional measurement techniques, the sample thermal conductivity can be extracted in air and without need for microfabrication. Further, the steady-state technique developed here enables a direct measurement of thermal conductivity (independent of density and specific heat) while simultaneously measuring convective heat transfer coefficient. The technique is applicable to a broad class of electrically conductive samples ranging from metallic wires to CNT fibers. Here, the impact of micro/macrostructure (collecting time, diameter, and density) on the thermal conductivity and the convection coefficient for the CNT fibers is investigated for the first time. These data complement previous work characterizing the mechanical and electrical properties of the CNT fibers directly spun from CNT aerogels in CVD. Moreover, we demonstrate a simple, effective acid treatment approach to enhance the electrical and thermal conductivities of the CNT fibers and films. The acid-treated specimens demonstrate up to a factor of ~3 for the fiber and ~6.7 for the thin film improvement in the thermal conductivities than the as-prepared samples due to the purification and densification during the acid treatment, which results in less defective structure and reducing contact resistance between nanotubes.

2. EXPERIMENTAL SECTION

Fabrication of CNT Fibers and Films. The CNT fibers are fabricated from CNT films, which are synthesized by the floating catalyst vapor deposition method. In a reducing hydrogen atmosphere, the nanotubes form an aerogel in the hot zone of the furnace at 1200 °C and the aerogel is stretched into cylindrical hollow socks. The CNT sock is pulled out of the furnace by a stainless rod and continuously collected on a paper roller to form a CNT film. CNT films collected for 1, 5, and 10 min are mechanically rolled from one end to the other to fabricate the CNT fibers with various diameters and densities. In order to study the effects of acid treatment on the thermal conductivity, the CNT fibers and films are immersed in 65 wt % nitric acid (HNO3, Sigma-Aldrich Pte Ltd.) at room temperature for 30 min and washed in deionized water.

Morphology Characterizations. The structures of the specimens are observed using a field emission scanning electron microscope (FE-SEM, Model S-4300, Hitachi), a transmission electron microscope (TEM, JEOL JEM-3010), and a Horiba Jobin Yvon Modular Raman Spectrometer. Nitrogen adsorption/desorption tests to determine the distribution of pores in the specimens before and after acid treatment, are conducted using a Nova 2200e Surface Area and Pore Size Analyzer (Quantachrome). To measure the bulk density of the specimens, the masses of the specimens are obtained with an analytical balance in accuracy of 0.01 mg and the dimensions of the specimens are measured by an Olympus optical microscope. The CNT volume fraction (f) is calculated from the bulk density of the CNT fiber or film, ρ, as

$$f = \frac{\rho}{\rho_{CNT}} \times 100\%$$

where ρCNT = 2.1 g cm⁻³ is the density of an individual CNT.

Electric Properties of the CNT Fibers and Films. Electrical resistances of the CNT fibers and films are measured by four-wire method using a Keithley 2420 source meter. For better electrical contacts, the two ends of the specimens are fixed on two separate glass slides with silver paint. The electrical conductivity (σ) and specific electrical conductivity (σ') is then calculated from eqs 2 and 3, respectively,

$$\sigma = \frac{L}{RA} \text{(S cm}^{-1})$$

(2)

$$\sigma' = \frac{\sigma}{\rho} \text{(S cm}^{-2} \text{g}^{-1})$$

(3)

where R, A, and L are the resistance, cross-sectional area, and length of the specimen.

The temperature coefficient of resistance (TCR or α) is measured by four-wire electrical resistance measurements across the temperature range of 295–350 K. The average TCR of the as-prepared specimens and acid-treated specimens was 0.001 15 ± 0.000 25 and 0.002 65 ± 0.000 40 K⁻¹, respectively.

Thermal Properties of the CNT Fibers and Films. Each CNT fiber is suspended between two pairs of copper blocks working as electrodes as shown in Figure 1a. For the CNT fiber samples, the length of suspended portion is ~1 cm; while for the film samples, the suspended portion is 2 cm in length and 0.5 cm in width. Current flowing through the sample heats the specimen. A Keithley 2420 source meter (Figure 1b) is used to source the current and measure the voltage drop across the sample. The temperature profile along the
specimen is measured by an infrared temperature measurement microscope system (InfraScope, Quantum Focus Instruments Corporation), as shown in Figure 1c. The high spatial resolution (11.7 μm/pixel at 1× magnification) of the infrared microscope enables hundreds of temperature data points along the length of a 1 cm long specimen, as shown in Figure 1d. The one-dimensional (1D) heat transfer along the length of the fiber is confirmed by the nearly uniform temperature in the direction perpendicular to the axis of the fiber. Blue crosses indicate data points averaged over each column of pixels in the 2D image. The bold solid red line indicates the best fit to the experimental temperature profile with an extracted thermal conductivity of 9.5 W m⁻¹ K⁻¹ and convection coefficient of 37 W m⁻² K⁻¹.

Figure 1. Experimental setup and example data from the steady state Joule heating infrared metrology technique. (a) Optical image of a CNT fiber suspended between two copper electrodes that also serve as heat sinks. (b) Schematic of the experimental setup. The Keithley 2420 source meter sources current through the sample leading to an electrical heating infrared metrology technique. (a) Optical image of a CNT fiber. Solid lines indicate temperature measured along three selected rows of pixels between the center and edge of the fiber. (c) Example infrared microscope image of a CNT fiber during Joule heating for a sample with a measured density of 0.28 g cm⁻³. Note the one-dimensional heat transfer along the length of the fiber as indicated by the nearly uniform temperature in the direction perpendicular to the axis of the fiber. (d) Temperature profile along the axis of the fiber. Solid lines indicate measured temperature along three selected rows of pixels between the center and edge of the fiber. Blue crosses indicate data points averaged over each column of pixels in the 2D image. The bold solid red line indicates the best fit to the experimental temperature profile with an extracted thermal conductivity of 9.5 W m⁻¹ K⁻¹ and convection coefficient of 37 W m⁻² K⁻¹.

3.1. Electrical Properties of CNT Fibers. Figure 2 shows the effect of the volume fraction of CNTs on the electrical conductivity determined according to eq 2. When the volume fraction increases from 5.5% to 41.4%, the electrical conductivities of the fibers increases from 150 to 1050 S cm⁻¹. While there is a clear increase in the electrical conductivity with increasing volume fraction, the specific electrical conductivity, defined as the ratio between fiber electrical conductivity and bulk density, is nearly independent of the volume fraction varying in the range of 1000–1500 S cm⁻² g⁻¹. The average specific electrical conductivity is ~1200 S cm⁻² g⁻¹ obtained by linearly fitting the data for electrical conductivity as a function of fiber bulk density. A similar trend of increasing electrical conductivity with volume fraction, but constant specific electrical conductivity, was previously observed by Miao for array-spun CNT fibers. Here, the measured specific electrical conductivity is comparable with

\[
T(x) = T_0 - \frac{p'}{h'} \left( \frac{\cosh(mx)}{\cosh(mx/2)} - 1 \right) + (T_{L/2} - T_0)
\]

where \(m^2 = (h' - \alpha p')/kA\), when \(h' - \alpha p' > 0\). We fit eq 6 to the experimental temperature profiles to measure the thermal conductivity \(k\) and convective heat transfer coefficient \(h\). Figure 1d shows an example of the best fit curve with an example experimental temperature profile. The traditional convection coefficient \(h\) in Watts per squared meter per Kelvin was then calculated from

\[
h = h'/P
\]

where \(P\) is the perimeter of the cross section of the specimen.

Note that the analytical solution in eq 6 assumes a constant convective coefficient along the length wire. As the maximum temperature of the wire is limited to a few Kelvin above the set base temperature, the variation in the natural convection coefficient is small. Essentially, the extracted heat transfer coefficient can be considered an average value for the fiber. This assumption is validated in detail in the Supporting Information.

The proposed method was first verified by measuring the thermal conductivity of the bare nickel chromiu resistance (BNC) wires (AWG 30, Consolidated Electronic Wire & Cable, United States). As shown in Table 1, all experimental values are very close to the values provided by the manufacturer, with standard deviations of less than 10%. Thus, the experimental setup and methods employed in the present work were considered to be valid and extended to the CNT fiber and film samples.

### Table 1. Data Sheet and Experimentally Measured Properties of Bare Nickel Chromium Resistance (BNC) Wires

<table>
<thead>
<tr>
<th>Diameter (μm)</th>
<th>Resistance (Ω cm⁻¹)</th>
<th>TCR (K⁻¹)</th>
<th>Thermal Conductivity (W m⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Value provided by manufacturer</td>
<td>254</td>
<td>0.2215</td>
<td>0.00015</td>
</tr>
<tr>
<td>Experimental value</td>
<td>255 ± 5</td>
<td>0.2195 ± 0.005</td>
<td>0.000146 ± 0.000002</td>
</tr>
</tbody>
</table>

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constant. The thermal conductivities of the fibers made from 1, S, and 10 min-films are 13 ± 1.2, 12.5 ± 1.5, and 13.7 ± 2.0 W m⁻¹ K⁻¹, respectively, which are nearly independent to the diameter and collecting time.

In contrast to diameter and collecting time, the volume fraction of CNTs has a great influence on the fiber thermal conductivity. Figure 3b shows the thermal conductivities of the CNT fibers as a function of volume fraction. When the volume fraction of CNT increases from 5.5% to 41.4%, the thermal conductivities of the fibers increase from 4.7 ± 0.3 to 28.0 ± 2.4 W m⁻¹ K⁻¹. Similar to the specific electrical conductivity, the specific thermal conductivity (k') is also nearly independent of the volume fraction as illustrated by the nearly linear relationship between the volume fraction and the thermal conductivity. The average specific thermal conductivity is estimated to be 32 W m⁻¹ K⁻¹ by linearly fitting the thermal conductivity as a function of the fiber bulk density.

Heat conduction in carbon materials is usually dominated by phonons due to the strong covalent sp² bonding resulting in efficient heat transfer by lattice vibrations. Here, we predict that the electronic contribution to the thermal conductivity (kₑ) is less than 5% of the total measured conductivity for all the specimens, as calculated via Wiedemann–Franz law: 
kₑ/σ ≈ LT,

where σ, Lₑ, and T are electrical conductivity, Lorenz number, and temperature, respectively.⁵⁶

The CNT fiber can be regarded as a two-phase system consisting CNTs and air with thermal conductivities of k_CNT and k_air (0.0259 W m⁻¹ K⁻¹). A simple model considering nanotubes conducting heat parallel with the air predicts that the thermal conductivity increases linearly with volume fraction of CNTs (f):⁶

\[ k_{\text{specimen}} = f_k^{\text{CNT}} + (1-f)k_{\text{air}} \approx f_k^{\text{CNT}} \]

A linear fit to the data in Figure 3b provides an estimate of 68 W m⁻¹ K⁻¹ for the thermal conductivity of the individual nanotubes in the fibers. This is within the reasonable range for individual MWNTs. Previous researchers have reported 34 W m⁻¹ K⁻¹ for the MWNT with a diameter of 14 nm and 160 W m⁻¹ K⁻¹ for the MWNT with a diameter of 11.4 nm.³⁸ However, it is much lower than other previous measurements of individual MWNTs.³⁹–⁴⁴

Previous research suggests that the density of nanotubes is not the only factor influencing the thermal conductivity of nanotube-based systems. The low apparent thermal conductivity of the CNT fibers compared to that predicted from the high values of thermal conductivity of the individual CNTs
reported in literature can be explained by the impact of contacts, as well as the quality and morphology of the CNT fibers.

Thermal contact resistance leads to temperature jumps at the interfaces between contacting nanotubes. The contact points may also introduce additional phonon scattering or damping phonon modes within a nanotube reducing the effective thermal conductivity of each nanotube. Although the coupling in nanotube bundles significantly increases the contact area, it may also lead to the deformation of nanotube shape due to van der Waals force between adjacent nanotubes. The deformation could lead to suppression of optical phonon modes and increased inter-CNT contact resistance, which results in substantially reduced thermal transport abilities for the individual CNT.

The CNT–CNT contact conductance \( G_{\text{CNT–CNT}} \) in this work is estimated to be on the order of 13–130 pW K\(^{-1}\), extracted by fitting the model of Chalopin et al. to our experimental results (see Figure 3b):

\[
k_{\text{specimen}} \approx \frac{0.18L}{2\pi D} \rho_{\text{graphene}} G_{\text{CNT–CNT}}
\]

where \( \rho_{\text{graphene}} = 7.6 \times 10^{-7} \text{ kg m}^{-2} \) is the surface mass density of graphene. Note that this model was developed for randomly oriented nanotube mats instead of aligned CNT films or fibers, and neglects the finite thermal conductivity of the individual CNTs. But, essentially, this value can be considered an upper bound to the thermal resistance for the contacts and it is comparable to the few reported experimental and simulation works (ranging from \( \sim 3–50 \) to >100 pW K\(^{-1}\)).

Mesoscopic models for aligned CNT macroassemblies, which can fully model the interactions between the individual CNT properties, specimen morphology including CNT length, diameter and alignment and CNT–CNT contacts on the thermal conductivity, are required in the future to better understand the heat conduction in CNT macroassemblies.

In addition to contact resistances, thermal conduction within nanotube fibers and films is complicated by CNT quality and the morphology of the nanotubes. MWNTs grown by CVD are generally more defective than those grown by arc-discharge or laser ablation methods. Simulations and measurements of individual CNTs with defects showed that the thermal conductivity decreased significantly with increasing defect concentration. CNT fibers or films consisting of longer nanotubes may exhibit even lower conductivity than the one consists of shorter nanotubes because of higher probability of a defect occurring within a longer tube. Additionally, the structural inhomogeneity of the CNT macroassemblies strongly impacts their apparent thermal conductivity. As shown in Figure 4, even though CNTs are assembled into bundles with high orientation preference (Figure 4a), we still observe dangling ends and interweaving in the structure (Figure 4b). These inhomogeneities may prevent the overall thermal conductivity from achieving the performance expected from that of individual CNTs.

### 3.3. Convective Heat Transfer in CNT Fibers

Natural convection from the CNT fibers is also investigated in this same experiment. The physics of solid to gas heat transfer changes considerably with size and environmental factors like temperature and pressure. Since most microelectronic and microelectro-mechanical devices operate in air, understanding the mechanism of convective heat transfer at macroscale is critical for accurate predictions of temperature and device performance.

Figure 5a shows the convection coefficients of the CNT fibers with various collecting times \( t \) and diameters vary from 26 to 193 W m\(^{-2}\) K\(^{-1}\), which is higher than the typical values for the natural convection coefficient at the macroscale \( (2–25 \text{ W m}^{-2} \text{ K}^{-1}) \). In general, most thermal conductivity measurements of fibers require a high vacuum environment to eliminate convection losses, which increases the experimental complexity. As a result, there are fewer studies (see Figure 5b) on the mechanism of convective heat transfer at microscale than at the macroscale. Li et al. reported convection coefficient of 1039–1143 W m\(^{-2}\) K\(^{-1}\) for CNT fibers an order of magnitude smaller in diameter than our fibers \((d \sim 36–43 \mu m\) compared to \(\sim 150–800 \mu m\) in this work). Hsu et al. found the heat transfer coefficient between an individual single-walled nanotube (SWNT) and the surrounding air molecules ranged from \(5.1 \times 10^3\) to \(7.9 \times 10^4 \text{ W m}^{-2} \text{ K}^{-1}\). Other studies on free convection from other microscale materials showed that the convection coefficient varies from 100 to 7000 W m\(^{-2}\) K\(^{-1}\) depending on the diameter of the microwire. Our observation is consistent with these results in the literature, suggesting that the convection coefficient for CNT fibers is also strongly influenced by scaling effects, as well as other structural and environmental factors.

As shown in Figure 5a, for fibers with the same collecting time (e.g., 10 min), the convection coefficient decreases with increasing diameter. This trend is consistent with the results calculated by the correlation of Churchill and Chu for free convection on long horizontal cylinders:

\[
\text{N}_D = \frac{0.60 + 0.387R_d^{1/6}}{1 + (0.559Pr^{9/16})^{8/27}}
\]

for \( R_d < 10^{12} \)

where \( \text{N}_D = hD/k_{\text{air}} \), \( R_d \), and \( Pr \) are the Nusselt number, Rayleigh number, and Prandtl number, respectively. Note that the correlation of Churchill and Chu is for free convection at a constant temperature, while the temperature distribution along the CNT fiber shows a cosh-shape. Since the average temperatures of the specimens were controlled within a small
Figure 5. (a) Impact of diameter and collecting time on the convection heat transfer coefficient. The trend of decreasing convection coefficient with diameter agrees well with the correlation of Churchill and Chu (calculated at 299.15 K),29 (dashed line), although exact values differ. Note that for the same diameter, a higher collecting time indicates more CNTs within the same outer fiber diameter. (b) Measured convection coefficients of this work compared with literature data29,56 and predictions29 for microwires. Note that the convection coefficient for CNT fibers is not only strongly influenced by scaling effects but also by other structural and environmental factors. (c) Effect of volume fraction on the convection coefficient. (inset) Cross-section of a CNT fiber with different volume fractions. (d) Convection coefficient of the CNT fiber as a function of effective diameter. The red hollow circles in part c and the solid red line in part d indicate the calculated convection coefficient using the Churchill–Chu correlation and the effective diameter of the fiber.

range (296.15–303.15 K), no significant impact of spatially varying convection coefficient is expected (see Figure S3 in the Supporting Information). Thus, a typical average fiber temperature (299.15 K) is chosen for use in the Churchill–Chu correlation. As shown in Figure 5a, most of our experimental results are larger than the corresponded calculated values, although the diameter scaling effect has been taken into account in this correlation.

In addition, the correlation of Churchill and Chu29 indicates that the convection coefficient monotonically increases with the increasing diameter, independent of other fiber properties. However, the convection coefficients of the CNT fibers in Figure 5a are also affected by the collecting time, which determines the number of CNTs inside the fiber. This suggests that the porous structure of the CNT fibers may affect the convective heat transfer considerably. Since it is difficult to count the number of individual CNTs inside a fiber, here we investigate the effect of the volume fraction, reflecting the number of individual CNTs per unit volume. As shown in Figure 5c, the convection coefficient increases with increasing volume fraction. Previous studies report that surface area to volume ratio demonstrates great impact on heat transfer coefficient.51,57 Unlike solid materials, the effective surface area of CNT fibers is difficult to calculate. The insets in Figure 5c show illustrations of the cross-section of a CNT fiber. The structure of the CNT fibers can be regarded as numerous CNT bundles consisting of aligned individual CNTs. Open pores, between the CNT bundles, interconnect the air inside and outside of the fiber. Thus, the free convection can be considered on not only the outer surface but also the surface of each or some CNT bundles inside. The convection coefficient reflects the degree of heat loss per unit area.

Assuming a fixed outer diameter and a fixed convection coefficient on CNT bundle surface, a fiber with higher volume fraction consists of more CNT bundles and thus could have a larger effective surface area for convection. This results in more total heat loss and a higher effective convection coefficient because only the outer perimeter ($P = \pi D$) is used to calculate $h$ in eq 7. For a better understanding of the convective heat transfer in a porous structure like the CNT fiber here, we suggest to consider an effective diameter ($D_{\text{eff}}$ (m)), which combines both the outer diameter ($D$ (m)) and volume fraction ($f$ (%)) by the following empirically obtained equation:

$$D_{\text{eff}} = D(0.000268D^{-1.6}f^{-1.8} + 0.061)$$

(11)

As shown in Figure 5c and d, the corresponding convection coefficients calculated by eqs 10 and 11 have a good consistency with the experimental data. To a certain extent, this estimate of effective diameter indicates synergistic effects between the outer diameter and the number of CNT inside the fiber on the convective heat transfer in these porous CNT fibers. The actual convection between CNT fibers and the air is complicated due to the interaction of many environmental variables, as well as the complex structure of the CNT fiber. Ultimately, a more detailed correlation may include many factors including CNT length, bundle size, bundle entanglement, pore size, and gas flow inside the pore structure.

The mechanism of heat transfer between microscale materials and air or other gases is also controversial. Some research assumes that the dominant mode of heat transfer at the microscale is conduction through the air, instead of the classic notion of advection, such that natural convection effects could be neglected at microscale.57 Models considering the
scaling effect and the microstructure of the CNT fiber are required in the future to further study the mechanism of heat transfer in CNT based assemblies.

3.4. Effects of Acid Treatment on Thermal Conductivity. To study the effects of acid treatment on the thermal conductivity, both CNT fibers and the CNT films from which they were fabricated are immersed in 65 wt % HNO₃ at room temperature for 30 min. The effects of acid treatment on physical properties of CNT fiber and films are summarized in Table 2. After acid treatment, the electrical conductivities of the specimens are enhanced by a factor of 2–3, while their thermal conductivities are enhanced by a factor of 3–6. Additionally, the specific electrical and thermal conductivities are enhanced by factors of ~2 and ~4, respectively. For the as fabricated samples discussed previously, the specific electrical and thermal conductivities are nearly independent of density. However, acid treatment significantly improves the specific conductivities indicating that the intrinsic conductivity of the CNTs or the interfacial resistance have been modified during the acid treatment.

Table 2. Effects of Acid Treatment on Physical Properties of CNT Fiber and Films

<table>
<thead>
<tr>
<th>sample</th>
<th>as-prepared</th>
<th>acid-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>fiber</td>
<td>film</td>
</tr>
<tr>
<td>density (g cm⁻³)</td>
<td>0.67</td>
<td>1.19</td>
</tr>
<tr>
<td>electrical conductivity (S cm⁻¹)</td>
<td>700</td>
<td>1988</td>
</tr>
<tr>
<td>specific electrical conductivity (S cm⁻² g⁻¹)</td>
<td>1045</td>
<td>1670</td>
</tr>
<tr>
<td>thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>25</td>
<td>113</td>
</tr>
<tr>
<td>specific thermal conductivity (mW m⁻² kg⁻¹ K⁻¹)</td>
<td>37</td>
<td>104</td>
</tr>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>78</td>
<td>124</td>
</tr>
</tbody>
</table>

Such significant improvements on both electrical and thermal conductivities of the specimens can be related to structural modifications, which are investigated using Raman spectroscopy based on the ratio I_p/I_G. As shown in Figure 6a, I_p/I_G decreases from 0.26 to 0.21 after acid treatment, suggesting that CNTs become less defective after this treatment. Chemical processing of CNTs by concentrated nitric acid induces several modifications to the structure including purification (i.e., to eliminate amorphous carbon adhering to the CNTs), functionalization, and decapping of the CNTs. Functionalization typically requires elevated temperature or long times (90–120 min or more), which may result in an increase in the ratio I_p/I_G after acid treatment. Unlike those studies, in this work, the CNT fibers and films are treated for just 30 min at room temperature and purification is expected to be the dominant effect in this initial short period of acid treatment. The impact of the nitric acid is further elucidated by TEM images, as shown in Figure 6c and d. Before the acid treatment, many small particles could be observed adhering to the CNT surface. These particles are believed to be amorphous carbon. After 30 min acid treatment, the CNT surface becomes cleaner and thinner, which proves that the short acid treatment odes impact the purity of the structure. Furthermore, there is an enhancement of 50% for the BET surface area of the acid-treated specimen (Table 2). The pore size distribution of specimen is also modified during the treatment (see Figure 6b).

Figure 6. Effects of acid treatment on (a) Raman spectra and (b) pore size distribution. TEM images of CNT (c) before and (d) after acid treatment. Note the amorphous carbon at the surface of the as-synthesized CNT in part c, which is not observed in the acid-treated sample in part d.

Table 2. Effects of Acid Treatment on Physical Properties of CNT Fiber and Films

Figure 6. Effects of acid treatment on (a) Raman spectra and (b) pore size distribution. TEM images of CNT (c) before and (d) after acid treatment. Note the amorphous carbon at the surface of the as-synthesized CNT in part c, which is not observed in the acid-treated sample in part d.
The denser structure contributes more conductive properties also can be attributed to the improving CNT–CNT contact conductance due to the better alignment, shorter intertube space, and larger effective contact area after densification.

Interfacial contact resistance can also be modified through the covalently bonded nanotubes, and there may be some slightly functionalized CNTs existing after the short time acid treatment. However, thorough functionalization was reported to suppress the electrical conductivity of the CNT fibers and also decrease the intrinsic nanotube thermal conductivity due to the destruction of the crystalline structure of CNT, which can be observed by TEM. Based on our characterizations of the structural modifications, functionalization is not the dominant reason for the observed enhancement of conductivities.

As shown in Figure 8, the thermal conductivity and specific thermal conductivity of our CNT fibers and films are comparable to those of other CNT fibers and selected highly conductive films. In particular, our acid-treated CNT film combines both high absolute thermal conductivity and high specific thermal conductivity, which is even higher than the typical values of conventional heat-transfer metals (copper, aluminum, and silver) and comparable to that of the highest performing CNT fibers and films reported in the literature. Interestingly, the specific thermal conductivity of our CNT film is much higher than that of our CNT fiber, which differs from the observation for the CNT fibers where the thermal conductivity increases nearly linearly with the increasing density and the specific thermal conductivity remains nearly constant in the density range of 0.11–0.87 g cm⁻³. This indicates some nonlinearity in the thermal conductivity with increased density in a wider density range (e.g., the density of the as-prepared film is around 1.2 g cm⁻³). The nonlinearity in the thermal conductivity with increased density was also reported by Marconnet et al. in their study of the thermal conductivity of aligned CNT–polymer nanocomposites as a function of varying CNT volume fraction. The lower specific conductivity may be ascribed to the structure of the CNT fiber and the inter-CNT contact resistance. Since the CNT fiber was rolling from the CNT film, it can be regarded as a cylinder structure consisting of multiple layers of films. Aliev et al. studied the effect of multilayered structure on the thermal conductivity of CNT sheets stacked on top of one another. They found that increasing the number of layers decreased the measured value of thermal conductivity, likely due to poor interfacial transport between the sheets. The same effect of decreasing thermal conductivity with increasing layers occurs for graphene layers when they are stacked in graphite. In that case, interlayer interactions quench the thermal conductivity by nearly an order of magnitude. The lower conductivity of multilayered structure indicates the presence of enhanced scattering of heat carriers at the tube–tube interconnections between layers. This result suggests that an improved fabrication method is required in the future to obtain highly dense CNT fibers with better intertube contacts and high thermal conductivity. In addition, the thermal conductivities in this work are measured near room temperature. For many applications, it is of great importance to study the thermal conductivity of the CNT fiber across a range of temperatures. The technique developed here can be extended to enable temperature-dependent measurements through control of the base temperature of the fiber and the environment.

4. CONCLUSIONS

We demonstrate a robust, fast electrothermal technique for simultaneously measuring the thermal conductivity of and convection coefficient from CNT fibers and films. The measured thermal and electrical performance demonstrates the promise for using these fibers and films in macroscale applications requiring effective heat dissipation such as electrical cables and multifunctional composites.

The thermal conductivity of the as-prepared fiber ranges from 4.7 ± 0.3 to 28.0 ± 2.4 W m⁻¹ K⁻¹, which is much lower than the expected from the high thermal conductivity of individual CNTs, is comparable to other CNT-based structures and rivals the specific thermal conductivity of metals. The

![Figure 7. SEM images of as-prepared (a and b) and acid-treated (c and d) CNT film at different magnifications.](Image)

![Figure 8. Thermal conductivity and specific thermal conductivity of this work compared with literature data for other CNT fibers and films made by different processes.](Image)
major factors limiting the apparent thermal conductivity of the CNT fibers are the interfacial contact resistance and structural inhomogeneity in the fibers.

The convective heat transfer coefficient for the as-prepared CNT fiber strongly depends on the diameter and volume fraction. A correlation between CNT volume fraction, diameter, and convective coefficient has been developed based on the experimental data. New models considering the microstructure of CNT fiber are required in the future for better understanding the mechanism of heat transfer in CNT based assemblies.

Nitric acid treatment is demonstrated to be a simple, effective approach to enhance the thermal conductivity of the CNT fibers and films. The thermal conductivity and specific thermal conductivity are enhanced by 670% and 450% respectively after acid treatment. This great improvement is attributed to the reducing CNT–CNT contact resistance, modified fiber structure, and increased density after the acid treatment. The acid-treated CNT film demonstrates thermal conductivity of 759 W m⁻¹ K⁻¹ and specific thermal conductivity of 474 mW m⁻² K⁻¹, which is even higher than the typical values of conventional metals and comparable with the highly conductive CNT assemblies reported in the literature. Compared to the CNT films, CNT fibers exhibit lower thermal conductivity and require the development of optimized fabrication method for more compacted fiber structures with improved intertube contacts to further improve thermal performance.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b04114.

Validation of one-dimensional heat transfer; method of emissivity calibration and thermal image acquisition; influence of variable local heat transfer coefficient on the temperature profile; influence of temperature on Churchill–Chu correlation; summary of the properties of the CNT fibers (PDF)

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