CARBON 77 (2014) 973–979

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

# Thermal manipulation of carbon nanotube fiber by mechanical stretching

*Yanan Yue* [*], *Kang Liu*, *Man Li*, *Xuejiao Hu*

*School of Power and Mechanical Engineering, Wuhan University, Wuhan, Hubei 430072, China*

A R T I C L E I N F O

*Article history:*
Received 16 March 2014
Accepted 9 June 2014
Available online 14 June 2014

A B S T R A C T

Thermal manipulation of materials is of great interest due to various requirements for heat dissipation. We report an experimental study of thermal manipulation of a highly oriented carbon nanotube (CNT) fiber by mechanical stretching based on the transient electro-thermal (TET) method. The thermal property of CNT fibers is measured under different elongation ratios and temperatures. Thermal conductivity enhancement as high as 28% is observed at all temperatures with applied mechanical stretching less than 5% in the axial direction. This enhancement in thermal conductivity is attributed to the better CNT alignment and the reduction in thermal resistance at CNT contacts, which is validated by the density/structural analysis.

## 1. Introduction

Individual carbon nanotube (CNT) exhibits exceptional mechanical, electrical and thermal properties [1], however, the implementation of CNTs requires these properties to be translated into macroscopic materials. Among efforts on CNT-based assemblies, the CNT fiber, which comprises axially aligned and highly packed CNTs, presents outstanding macroscopic properties, including high specific modulus, specific strength, electrical and thermal conductivity [2–5], which makes it a good candidate for broad industrial applications, such as reinforcements for high-performance composites, biosensors, transmission lines, and microelectronics [6–9]. Some applications, such as micro-electronics which work under high power densities, have high demands for heat dissipation. The clear understanding of the fundamental thermal transport properties, especially under different circumstances is of great importance.

Tremendous efforts have been devoted to the study of mechanical and electrical properties of CNT fibers, while only few studies have been focused on its thermal property analysis. A few works include: the measurement of thermal conductivity in the acid spun method as 20 W/(mK) [10] and in the dry-spinning method as 26 W/(mK) [11] and the measurement of CNT/PVA composites as 10 W/(mK) [12]. The highest value in literatures is reported by Jakubinek et al. as 60 ± 20 W/(mK) [4]. All values are one or two orders of magnitude lower than individual CNTs. It is because the thermal resistance of inter-tube is much higher than that of the inner-tube, and the inter-tube thermal transport dominates the energy dissipation of CNT fibers [4,11–13]. It is reasonable to seek the enhancement of thermal transport property of CNT fibers by reducing the internal contact resistances of CNT–CNTs.

It has been validated that mechanical stretching is an effective way to improve alignment and enhance thermal transport of disordered soft materials. For example, Badaire and Jin et al. observed the improvement of alignment in CNT-polymer composites [12,14]. Liu et al. found the improvement of thermal diffusivity as high as 263% at the stretching ratio of 63.8% for silkworm silk [15]. It is speculated that the stretching effect might take effect on the thermal performance of CNT fibers

---

[*] *Corresponding author*: Fax: +86 27 68772268.
E-mail address: yyue@whu.edu.cn (Y. Yue).

http://dx.doi.org/10.1016/j.carbon.2014.06.013
0008-6223/© 2014 Elsevier Ltd. All rights reserved.

and it is interesting to find whether this speculation is real and to what extent this effect could be. In this work, we use the transient electro-thermal (TET) method to measure the thermal conductivity of CNT fiber under stretching to explore the feasibility of the thermal manipulation of this material.

## 2. Experimental principles and details

### 2.1. *Experiment principle*

The TET technique developed by Wang is an efficient approach to measure thermal property of microwires [15,16]. As shown in Fig. 1(a) for the experimental principle and setup: the sample is suspended between two electrodes (copper) with ends firmly adhered by silver paste. The copper is used as the electrodes and also the heat sink for heat dissipation. Comparing with the sample, the copper electrodes have higher volume and heat capacity, ensuring that the sample ends stay at room temperature. The electrodes are connected to the DC current source, which supplies the Joule heating.

In TET experiment, a step current is applied on the sample. The temperature increase of sample experiences a transient process before reaching steady-state. The temperature rise of sample leads to the resistance change, which can be monitored by measuring voltage. The transient process during temperature rise can be used to determine thermal diffusivity while the steady state period can be used for calculating thermal conductivity by:

$$k = \frac{I^2RL}{12A\Delta T} \tag{1}$$

where $I$ is step current, $R$ is electrical resistance. $A$ and $L$ are cross-sectional area and length of CNT fiber, respectively. $\Delta T$ is the temperature rise of sample, which can be obtained from the voltage increase and temperature coefficient of resistance.

### 2.2. *Experimental details*

Fig. 1(b) shows the image of CNT fiber sample with initial length of 5.09 mm. The sample is purchased from Jcnano Company prepared in the floating catalyst method with good elasticity. Sample stage used in the experiment is controlled by a micro-stage with spatial resolution of 1 μm. To ensure the accuracy of measurement, the sample needs to be fixed on electrodes, and the elongation can be precisely controlled by the micro-stage. In the experiment, four samples were tested and the average elongation of breaking is 5%. Fig. 2(a)–(d) are SEM images of the sample. It can be seen from (a) and (b) that the sample is tightly twisted and the diameter of the sample is a little nonuniform. To accurately determine diameter of the sample, 26 values along the fiber are taken for averaging as 17.8 μm. Fig. 2(c) and (d) are taken at the breakpoint after the stretching experiment. The inside structure shows that most of the CNTs have good alignment while there are some twisted ones. The diameter of individual CNT is estimated from Fig. 2(d) as 20 nm.

Before thermal measurements, a calibration experiment is conducted to get the temperature coefficient of electrical resistance. In the calibration experiment, the sample is heated from room temperature to 90 °C with electrical resistance recorded at corresponding temperatures, shown as Fig. 3. Usually, the relationship between electrical resistance of materials and temperature can be regarded as linear within a low temperature range. As shown in Fig. 3, linear fitting of

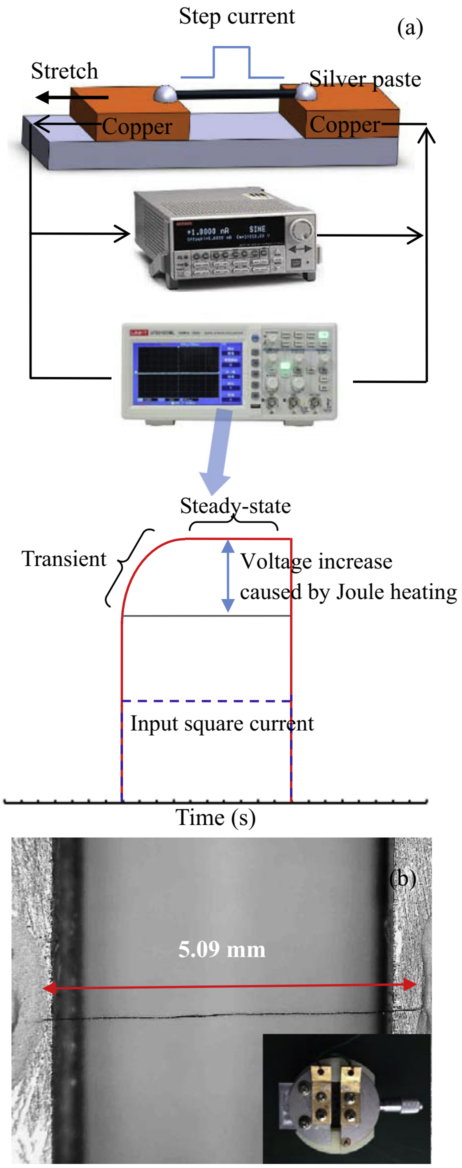

**Fig. 1 – (a) Schematic of the TET experiment principle. The current source supplies a step current for Joule heating and the oscilloscope is used to record voltage evolution. The temperature response to Joule heating can be recorded and used for thermal property measurement. The transient part can be used to determine thermal diffusivity and the steady-state period (voltage increase) can be used to calculate thermal conductivity. (b) Sample image of the CNT fiber. Sample ends are attached on copper electrodes by silver paste. The inset shows the image of the stretching stage used in the experiment. There is a micro-stage beneath the electrode to control elongation precisely. (A color version of this figure can be viewed online.)**

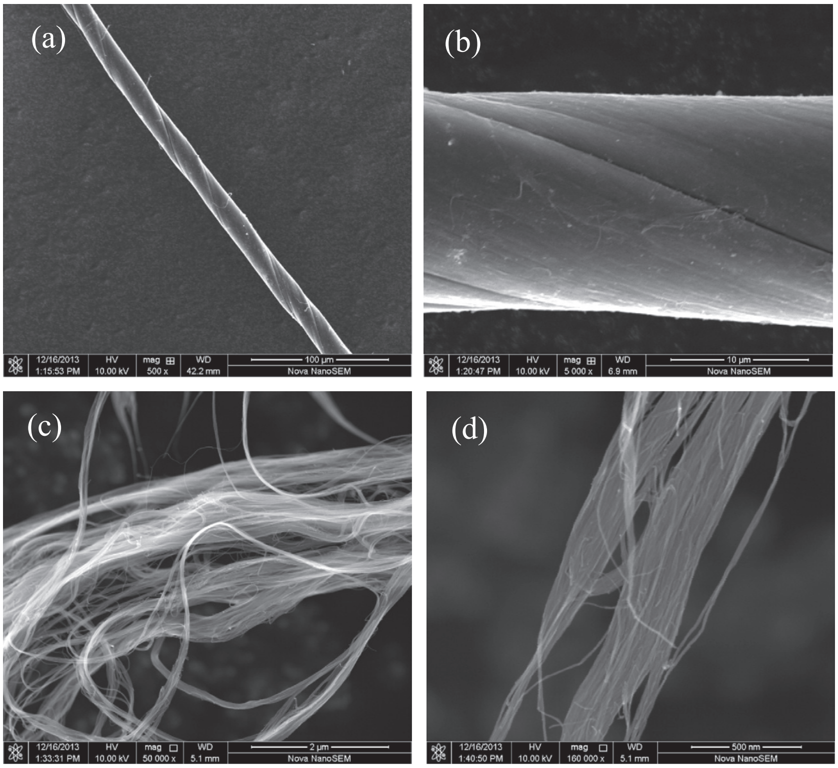

**Fig. 2 – SEM images of the CNT fiber measured in experiments: (a) and (b) show the surface morphology; (c) and (d) show the inner structure of the CNT fiber at break point.**

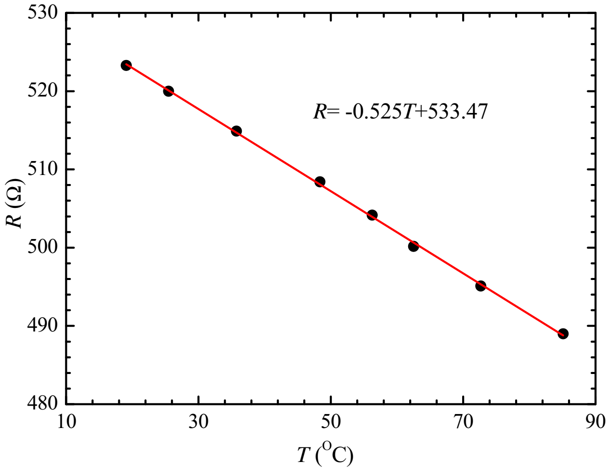

**Fig. 3 – Temperature coefficient of CNT fiber's resistance is calibrated as −0.525 Ω/K. (A color version of this figure can be viewed online.)**

relationship between resistance and temperature is conducted, and the temperature coefficient is obtained as −0.525 Ω/K.

The measurement experiments are performed in a vacuum chamber with $10^{-3}$ Torr, ensuring that the heat loss due to convection effect can be neglected. Meanwhile, an aluminum foil is used to cover the sample stage throughout the experiments to minimize radiation heat loss. During the test, it is found that there is a little change on the resistance of sample during stretching. To ensure that the fiber is straight at the first measurement point, the fiber is carefully adjusted until its electrical resistance starts to change. The fiber is stretched by 30 μm each time and the data acquisition is repeated for ten times for voltage averaging to eliminate the effect of current noise.

## 3. Results and discussion

### 3.1. *Resistance and temperature response to mechanical stretching and Joule heating*

Fig. 4(a) shows the resistance response of the sample when a step current is applied. The different colors represent for different elongations. It is found that the final resistances of sample at different elongations are different even supplied with same current, which proves that the temperature of the sample is different even at the same heating level and stretching effect affects thermal transport in the CNT fiber. As aforementioned, the mechanical stretching also changes the original resistance. Thus, it needs to be clarified that the difference in thermal transport is induced by stretching rather than different heating effect (from the original resistance difference because of different stretching). The inset shows the magnified figure of the original resistance at different elongation ratios. By comparing the resistance of elongation 0.012 and 0.035, it is found that the resistance difference after Joule heating is much higher than the original resistance difference, which is the evidence for the stretching effect on the temperature (resistance) response.

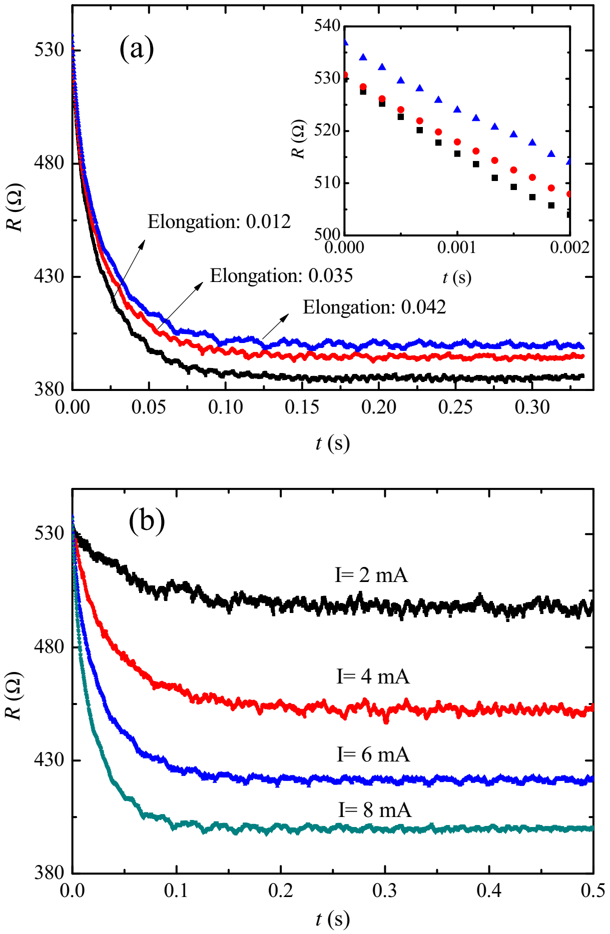

**Fig. 4 – (a) Resistance change of CNT fiber under Joule heating (8 mA) at different elongations. (b) Resistance change of CNT fiber under different currents with elongation of 3.5%. (A color version of this figure can be viewed online.)**

In addition, the heating level (or say temperature) of CNT fiber also affect thermal transport. Because thermal property of materials, no matter metals, semiconductors or insulators, have some temperature dependence. How this effect would be when the sample is under stretching is unclear. To perform the study of thermal manipulation under different temperatures, the average temperature of CNT fiber is precisely controlled by adjusting feeding current. Fig. 4(b) presents the result of resistance evolution of different currents from 2 to 8 mA at same elongation (3.5%). It can be easily understood that different heating gives different temperature rise (the resistance drop). However, the resistance drop for each 2 mA intervals (from 2 to 8 mA) is less significant as shown in Fig. 4(b), which infers that either thermal property or resistance of the material have changed under different heating levels (temperatures). In addition, it is observed that the mechanical stretching changes initial resistance as shown in Fig. 4(a). Therefore, the variance in final electrical resistance (temperature) is a combined effect of the initial resistance change from stretching and the thermal property change (due to stretching). To keep consistency in the measurement result, the initial resistance is recorded at each elongation before Joule heating experiment and is subtracted from the final resistance to count temperature rise induced by thermal property change.

### 3.2. *Thermal conductivity enhancement by mechanical stretching*

To get coupling effect of temperature and mechanical stretching, the fiber is fed by different currents at different elongations. Temperature rise of the sample is calculated from the temperature coefficient of electrical resistance, and thus, thermal conductivity of CNT fiber at different elongations and temperatures is obtained. Fig. 5 summarizes thermal conductivity of CNT fiber under three temperatures: 93 °C, 181 °C and 253 °C. Relatively higher data uncertainty at lower temperatures is because of the inherent noise. It can be seen that the thermal conductivity increases significantly with elongations for all temperatures. The thermal conductivity measured at 93 °C is 39.8 W/(mK), which is comparable with the measured value: 60 W ± 20 W/(mK) for the diameter of 10 μm, and 25 ± 5 W/(mK) for the diameter of 34 μm in [4], but slightly higher than results of [10]: 20 W/(mK) and [11]: 26 W/(mK). The difference stems from the material composition and structure, and also experimental conditions.

Fig. 5 shows that thermal conductivity of CNT fiber increases significantly with temperatures. Thermal conductivities obtained at high temperatures involve some uncertainty due to radiation heat loss. Although the aluminum foil is used in the experiment for radiation protection, the radiation from sample to the surroundings is still significant. For better understanding of uncertainty of experimental data

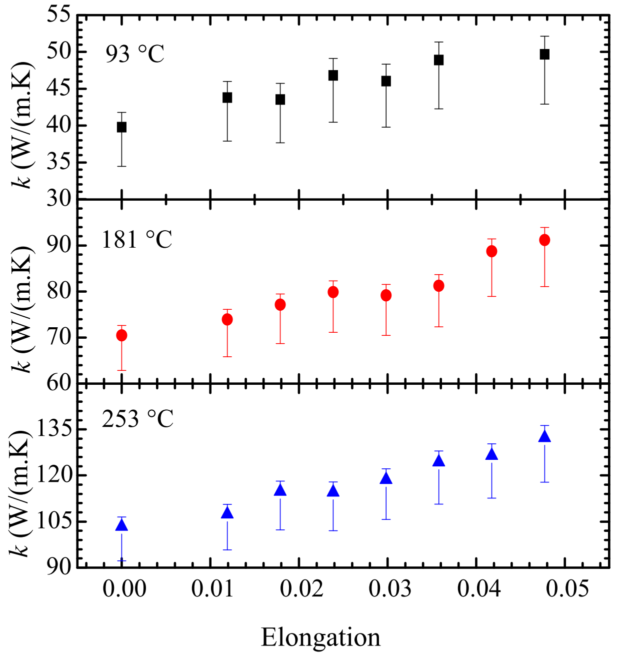

**Fig. 5 – Measurement results for the thermal conductivity of CNT fiber at different elongations and temperatures. The upper limit of error bars is from the standard deviation during data fitting. The lower limit of error bar involves the uncertainty of measurement result due to radiation heat loss. (A color version of this figure can be viewed online.)**

due to radiation heat loss, we take a rough calculation for this effect. The heat loss due to radiation can be estimated by $\varepsilon\sigma A_s(T^4 - T_0^4)$, where $\varepsilon$ is emissivity, $\sigma$ is Stefan–Boltzmann constant ($5.67 \times 10^{-8}$ W/m$^2$K$^4$), $A_s$ is surface area of the sample, $T$ and $T_0$ are sample temperature and room temperature, respectively. CNT fiber can be regarded as similar property as carbon black, we take $\varepsilon$ as 1 for calculating the maximum radiation heat loss. The radiation heat loss is estimated as $1.69 \times 10^{-4}$, $5.60 \times 10^{-4}$ and $1.10 \times 10^{-3}$ W for temperatures 93 °C, 181 °C and 253 °C, respectively. Comparing with corresponding Joule heating, thermal conductivity can be overestimated by 8.43%, 7.88% and 7.77% at maximum for these temperatures.

The surface area of sample is changed by mechanical stretching, therefore, the radiation heat loss would be different for sample at different elongations. To investigate if there is contribution of radiation heat loss due to stretching to the improved thermal conductivity, we calculate the ratio of radiation loss to Joule heating at the highest elongation as 8.63%, 8.06% and 7.96% for these temperatures. Comparing these values with above results before stretching, the difference is about 2%, which is negligible considering with large improvement of thermal conductivity. Therefore, the tendency for the thermal conductivity improvement due to mechanical stretching at high temperatures is not affected much by radiation heat loss. The effect of radiation heat loss on the evaluation of thermal conductivity has been shown in Fig. 5 as the lower limit for the uncertainty.

### 3.3. *Physical interpretation of experimental observations*

If explaining the thermal transport of CNT fiber via Umklapp scattering, thermal conductivity should decrease as temperature increases. In our measurement, the enhanced thermal conductivity with temperature means that the phonon transport is mainly dominated by the phonon boundary scattering and defect scattering, rather than Umklapp scattering. For further analysis of stretching's effect on the thermal conductivity improvement, the results are integrated into one figure, as shown in Fig. 6. The $y$ axis is thermal conductivity improvement: $\Delta k_p = (k - k_0)/k$, where $k_0$ is initial thermal conductivity before stretching. The data shows that thermal conductivity increases significantly (23–28%) with elongation of 4.7%, and the slopes of linear fitting are 5.23, 5.95 and 5.83 for temperatures 93 °C, 181 °C and 253 °C, respectively.

It remains a question how mechanical stretching changes the thermal transport inside CNT fiber. The heat conduction involves the transfer of energy carriers inside a material. As a conductive material, the energy carriers inside it are electrons and phonons. The thermal transport inside CNTs is mainly dominated by phonons [17,18], while the electrical conductivity comes from the movement of free electrons. For CNT fibers, since the stretching effect has direct effect on the resistance, it needs to be clarified whether mechanical stretching will greatly enhance the energy transport by electrons, hence contributes in a higher proportion to the thermal conductivity improvement.

To validate this speculation, the electrical conductivity ($\sigma$) at different elongations is calculated as shown in Fig. 7. Before stretching, the fiber has the electrical conductivity of 395 S/cm, which is consistent with the results in [4]. The value increases from 395 to 413 S/cm, about 4.4% increment with elongation of 4.7%. Similar results were observed in [4] for the electrical conductivity decrease with diameter (our slope: −4206 S/mm$^2$). According to the Wiedemann–Franz law, the thermal conductivity ($k$) induced by electrons can be related to the electrical conductivity ($\sigma$) by $k/\sigma T \approx L_0$, where $L_0 = 2.45 \times 10^{-8}$ V$^2$/K$^2$. Taking the highest electrical conductivity (413 S/cm) into calculation, the thermal conductivity due to electron transport is calculated as $4 \times 10^{-3}$ W/(mK), which can be neglected compared with our measured values. It means that the electrons induced thermal conductivity does not contribute much to the thermal conductivity improvement during stretching, and the change mainly comes from the phonon transport.

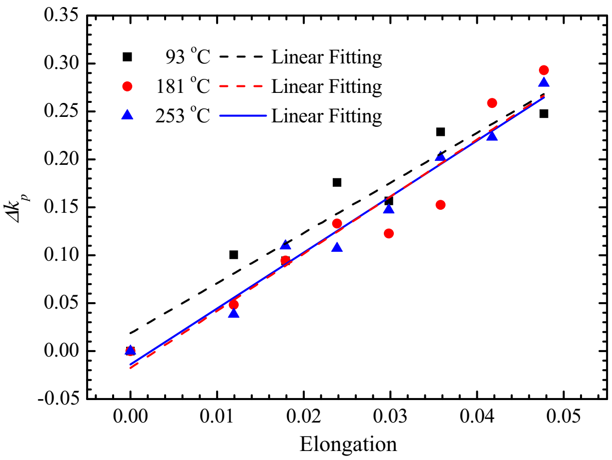

**Fig. 6 – Comparison of thermal conductivity improvement by mechanical stretching at different temperatures. Slopes of linear fittings are 5.23, 5.95 and 5.83 for temperatures 93 °C, 181 °C and 253 °C, respectively. (A color version of this figure can be viewed online.)**

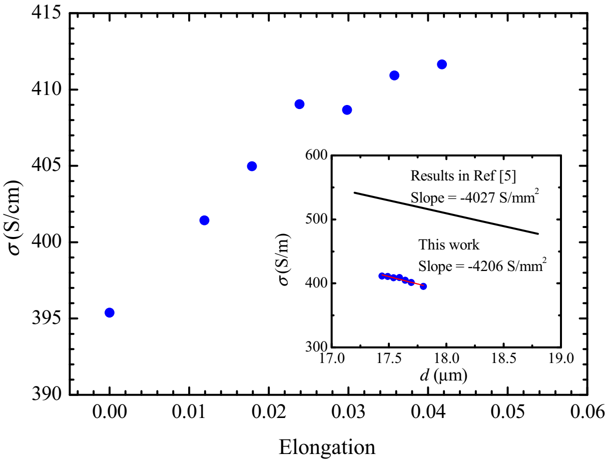

**Fig. 7 – Electrical conductivity of the CNT fiber at different elongations. The inset shows the relative diameter dependence and the comparison with results in [5]. (A color version of this figure can be viewed online.)**

Thermal conductivity can be enhanced by reducing phonon scatterings, including boundary scattering, impurity scattering and phonon–phonon scattering, which can be understood via thermal conductivity relation derived from the kinetic theory: $k = Cvl/3$, where $C$ is the volumetric heat capacity, $v$ is phonon group velocity, and $l$ is phonon mean free path (MFP). $C$ and $v$ can be regarded as constant without considering temperature effect, therefore, the phonon MFP is the main factor for the thermal conductivity improvement. It is reasonable to take the volumetric heat capacity of graphite as 1.56 J/cm$^3$K [19] and assume the phonon group velocity as $10^4$ m/s [20], the effective phonon MFP of CNT fiber is calculated in the order of 10 nm, comparable to the diameter of CNTs inside the material. It needs to be mentioned that calculated phonon MFP is an apparent value which combines effects of phonon–phonon scattering, boundary scattering and phonon-defect scattering. Mechanical stretching can effectively improve the thermal transport property, which in other words, increase the effective phonon MFP. It can be realized in two pathways: good alignment and tight contact. As discussed earlier, the phonon energy transport inside the CNT-based bundles or fibers is dominated by the boundary/defect scattering. The thermal transport is mainly determined by the thermal contact resistance of the CNT–CNTs. As shown in Fig. 1(c) and (d) for SEM images of inner structures, there is still much room for better alignment. Better alignment can optimize the inner structure, increase the contact areas and thus improve the integral property. Meanwhile, a tight contact effectively reduces the contact resistance between CNTs, hence improves the electrical conductivity (as observed in the experiment). Mechanical stretching can effectively improve the alignment of CNT fiber and the internal force gives pressure on CNT contacts, and reduces thermal contact resistance.

To get comprehensive understanding of thermal transport inside CNT fiber, thermal diffusivities of CNT fiber at different elongations are calculated. As previously introduced in TET technique, the steady-state period of voltage signal is used for thermal conductivity calculation, while the transient period of the voltage signal can be processed to determine thermal diffusivity of CNT fiber from the same group of data. The principle for details of thermal diffusivity calculation can be found in [15,16]. Fig. 8(a) shows the results for the heating current of 6 mA as an example. There is an obvious trend for the thermal diffusivity improvement with mechanical stretching. Since thermal conductivity and thermal diffusivity are obtained, the density of CNT fiber can be readily calculated from $k/\alpha c_p$, where $k$ is thermal conductivity, $\alpha$ is thermal diffusivity and $c_p$ is specific heat. Here, we take the specific heat of graphite (709 J/kgK) for a rough estimation [21], and the results of density at different elongations are shown in Fig. 8(b). It can be seen that the density of CNT fiber is much lower than that of graphite bulk (2210 kg/m$^3$) [19], which means that there is high porosity inside the fiber. Moreover, the increase of density during stretching is significant, which confirms our previous analysis that the mechanical stretching does reduce porosity, and thus improve alignment of CNTs and thermal conductance at CNT contacts. In our experiment, it is found that sample still exhibits original thermal properties after the relaxation from stretching. Therefore, it is feasible to manipulate thermal property of CNT fiber by precisely adjusting the stretching force.

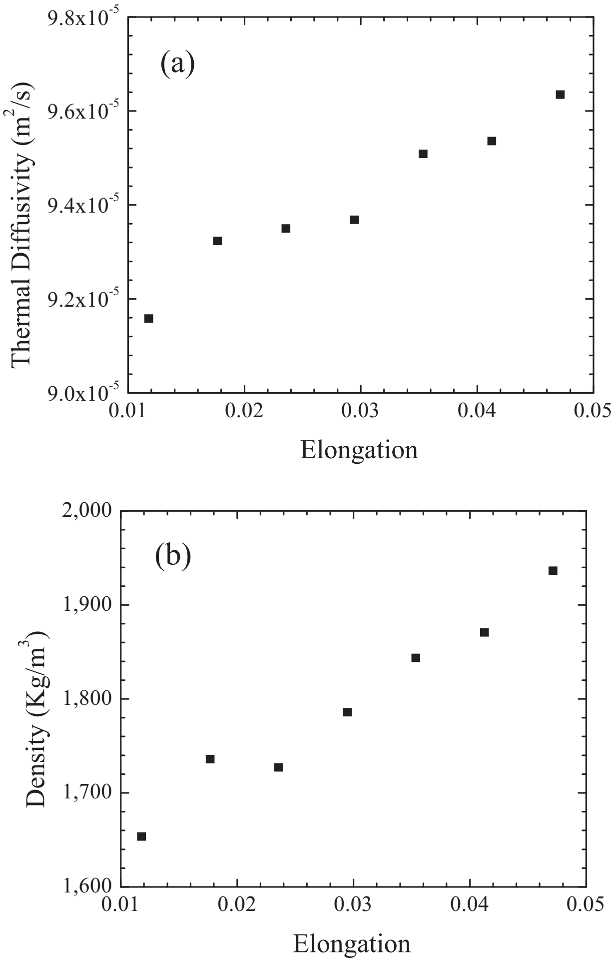

**Fig. 8 – (a) Thermal diffusivity of CNT fiber increases with elongation (6 mA). (b) Density of CNT fiber increases with elongation (6 mA), indicating that mechanical stretching can effectively reduce porosity and improve the alignment of inside CNTs.**

## 4. Conclusion

In this work, the thermal conductivity of highly oriented CNT fiber is investigated by the transient electro-thermal method. The thermal manipulation of CNT fibers with thermal conductivity enhancement as high as 28% is achieved by the mechanical stretching (less than 5%) in the axial direction. This enhancement is attributed to the alignment improvement and reduction in thermal contact resistance of CNTs, which is validated from density analysis during stretching. Besides, the effect of stretching on thermal conductivity is studied at different temperatures, and a similar tendency for different temperatures is observed. This finding provides a pathway for manipulating thermal performance of CNT fiber for different thermal dissipation needs in broad industrial applications.

## Acknowledgements

The financial supports from Start-up of Wuhan University and National Science Foundation of China (No. 51206124) are gratefully acknowledged. Y.Y. proposed the idea. Y.Y. and K.L. conceived and designed the experiments. K.L. performed the experiments. M.L. helped on the experimental setup. Y.Y. and K.L. wrote the paper. K.L. is regarded as the co-first author (his contribution is not equal to the first author, just specify that he is the first-student author in this work). Y.Y. and X.H. supervised the research.

## REFERENCES

[1] Jayasinghe C, Li W, Song Y, Abot JL, Shanov VN, Fialkova S, et al. Nanotube responsive materials. MRS Bull 2010;35(09):682–92.

[2] Zhang X, Li Q, Holesinger TG, Arendt PN, Huang J, Kirven PD, et al. Ultrastrong, stiff, and lightweight carbon-nanotube fibers. Adv Mater 2007;19(23):4198–201.

[3] Koziol K, Vilatel J, Moisal A, Mott M, Cunniff P, Sennett M, et al. High-performance carbon nanotube fiber. Science 2007;318(5858):1892–5.

[4] Jakubinek MB, Johnson MB, White MA, Jayasinghe C, Li G, Cho W, et al. Thermal and electrical conductivity of array-spun multi-walled carbon nanotube yarns. Carbon 2012;50(1):244–8.

[5] Miao M. Electrical conductivity of pure carbon nanotube yarns. Carbon 2011;49(12):3755–61.

[6] Lu W, Zu M, Byun J, Kim B, Chou T, et al. State of the art of carbon nanotube fibers: opportunities and challenges. Adv Mater 2012;24(14):1805–33.

[7] Behabtu N, Green MJ, Pasquali M. Carbon nanotube-based neat fibers. Nano Today 2008;3(5–6):24–34.

[8] Liu L, Ma W, Zhang Z. Macroscopic carbon nanotube assemblies: preparation, properties, and potential applications. Small 2011;7(11):1504–20.

[9] Chou T, Gao L, Thostenson ET, Zhang Z, Byun J. An assessment of the science and technology of carbon nanotube-based fibers and composites. Compos Sci Technol 2010;70(1):1–19.

[10] Ericson LM, Fan H, Peng H, Davis VA, Zhou W, Sulpizio J, et al. Macroscopic, neat, single-walled carbon nanotube fibers. Science 2004;305(5689):1447–50.

[11] Aliev AE, Guthy C, Zhang M, Fang S, Zakhidov AA, Fischer JE, et al. Thermal transport in MWCNT sheets and yarns. Carbon 2007;45(15):2880–8.

[12] Badaire S, Pichot V, Zakri C, Poulin P, Launois P, Vavro J, et al. Correlation of properties with preferred orientation in coagulated and stretch-aligned single-wall carbon nanotubes. J Appl Phys 2004;96(12):7509–13.

[13] Shaikh S, Li L, Lafdi K, Huie J. Thermal conductivity of an aligned carbon nanotube array. Carbon 2007;45(13):2608–13.

[14] Jin L, Bower C, Zhou O. Alignment of carbon nanotubes in a polymer matrix by mechanical stretching. Appl Phys Lett 1998;73:1197.

[15] Liu G, Huang X, Wang Y, Zhang Y, Wang X. Thermal transport in single silkworm silks and the behavior under stretching. Soft Matter 2012;8(38):9792–9.

[16] Guo J, Wang X, Wang T. Thermal characterization of microscale conductive and nonconductive wires using transient electrothermal technique. J Appl Phys 2007;101(6):063537.

[17] Biercuk MJ, Llaguno MC, Radosavljevic M, Hyun JK, Johnson AT, Fischer JE. Carbon nanotube composites for thermal management. Appl Phys Lett 2002;80:2767–9.

[18] Hone J, Whitney M, Piskoti C, Zettl A. Thermal conductivity of single-walled carbon nanotubes. Phys Rev B 1999;59:R2514.

[19] Incropera FP, DeWitt DP, Bergman TL, Lavine AS. Fundamentals of heat and mass transfer. sixth ed. Hoboken, NJ: John Wiley & Sons; 2006. 933.

[20] Hone J. Phonons and thermal properties of carbon nanotubes. In: Dresselhaus M, Dresselhaus G, Avouris P, editors. Carbon Nanotubes. Berlin Heidelberg: Springer; 2001. p. 273–86.

[21] Mizel A, Benedict LX, Cohen ML, Louie SG, Zettl A, Budraa NK, et al. Analysis of the low-temperature specific heat of multiwalled carbon nantubes and carbon nanotube ropes. Phys Rev B 1999;60:3264–70.