Thermal Property of Carbon Nanotube Fibers from Chemical Vapor Deposition Synthesis

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Keywords: carbon nanotube fibers, chemical vapor deposition synthesis, thermal property

Abstract. In this study, thermal property of the carbon nanotube (CNT) fibers from chemical vapor deposition synthesis was investigated. Thermal conductivity of the CNT fibers was measured using the "T"-type method; a value of 75.9 $WK^{-1}m^{-1}$was obtained at room temperature. Temperature dependence of the thermal conductivity of the CNT fibers was also measured; the thermal conductivity first increased and then decreased in the temperature range 80–320 K. Moreover, thermal conductivity of the CNT fibers increased after the treatment with an HCl solution.

Introduction

Carbon nanotubes (CNTs) with unique one-dimensional nanotube structures possess super strength[1], high electrical[2] and thermal conductivities[3],and multifunctional properties. CNT fibers, as the oriented assembly of CNTs, have several potential applications such as in artificial muscles[4],supercapacitors[5], ultrahigh conductivity fibers[6],stretchable conductors[7], and high-performance structural fibers[8] due to the outstanding performance of individual CNTs.

Currently, CNT fibers are synthesized by four main routes:1)spinning from a CNT solution[9],2)spinning from an aligned CNT array[10],3)spinning from the CNT aerogel formed by chemical vapor deposition(CVD) reactor[11,12], and 4)twisting/rolling from a CNT film[13]. CNT fibers obtained from the CVD method are the most suitable for large-scale commercial production because of their facile synthesis and a stable continuous spinnable process. At present, the fabrication of CVD CNT fibers has been optimized; however, their properties have not been studied. The first requirement for the applications of CVD CNT fibers is to understand their properties, particularly thermal property. Therefore, the thermal property of CVD CNT fibers was investigated in this study.

Experimental

CNT fibers were fabricated by the CVD synthesis method. A mixture of carbon source and catalyst was injected into a high-temperature reactor along with H_2 stream, affording continuous fibers at the bottom of the reactor. The fiber was pulled out of the reactor after on-line densification with acetone. A more detailed description of the synthesis process can be found elsewhere[12].

The as-spun fiber was treated with HCl as follows: The fiber was immersed in an HCl solution for ~30 min, followed by drying in an oven. The cross-section and surface morphologies of CNT fibers were characterized using an SEM (JSM-6700F); further characterizations were carried out using a transmission electrical microscope (TEM, Tecnai-G20 F20) and Raman spectrometer (Renishaw).

The measurement principle of the thermal conductivity can be found in supporting materials. The thermal conductivity was measured using a "T"-type device in a thermostat bath. Molecular and vacuum pumps were used for the continuous removal of air in the thermostatic bath, thus decreasing the pressure to 10^{-4} Pa. Simultaneously, a liquid nitrogen circulation system and microcontrolled heater were used to adjust the temperature inside the bath. The voltage and current

were measured using a digital multimeter. A more detailed description can be found in literature[14].

Results and discussion

The structure of as-spun CNT fiber

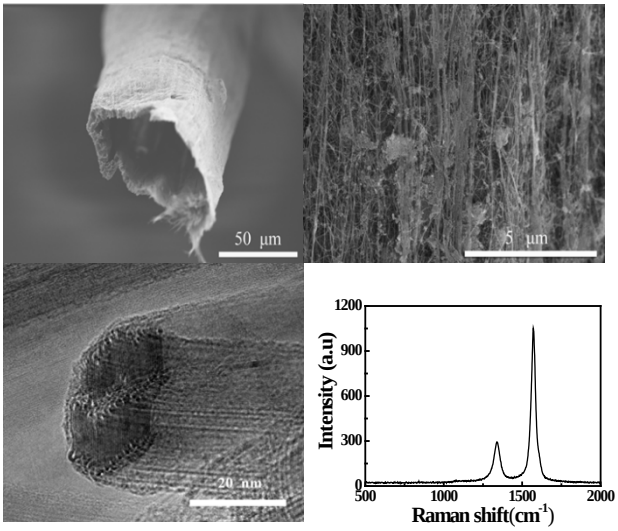

Figure. 1. a) Scanning electron microscopy (SEM) image of the cross-section of CNT fiber. b) SEM image of the surface of fiber. c) Transmission electron microscopy image of the cross-section of CNT bundle. d) Raman spectrum of fiber.

The fibers are continuous and soft, like cotton yarns. Three hierarchy structures were observed in the SEM and high-resolution TEM. At the macroscopic scale, the fibers are hollow, with a fiber wall of 1–10 μm (Fig.1a).The fiber wall consists of large quantities of CNT bundles in the diameter range 10–100 nm, and the bundles are slightly aligned with the fiber axis(Fig.1b). At the microscopic scale, the bundles comprise of stacked large-diameter double-wall CNTs (Fig.1c).The crystallization of the fiber was characterized by the Raman spectrum(Fig.1d).The intensity ratio of G to D(I_G/I_D)was found to be 4.3,indicating that the obtained CNT fibers have less defect than the CNT fiber from array[16].

Thermal conductivity of CNT fibers

1) Thermal conductivity of CNT fibers at room temperature

The CNT fibers from CVD synthesis process have a thermal conductivity of 75.9 $WK^{-1}m^{-1}$ at room temperature, which is comparable to the reported values, 50 and 19 $WK^{-1}m^{-1}$, of CNT fibers from array[17] and a typical solution[18], respectively, but lower by one order of magnitude(600 $WK^{-1}m^{-1}$) than the CNT fibers synthesized by improved spinning from a solution[6].This can be attributed to the worse packing of the CNT fibers in this study. However, the thermal conductivity is much different from both the theoretical and experimental values for individual CNT. Notably, the thermal conductivity of individual CNT can reach 6600 $WK^{-1}m^{-1}$ in theory[19], while the experimental thermal conductivity values range from 1400 to 3500 $WK^{-1}m^{-1}$[15,20,21]. This is probably because the interface between the adjacent CNTs plays a dominant role in the thermal conductivity of any assembly of CNTs. The contact between CNTs provides the defects within the fiber that enhance phonon scattering and in turn reduce the phonon mean free path.

2) Temperature dependence of thermal conductivity of CNT fiber

The thermal conductivity of the CNT fibers was measured at different temperatures from 76 to 320K. The thermal conductivity values versus temperature are plotted in Figure 2. The thermal conductivity of the as-spun fiber first increased from 41.4 $WK^{-1}m^{-1}$ at 80 K to 85.5 $WK^{-1}m^{-1}$ at 225K and then decreased to74.1 $WK^{-1}m^{-1}$ at 320 K; thus, the crossover temperature was observed at 225K. This temperature dependence of the as-spun fiber is different from those of the CNT fibers from array[17] and a solution[18].In both cases, the thermal conductivity increases with temperature, and no crossover temperature was observed in the tested temperature range. However, the temperature dependence of the as-spun fiber is similar to that of the fiber synthesized by improved

spinning from a solution[6], where the thermal conductivity also first increased and then decreased with a crossover temperature at 220 K. In general, two factors contribute to the thermal conductivity of CNT fibers: the thermal conductivity of CNTs themselves and the thermal conductivity due to the contact between the adjacent CNTs. The thermal conductivity due to the contact between the adjacent CNTs should not change with temperature because the contact itself has no relation with the temperature. Therefore, the temperature dependence of the thermal conductivity of the CNT fibers can be attributed to the individual CNTs themselves. This view is supported in the literature[20], where the thermal conductivity of individual CNTs also first increased and then decreased in a range of temperature. Moreover, the crossover temperature was at ~270K,consistent Figure 2 Temperature dependence of thermal conductivity of the as-spun fiber with the value (225K) of the CNT fibers in this study.

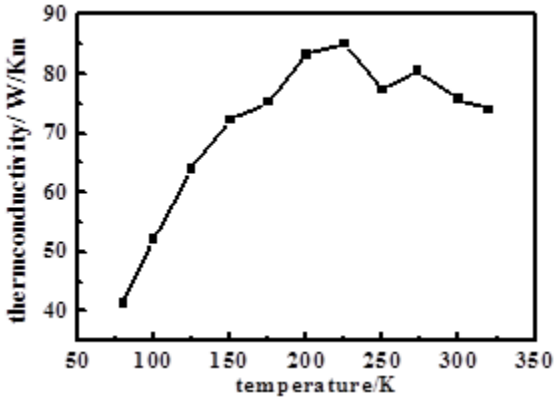

Figure 2 Temperature dependence of thermal conductivity of the as-spun fiber

3)Thermal conductivity of CNT fibers after HCl treatment

The CNT fibers were treated with HCl, and the temperature dependence of the thermal conductivity was measured as shown in Figure 3. The thermal conductivity of the HCl-treated CNT fibers first increased and then decreased with temperature, similar to the as-spun fiber. However, the HCl-treated CNT fibers exhibited a higher thermal conductivity throughout the temperature range than the as-spun fiber. In particular, the HCl-treated CNT fibers had a thermal conductivity of 138 $WK^{-1}m^{-1}$ at room temperature, an increase by 84% compared to the as-spun fiber. The result indicates that HCl can significantly enhance the thermal conductivity of CNT fibers. The reason is not clear. This is probably because HCl removes the Fe particles, the residual catalyst, formed during the synthesis of CNT fibers; therefore, the phonon scattering caused by the Fe particles was reduced, thus increasing the thermal conductivity.

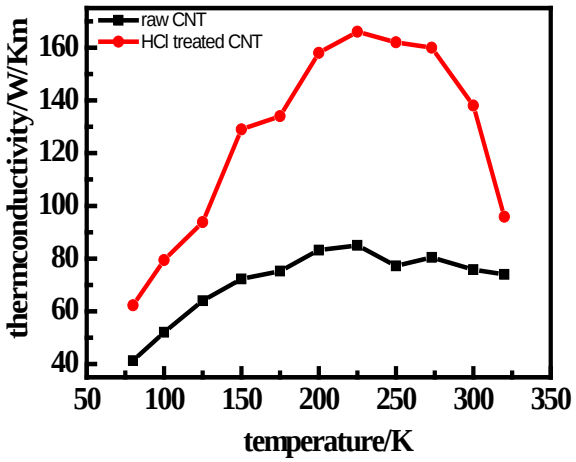

Figure 3 Temperature dependence of the HCl-treated CNT fibers and comparison with the profile of the as-spun fiber

Conclusion

The CNT fibers from CVD synthesis process consist of stacked CNT bundles and have a thermal conductivity of 75.9 $WK^{-1}m^{-1}$at room temperature, much lower than that of individual

CNTs. This is due to the contact between CNTs. The temperature dependence of the thermal conductivity of the CNT fibers first increased and then decreased with temperature; this behavior can originate from the individual CNT. The thermal conductivity of the CNT fibers could be enhanced by treating with HCl, probably because HCl partially removed the residual Fe particles.

Acknowledgement

The author is grateful to Professor Li Ya-Li at Tianjin University for providing CNT fibers from CVD synthesis process and Dr. Wang JianLi at Tsinghua University for his help with thermal measurements.

References

[1] Yu MF, Files BS, Arepalli S, Ruoff RS. Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties. Phys Rev Lett 2000;84(24): 5552–5555.
[2] Collins PG, and Avouris P, Nanotubes for electronics. Scientific American 2000;283(6): 62.
[3] Balandin AA, Thermal properties of graphene and nanostructured carbon materials. Nat Mater 2011;10(8): 569–581.
[4] Lima MD, li N, Endrade MJ, et al. Electrically, chemically, and photonically powered torsional and tensile actuation of hybrid carbon nanotube yarn muscles. Science 2012;338:928–932.
[5] Dalton AB, Collins S, Munoz E, et al. Super-tough carbon-nanotube fibres.Nature2003; 423(6941): 703.
[6] Behabtu N, young CC, Tsentalovich DE, et al. Strong, light, multifunctional fibers of carbon nanotubes with ultrahigh conductivity. Science 2013;339:182–186.
[7] Zu M, Li QW, Wang GJ,etal. Carbon nanotube fiber based stretchable conductor. Adv Func Mater 2013;23:789–793.
[8] Koziol K, Vilatela J, moisala A, et al. High-Performance carbon nanotube fiber. Science 2007;318:1892–1895.
[9] Ericson LM, Fan H, Peng HQ, et al. Macroscopic, neat, single-walled carbon nanotube fibers. Science 2004;305(5689): 1447–1450.
[10] Zhang M, Atkinson KR, Baughman RH, Multifunctional carbon nanotube yarns by downsizing an ancient technology. Science 2004;306(5700): 1358–1361.
[11] Li YL, Kinloch IA, and Windle AH, Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis. Science 2004; 304(5668): 276–278.
[12] Zhong XH, Li YL, Liu YK, et al. Continuous multilayered carbon nanotube yarns. Adv Mater 2010;22(6): 692–696.
[13] Ma WJ, Liu LQ, Yang R, et al. Monitoring a micromechanical process in macroscale carbon nanotube films and fibers. Adv Mater 2009;21(5): 603–608.
[14] Wang JL, Gu M, Ma WG, Zhang X, et al. Temperature dependence of the thermal conductivity of individual pitch-derived carbon fibers. New Carbon Mater 2008;23(3):259–263.
[15] Fujii M. Zhang X. Xie HQ, Ago H, Takahashi K etal. Measuring the Thermal Conductivity of a Single Carbon Nanotube. Phys Rev Lett 2005;(95):065502–065504.
[16] Li QW, Li Y, Zhang XF, Chikkannaavar SB et al. Structure-dependent electrical properties of carbon nanotube fibers. Adv Mater 2007;19(20): 3358–3363.
[17]Aliev AE, Guthy C, Zhang M, Fang SL etal. Thermal transport in MWCNT sheets and yarns. Carbon 2007;45:2880–2888.
[18]Zhou W, Vavro J, Guthy C Winey KI etal. Single wall Carbon nanotube fiber extruded from super-acid suspensions: preferred orientation, electrical, and thermal transport. Journal of Applied Physics,2004,95(2): 645–655.
[19] Berber S, Kwon YK, Tomank D. Unusually high thermal conductivity of carbon nanotubes. Phys Rev Lett 2000;84(20):4613–4616.
[20]Pop E, Mann D, Wang Q, Goodson K, etal. Thermal conductance of an individual single-wall carbon nanotube above room temperature. Nano Lett 2006;6(1):95–100.
[21] Li QW, Liu CH, Wang XS, Fan SS. Measuring the thermal conductivity of individual carbon nanotubes by the Raman shift method. Nanotech 2009,20(14):572.