Thermal transport in carbon materials: Effect of low temperature and nanostructures

Yangsu Xie
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd
Part of the Engineering Commons

Recommended Citation
https://lib.dr.iastate.edu/etd/16533

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Thermal transport in carbon materials: Effect of low temperature and nanostructures

by

Yangsu Xie

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Mechanical Engineering

Program of Study Committee:
Xinwei Wang, Major professor
Nicole Hashemi
Hui Hu
Gap-Yong Kim
Yue Wu

Iowa State University
Ames, Iowa
2017

Copyright © Yangsu Xie, 2017. All rights reserved.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>ix</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Phonon as the Heat Carriers in Nanostructured Carbon Materials</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Thermal Conductivity and Challenges</td>
<td>3</td>
</tr>
<tr>
<td>1.3 New Nanostructured Carbon Materials and The Unique Properties</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Scope of Present Work</td>
<td>11</td>
</tr>
<tr>
<td>CHAPTER 2 THE THERMAL REFFUSIVITY AND PHONON SCATTERING THEORY</td>
<td>13</td>
</tr>
<tr>
<td>CHAPTER 3 IDEAL THERMAL CONDUCTIVITY OF GRAPHENE FOAM</td>
<td>17</td>
</tr>
<tr>
<td>3.1 Sample Characterization</td>
<td>17</td>
</tr>
<tr>
<td>3.2 Experimental Details of TET Technique and Cryogenic System</td>
<td>20</td>
</tr>
<tr>
<td>3.3 Results and Discussion</td>
<td>24</td>
</tr>
<tr>
<td>3.3.1 Thermal diffusivity of graphene foam</td>
<td>24</td>
</tr>
<tr>
<td>3.3.2 Thermal reffusivity model for determining the defect levels</td>
<td>27</td>
</tr>
<tr>
<td>3.3.3 Ideal thermal conductivity of graphene</td>
<td>30</td>
</tr>
<tr>
<td>CHAPTER 4 INTERFACE-MEDIATED EXTREMELY LOW THERMAL CONDUCTIVITY OF GRAPHENE AEROGEL</td>
<td>34</td>
</tr>
<tr>
<td>4.1 Sample Synthesizing Method and Material Characterization</td>
<td>35</td>
</tr>
<tr>
<td>4.1.1 Synthesis of graphene aerogel using EDA based chemical reduction</td>
<td>35</td>
</tr>
<tr>
<td>4.1.2 Structure characterization</td>
<td>36</td>
</tr>
<tr>
<td>4.2 Thermal Characterization Method</td>
<td>41</td>
</tr>
<tr>
<td>4.2.1 The transient electro-thermal technique</td>
<td>41</td>
</tr>
<tr>
<td>4.2.2 The steady-state electro-thermal technique</td>
<td>44</td>
</tr>
<tr>
<td>4.3 Results and Discussion</td>
<td>45</td>
</tr>
<tr>
<td>4.3.1 Extremely low thermal conductivity</td>
<td>45</td>
</tr>
<tr>
<td>4.3.2 Thermal diffusivity and reffusivity of graphene aerogel</td>
<td>50</td>
</tr>
<tr>
<td>CHAPTER 5 SWITCH ON THE HIGH THERMAL CONDUCTIVITY OF GRAPHENE PAPER</td>
<td>56</td>
</tr>
<tr>
<td>5.1 Graphene Paper Structure</td>
<td>56</td>
</tr>
<tr>
<td>5.2 Switch On: Analyzed Using Thermal Diffusivity and Reffusivity</td>
<td>59</td>
</tr>
</tbody>
</table>
5.2.1 Thermal diffusivity switch-on observation and physics ........................................ 59
5.2.2 Structure evolution revealed by thermal diffusivity ............................................ 69
5.3 Thermal Conductivity: Switch-On........................................................................... 71
5.4 Comparison Study Against Graphene Oxide and Partly Reduced Graphene Paper 78
5.4.1 Thermal conductivity comparison ...................................................................... 78
5.4.2 Thermal diffusivity and in-plane domain size .................................................... 79
5.4.3 Structure study and physics interpretation ............................................................ 80

CHAPTER 6 CURRENT-INDUCED THERMAL ANNEALING ON IMPROVING THE
STRUCTURE AND THERMAL CONDUCTIVITY OF CNT BUNDLES ............. 85

6.1 Synthesis and Structure Characterization ............................................................... 85
6.2 Thermal Characterization and Annealing Method ................................................... 90
6.3 CITA Results And Discussion .............................................................................. 93
6.3.1 The reduced electrical resistance ....................................................................... 93
6.3.2 The enhanced effective thermal diffusivity and phonon scattering principle ...... 97
6.3.3 The unevenly distributed annealing effect along length direction ....................... 100
6.4 Thermal Conductivity Evaluation By Numerical Calculation .............................. 103
6.4.1 The averaged and localized annealing effect ...................................................... 103
6.4.2 The intrinsic thermal diffusivity and conductivity of graphite walls in CNT
bundles after annealing ................................................................................................. 107

CHAPTER 7 CONCLUSION AND FUTURE WORK ............................................. 111

7.1 Conclusion ............................................................................................................. 111
7.1.1 Conclusion on graphene foam ........................................................................... 111
7.1.2 Conclusion on graphene aerogel ....................................................................... 112
7.1.3 Conclusion on graphene paper .......................................................................... 113
7.1.4 Conclusion on CNT bundles ............................................................................. 114
7.2 Future Work .......................................................................................................... 115
7.2.1 Scope of future work ......................................................................................... 115
7.2.2 Parallel heat transfer in CNT bundles ............................................................... 115
7.2.3 Graphene based super-insulation material ....................................................... 118

REFERENCES .......................................................................................................... 121
LIST OF FIGURES

Figure 1.1.1 phonon dispersion relation of the graphene sheet. The solid lines show the results of the ab initio force constant approach for the soft potential. [9] The open squares represent the reflection electron-energy-loss spectroscopy data of Oshima et al. [12] and the solid circles correspond to the high-resolution electron-energy-loss spectroscopy data of Siebentritt et al. [13] ........................................................................................ 3

Figure 3.1.1 SEM, Raman and XRD spectra images of the GF sample studied in this work. (a) and (b): SEM images of GF cellular structure and wall structure respectively. (c): Raman spectrum of the GF sample. Raman condition: CW laser at 532 nm wavelength, 100× lens, and 10s integration time. I_G/I_2D is the ratio of integrated intensity of G band to that of 2D band. The value of I_G/I_2D indicates the GF is composed of about 4-layer graphene. (d): XRD spectrum of the GF sample. The fitting result reveals a pronounced peak at 26.6°, yielding an interlayer spacing of 3.35 Å. (e) and (f): X-ray photoelectron spectra of GF. (e) the C1s spectrum, indicating different bonds for carbon atoms in the sample. (f) the N1s spectrum, suggesting the presence of NH-C=O functional group at the surface of the samples. ............................................................................................................. 19

Figure 3.2.1 (a) Schematic of the experiment setup and data collecting for the TET technique. The whole sample base is mounted on the cold head of the CCR system. A current source supplies the step current and an oscilloscope records the voltage evolution for the GF sample. (b): Microscope image of the GF sample (sample 1) suspended between two gold-coated silicon electrodes. (c): The raw voltage against time data collected by the oscilloscope for sample 1 at environmental temperature of 195 K. The inset demonstrates the linear relationship between resistance and temperature for sample 1 from 295 K to 10 K. (d): Theoretical fitting of the normalized temperature rise for sample 1 at different environmental temperatures: 295 K, 195 K, 10 K. Dots represent the experimental data, and solid lines show the fitting result........................................................................................................ 21

Figure 3.3.1 The measured thermal diffusivity α_real against temperature T for the three GF samples and the resulting real thermal diffusivity of GF (α_real). α_real follows a linear increase with the decreasing temperature from 299 K to 104 K. Under 104 K, α_real tends to be stable with a slight decrease from 43 K to 17 K. The top right inset is the measured thermal diffusivity against length square (L^2) for the three GF samples at temperature of 54 K, to show one of the fitting process for determining the real thermal diffusivity of the sample. Triangles are for the experimental data, and the solid line represents the linear fitting. ........................................................................................................ 25

Figure 3.3.2 The intrinsic thermal diffusivity of graphene changes with temperature. (b) Thermal diffusivity of graphene compared with (c) the thermal diffusivity of other literature values for pyrolytic graphite. [87, 90, 91] The solid symbols are the
experiment data, and the solid lines show the theoretical fitting of the data. As temperature approaches zero, the intersection point of the fitting line and vertical axis is taken as the residual thermal reffusivity (\( \Theta_0 \)).

Figure 3.3.3 (a) The ideal thermal diffusivity of graphene. (b) The experimental data for specific heat of graphite [94]. (c) The ideal thermal conductivity of graphene (\( \kappa_{\text{ideal}} \)) against temperature compared with that we obtained from other literature data of pyrolytic graphite.[87, 90, 91] The data inside the orange rectangle (below 80 K) is less reliable due to the error of \( \alpha_G \) at low temperatures and the undecided difference of specific heat between graphene and graphite.

Figure 4.1.1 (a) and (b): SEM images of GAs cellular and wall structure. (c): Raman spectrum. (d): XRD spectrum. (e) X-ray photoelectron spectra of GA. (f) The XPS C1s spectrum, indicating different bonds for carbon atoms in the sample. (g) The XPS N1s spectrum, suggesting the presence of the pyridinic (N1), pyrolic and quaternary nitrogen (N2), and pyridine-N-oxide (N3) at the sample surface. (h) A GA on a dandelion. (i) The compressing test with a 10-gram weight.

Figure 4.2.1 (a) The schematic of the experiment set up. (b) The normalized temperature profiles for sample 1-1 at different temperatures: 295 K, 95 K and 10 K. The symbols are experimental data and the lines are the theoretical fittings. (c) The first derivative of electrical resistance against temperature profiles obtained by differentiating R-T curve. Some errors are less than \( \pm 2\% \), so these error bars are not very visible. (d) The measured thermal conductivity of the five GA samples in this work. The inset shows one of the examples for the linear fitting (for group 1 at real temperature of 298.6 K) to obtain its real thermal conductivity.

Figure 4.3.1 (a) The thermal conductivity of the two groups of GAs. The inset shows the \( \kappa \) of pyrolytic graphite for comparison. (b) The intrinsic thermal conductivity of GAs by taking out the porosity effect. (c) The specific heat of the two GA samples. The literature data for graphite and amorphous carbon are also plotted for comparison. The data inside the yellow rectangular is less reliable due to the large data fluctuation at very low temperature. (d) The schematic drawing that illustrates the heat transfer process inside GA. At the interfaces of the flakes, intensive interface-mediated phonon scatterings occur.

Figure 4.3.2 (a) The thermal diffusivity of the two groups of GAs compared with that of graphene foam (GF) and pyrolytic graphite. (b) The electrical resistivity against temperature for the five GA samples. The linear \( \rho_e -T \) data of graphene foam is also plotted at the bottom panel for comparison.

Figure 5.1.1 Morphology and structure characterization of GP sample. (a) and (b): SEM images. The inset shows an AFM topology image. \( \delta = 0.23 \) nm is the average height variation of the surface along the blue line. (c) The Raman spectrum. The inset shows the XRD spectrum. (d) x-ray photoelectron spectra. The inset shows the XPS F 1s spectrum. (e) The XPS C 1s spectrum, indicating different bonds for
carbon atoms in GP sample. (f) The XPS O 1s spectrum, suggesting the residual oxygen-containing functional groups. ................................................................. 58

Figure 5.2.1 (a) The schematic of four-probe TET experiment and sample set up in the cold jacket of CCR system. Four-probe I - V measurement is employed in the experiment to avoid the influence of contact resistance. (b)-(c) The evolution of voltage against time for S2 at different temperatures. As temperature goes down, the profile transforms from pure voltage increasing to pure voltage decreasing pattern. ................................................................. 61

Figure 5.2.2 (a) The thermal diffusivity of GP. (b) The resistance against temperature profile of GP. (c) The schematic drawing illustrates the reversible structure separation process. (d) The thermal diffusivity of GP after switch-on. (e) The thermal diffusivity of GP before switch-on. ................................................................. 63

Figure 5.3.1 (a) The experimental specific heat data of graphite and the calculated specific heat data of single-layered graphene from literature for comparison.[8] This experimental data of graphite is used for calculating the thermal conductivity of GP. (b) The switch-on of the thermal conductivity of two GP samples. At low temperatures, κ presents a T 1.5 trend as shown by the solid black line in the figure. The literatures reported thermal conductivity of graphene is presented in the figure to help the readers better understand the level of our thermal conductivity. The thermal conductivity of our GP should be lower than that of graphene due to the intrinsic structure phonon scattering. The black solid circles, solid square and hollow triangle are the literatures reported κ for suspended mechanically exfoliated mono-layered graphene.[20, 136] The black solid upward triangle and downward triangle are literature κ of suspended isotopically pure 12C (0.01% 13C) graphene and 99.2% 13C graphene respectively.[7] The orange solid circle present reported κ of supported mono-layered graphene.[17, 137] The orange triangles are κ of supported three-layered graphene.[50] ...................................................................................... 73

Figure 5.4.1 The thermal conductivity of (a) PRGP and (b) GOP. The thermal diffusivity of (c) PRGP and (d) GOP. The measurement uncertainty is about ±10%. The error bar is omitted for clarity purpose. ................................................................. 79

Figure 5.4.2 SEM images of (a) PRGP and (b) GOP. (c) XRD spectrum of PRGP and GOP. XPS survey of (d) PRGP and (e) GOP. (f) The Raman spectrum of PRGP and GOP, indicating the presence of defects and impurities in the samples. ........... 82

Figure 6.1.1 Morphology and structure characterization of CNT bundles. (a)-(b) SEM images of the CNT bundles under ×500 and ×15000 magnifications. (c)-(d) TEM images. The yellow arrows indicate the amorphous region. (e) Raman spectrum indicating three pronounced peaks. (f) XRD spectrum. (g) The X-ray photoelectron spectra. In the insets are the deconvoluted spectrums for O 1s and C 1s. ................. 88

Figure 6.2.1 Experimental set-up and principle of the transient electro-thermal (TET) technique for in-situ thermal characterization. (a) A digital camera photo of the
MWCNT bundles array. (b) A microscopy image of a suspended CNT bundle sample. (c) A schematic of experimental set-up. (d) Selected normalized temperature profiles of TET of S1 after different currents annealing. The dots are raw data and lines are fitting curves from TET model. The corresponding thermal diffusivity values ($\alpha$) are also presented in the figures.

Figure 6.3.1 The resistance profiles of S3 during the large current annealing from 120 mA to 1250 mA. Two-stage evolution is observed.

Figure 6.3.2 The experimental result of large current annealing effect. (a) The electrical resistance against annealing current and (b) effective thermal diffusivity of CNT bundles against annealing current. (c) The thermal diffusivity and electrical resistance of S4 at low temperatures without annealing.

Figure 6.3.3 The morphology and characterization of the structure after CITA. (a)-(b) The SEM images of the breaking point due to the high temperature annealing and melting under low to high magnifications. The insets in figure (a) is the SEM and Raman signal of the amorphous carbon film sputtered on the glass substrate from the molten CNT bundle. (c) Change of the Raman signal with the distance from the breaking point (DFB). The Lorentz fitting result of the Raman signals, including (d) the ratio of intensity of the D peak to the G peak. (e) The Raman shift of G peak. (f) The full width at half maximum (FWHM) of G peak.

Figure 6.4.1 (a) The effective thermal diffusivity of CNT bundles against the averaged annealing temperature. It shows an averaged effect of annealing. (b) Right y axis: the thermal conductivity of the center point of sample against the annealing temperature at center point. It shows the localized annealing effect at the center point. Left y axis: calculated intrinsic thermal conductivity of graphite walls ($\kappa_{\text{intr}}$) against the localized annealing temperature. The orange rectangular shows the fast annealing zone, within which $\kappa_{\text{intr}}$ has the highest increasing rate with the increased temperature. The green rectangular indicates a saturated annealing state of S1.

Figure 7.2.1 (a) A schematic of the root growth mechanism illustrates that the initially straight CNTs develop curved morphologies in latter stages of growth. (b) The schematic of parallel thermal transport path in CNT bundles. (c) One of the TET signals from parallel heat transport in CNT bundles sample.

Figure 7.2.2 A schematic of the graphene based super-insulation material. The outer layer material will be graphene paper (GP) with high in-plane thermal conductivity and the interior material will be graphene aerogel (GA) with lightweight and extremely low thermal conductivity.
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1</td>
<td>Details of GF samples characterized in this work.</td>
<td>25</td>
</tr>
<tr>
<td>Table 2</td>
<td>Details of GA samples characterized</td>
<td>43</td>
</tr>
<tr>
<td>Table 3</td>
<td>Details of the GP, GOP and PRGP samples measured in this work.</td>
<td>60</td>
</tr>
<tr>
<td>Table 4</td>
<td>The details of the measured CNT bundle samples</td>
<td>90</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

Foremost, I would particularly like to thank my major advisor, Dr. Xinwei Wang, for his excellent guidance not only in research but also in life. He always provided me with valuable advices and helped me whenever I encountered problems in my projects, and taught me patiently with his good knowledge and serious research attitude. His guidance and encouragement will continue to motivate and inspire me in my future life. I would also like to express my sincere gratitude to my co-advisor Dr. Nicole N Hashemi for her excellent guidance, and for her good advice and warm encouragement on my research. I am grateful to Dr. Hui Hu, Dr. Gap-Yong Kim and Dr. Yue Wu for being my committee members and giving me helpful comments on my study. I appreciate the support from all my committee members through all these years. I would also like to thank my undergraduate advisor Dr. Haisheng Fang for always giving me valuable advice and support on my research and career choice.

In addition, I would like to thank all my colleagues, Zaoli Xu, Shen Xu, Huan Lin, Chong Li, Hongchao Wang, Zhe Cheng, Jing Liu, Tianyu Wang, Bowen Zhu, Pengyu Yuan, Ridong Wang, Meng Han, Chris Reilly, Mahdi Ramezani, Chenghao Deng, and Wangyujue Hong for their help and friendship. I give my best wishes to all of them for their bright future. Also I thank the department faculty and staff for making my time at Iowa State University such a memorable and wonderful experience.

I want to express my deepest gratitude to my dear parents, my fiancé Boyan, my sister, and other families for unconditionally loving me, patiently listening to me, and wholeheartedly supporting me, and to all my friends in the US, in China, and in Europe for always being there
for me to share my happiness and hard times. Without you, I would not be able to accomplish this work.

I am grateful to the support from China Scholarship Council. Support of this work by the Iowa Energy Center, Army Research Office, Office of Naval Research, the National Science Foundation and the Department of Energy is also gratefully acknowledged.
ABSTRACT

To realize their potential applications in electronic, energy, environmental and medical devices, new nanostructured carbon materials have been synthesized and studied. In this work, the excellent thermal properties of four typical new nanostructured carbon materials including graphene foam, graphene aerogels, graphene paper with different reduction level, and carbon nanotube bundles have been studied in detail by using phonon scattering mechanisms analysis. The effect of low temperature, different nanostructures and thermal strain are the focus.

Specifically, for the first time, the defect level in graphene foam is identified by evaluating the thermal reffusivity at the 0 K limit. The ideal thermal diffusivity and conductivity (κ) of graphene presented in the 3D graphene foam structure in the range of 33-299 K is also reported and discussed. We synthesized ultra-light graphene aerogels material, although its density is about two times higher than air, its κ at room temperature is about 80% lower than that of air. At low temperatures, its κ even reaches a lower level of $2 \times 10^{-4} - 4 \times 10^{-4}$ W m$^{-1}$ K$^{-1}$, which is the lowest κ ever reported. The mechanism of this extremely low κ is explored by studying the temperature variation of κ, α, and specific heat ($c_p$) from RT to as low as 10.4 K. A high κ switch-on phenomenon in high-purity graphene paper when its temperature is reduced from RT to 10 K is investigated and reported. The switch-on behavior is attributed to the thermal expansion mismatch among pure graphene flakes and the impurities embedded flakes. By conducting comparison studies with pyrolytic graphite, graphene oxide paper and partly-reduced graphene paper, the whole physical pictures are illustrated clearly. The sequential process of current-induced thermal annealing on improving the structure, electrical and thermal conductivity of CVD grown CNTs is studied for the first time. By
combining large current annealing in vacuum environment and in-situ afterwards transient electro-thermal characterization, the dynamic electrical and thermal properties of the same sample annealed at different temperatures are obtained. The future work about the parallel heat transport in the carbon nanotube bundles and a super-insulation material is also discussed at the end of this work.
CHAPTER 1 INTRODUCTION

1.1 Phonon as the Heat Carriers in Nanostructured Carbon Materials

As with the discovery and rise of new carbon allotropes such as graphene and carbon nanotubes (CNTs), rapid growth of interest has been attracted by the fascinating properties of these new materials and their derivatives. Graphene, a form of carbon with monolayer honeycomb lattice, has been a focus of extensive investigations since its discovery in 2004. It has numerous intriguing properties, such as extremely high thermal conductivity,[1] large specific surface area,[2] quantum electronic transport,[3] a tunable band gap,[4] extremely high mobility.[5] To fulfil the promising applications in various areas, different graphene based materials with excellent properties have been synthesized and studied. Understanding the fundamental physics and underlying mechanism controlling those amazing properties of the graphene based materials paves the way for their future applications.

In solid materials heat is carried by acoustic phonons (ion-core vibrations in a crystal lattice) and electrons.[6] In metals, contribution from electrons is dominant owing to large concentrations of free carriers. In carbon materials, however, the strong covalent sp$^2$ bonding leads to high values of in-plane group velocities and low crystal lattice unharmonicity for in-plane vibrations. Consequently, the main heat carriers in carbon materials are usually acoustic phonons.[7] When the temperature of a supported-graphene changes, phonon population frequencies and phonon dispersion change, which contributes to the thermal properties variation with temperature. Graphene has three acoustic and three optical phonon modes, in which longitudinal (L) modes correspond to the atomic displacement along the wave propagation direction, transverse (T) modes are along in-plane but perpendicular to the wave propagation direction, and flexural (Z) modes correspond to out-of-plane atomic
displacement.[8] The phonon dispersion relation between the phonon energy (or frequency) and the phonon wave vector of graphene sheet from Dubay et al.[9] is shown in figure 1.1.1. Phonon group velocity can be calculated from this dispersion, which gives an average groups velocity of $9171 \text{ m/s}$ for graphene.[10] Specific heat ($c_p$) is defined by the phonon density of states, which leads to different temperature dependence for 1D, 2D and 3D structure. [6] To date, there is no direct experimental measurement of the specific heat of graphene. $c_p$ of graphene increases with the increasing temperature. At low temperature, it is expected that $c_p$ of isolated graphene has a linear behavior with temperature when quadratic ZA modes dominate, subsequently changes to a $\sim T^2$ relationship due to the effect of LA and TA. Above $100 \text{ K}$, $c_p$ of graphene is expected to be similar to that of graphite.[8] At high temperatures, $c_p$ becomes nearly constant when approaching the Debye temperature. For graphene, the Debye temperature is calculated to be about $2100 \text{ K}$. [8]

In ballistic, scattering-free phonon propagation, where sample size is smaller than the mean free path of phonon ($l_s$), the thermal conductivity of graphene is proportional to the sample length. However, in graphene materials where sample size is much larger than $l_s$, phonons can encounter various kinds of scattering mechanisms during propagation. If phonons are only scattered by other phonons, the resulting thermal conductivity is the intrinsic thermal conductivity of graphene. The intrinsic $\kappa$ is only limited by the crystal-lattice anharmonicity, which can be described by the Umklapp scattering rates. In real carbon nanostructures, the phonons propagation is not only limited by phonon-phonon interaction, but also mainly by scattering from defects, boundaries, rough edges and substrates coupling. The resulting $\kappa$ is expected to be lower than the intrinsic thermal conductivity, called extrinsic thermal conductivity. Temperature has a significant role in determining the phonon population and the
intensity of phonon scattering. Another factor needed to be considered is the thermal strain induced by the thermal expansion mismatch between the substrate and graphene. Kuang et al. investigated the effect of tensile strain on the enhancement of the intrinsic $\kappa$ of multi-layered graphene. From their calculation, the increasing tensile strain leads to decreased heat capacity and increased lifetime of flexural phonons, which could enhance the intrinsic $\kappa$ for multi-layered graphene.[11]

Figure 1.1.1 phonon dispersion relation of the graphene sheet. The solid lines show the results of the ab initio force constant approach for the soft potential.[9] The open squares represent the reflection electron-energy-loss spectroscopy data of Oshima et al.[12] and the solid circles correspond to the high-resolution electron-energy-loss spectroscopy data of Siebentritt et al.[13]

1.2 Thermal Conductivity and Challenges

The highest thermal conductivity ($\kappa$) is of significant importance for graphene’s applications. Different approaches have been developed to characterize $\kappa$ of suspended and supported graphene.
For suspended graphene, a large thermal conductivity from 1500 to 5000 W m$^{-1}$ K$^{-1}$ was obtained experimentally at near room temperature (RT).[14-20] The first experimental measurement was conducted at University of California Riverside[14] using a “noncontact technique based on micro-Raman spectroscopy”. In their experiment, an extremely high thermal conductivity of suspended single-layer graphene was found in a range of $(4.84 \pm 0.44) \times 10^3$ to $(5.30 \pm 0.48) \times 10^3$ W mK$^{-1}$ at RT. This value exceeds the measured thermal conductivity of other carbon materials, such as CNTs and diamond. As for isotopically pure $^{12}$C graphene, the in-plane thermal conductivity was determined higher than 4000 W mK$^{-1}$ at 320 K by Chen et al. using optothermal Raman technique.[20] Cai et al. obtained $\kappa$ of single layered graphene (SLG) grown by chemical vapor deposition. For suspended samples, $\kappa$ exceeded $(2500+1100/-1050)$ W m$^{-1}$ K$^{-1}$ at near 350 K and $(1400+500/-480)$ W m$^{-1}$ K$^{-1}$ at about 500 K.[17] For the supported graphene, however, $\kappa$ is reduced to a much lower level owing to the phonons leaking across the graphene-support interface and strong interface scattering of flexural modes.[21] In Cai et al.’s work, when graphene sample was supported on Au-coated SiNx, $\kappa$ was determined as $(370 + 650/-320)$ W m$^{-1}$ K$^{-1}$ at RT, which is considerably lower due to the substrate effect.[17] Seol et al. investigated $\kappa$ of mono-layered graphene supported on a silicon dioxide. The $\kappa$ was measured to be about 600 W m$^{-1}$ K$^{-1}$ near RT,[21] which is 60%-88% lower compared to the $\kappa$ of suspended graphene. Jang et al. measured $\kappa$ of graphene and ultrathin graphite encased within silicon dioxide to be lower than 160 W m$^{-1}$ K$^{-1}$ at 310 K.[22] The top layer oxide deposition resulted in an extra 64% and 38% reduction in $\kappa$ of three-layered and four-layered graphene flakes compared to supported samples. Pettes et al. studied the influence of polymeric residue on $\kappa$ of bilayer graphene. The $\kappa$ was about 600 W m$^{-1}$ K$^{-1}$ and presented a $T^{1.5}$ behavior from 50 to 125 K.[23]
Therefore, substrate or impurities deposition can suppress the $\kappa$ of graphene to a great extent. If the substrate effect is controllable, a thermal switch using graphene will be feasible. At a predetermined temperature, heat will transfer with an extremely high rate from a heat source to a heat sink. In this work, the heat switch utilizing the substrate effect of graphene is proposed by studying the switch-on behavior of high purity graphene paper.

Among the above experimental results, large discrepancy exists. So far the value of measured $\kappa$ of graphene ranges from dozens to thousands of W mK$^{-1}$. Besides the substrate effect which can be controlled by suspending or supporting graphene samples, other factors also contribute to the discrepancy: mainly the sample defects, different isotopes composition, varying grain size and orientation, different temperature and uncertainties in the measurements. Some factors can be controlled and compared. However, the defect level in the samples is extremely difficult to measure quantitatively. Defects including charged impurities,[24] functionalized groups,[25] Stone–Wales defect, vacancy defect, stains, etc. , are complex and random, hard to interpret in detail. Obtaining the ideal thermal conductivity of different graphene samples experimentally remains challenging.

Given the difficulty of the experiment, theoretical modeling and simulation play an important role for investigating the ideal thermal properties of graphene. Nika et al. calculated the thermal conductivity of graphene using valence-force field method. The obtained thermal conductivity of single-layer graphene ranges from 2000 to 5000 W mK$^{-1}$ depending on different flake sizes, edges roughness and defect concentration.[26] Zhang et al. characterized the thermo-physical properties of 2D graphene nanoribbons using the transient molecular dynamics technique. Quantum correction was applied in temperature calculations, a thermal conductivity of 149 W m$^{-1}$ K$^{-1}$ at 692.3 K and 317 W m$^{-1}$ K$^{-1}$ at 300.6 K was obtained for the
1.99-nm-wide GNR with infinite length.[27] Other results using MD simulations,[28] Boltzmann transport equation[29] and Ballistic theory[30] predicted the ideal thermal conductivity. It was found that without defects scattering, $\kappa$ spans a range of 2400 to 10000 W mK$^{-1}$ depending on different graphene flakes sizes. For the purpose of predict and analyze the thermal performance of different graphene based materials, it is significantly important to better understand and characterize the defect levels of different graphene materials. In this work, the defect level of different graphene based materials will be analyzed quantitatively by using a novel physical model named thermal reffusivity model.

Besides the fascinating ultra-high thermal conductivity of graphene, the highest mechanical strength to weight ratio is another promising aspect for graphene’s potential application. Graphene has an intrinsic tensile strength of 130 GPa and young’s modulus of 1 TPa.[31] To utilize this excellent property, graphene and its derivatives are widely used as basic building block of other important 3D bulk materials. Graphene aerogel (GA) with high porosity and randomly oriented microstructure is synthesized and studied. In spite of the extremely high thermal conductivity of its building block, GA with ultra-high porosity is reported to have low thermal conductivity and strong mechanical strength.

Aerogels have always been highly insulating materials with a thermal conductivity lower than still air.[32] Before GA, the most typical aerogel is silica aerogel, which is known as the best insulator so far. Compared to its peers, GA is expected to be a more outstanding thermal insulating material considering its high porosity, flexible and strong mechanical properties and the controllable functional groups at the surfaces. Fan et al. investigated the impact of thermal annealing on the thermal conductivity of GA. Their GA with a density of 14.1-52.4 mg·cm$^{-3}$ was synthesized by a chemical reduction method and dried with
supercritical CO\textsubscript{2}. The value for the measured thermal conductivity at RT was 0.12-0.36 W·m\textsuperscript{-1}·K\textsuperscript{-1},\cite{33} which is remarkably low compared with the ultrahigh thermal conductivity of graphene.\cite{14} Another research group studied the effect of different reducing agents and thermal annealing on the properties of GAs. Their GAs with density of 16-41 kg·m\textsuperscript{-3} have a thermal conductivity of about 0.1 W·m\textsuperscript{-1}·K\textsuperscript{-1}.\cite{34} However, these numbers still show little advantage over other aerogels reviewed above in terms of insulation. Wicklein et al. synthesized a strongly anisotropic foams by freeze-casting suspensions of cellulose nanofibers, graphene oxide and sepiolite nanorods. The material is lightweight (7.5 kg·m\textsuperscript{-3}), super-insulating (with a thermal conductivity of 15 mW·m\textsuperscript{-1}·K\textsuperscript{-1}), and fire retardant, which is very promising as an advanced high-performance thermally insulating material.\cite{35} It is expected that the thermal conductivity of GA will be reduced to a much lower level if the porosity of GA is increased. It will be an interesting research to explore the lowest thermal conductivity that GA can reach and study the underlying physical mechanisms controlling the low thermal conductivity.

1.3 New Nanostructured Carbon Materials and The Unique Properties

As one of the most promising 3D structure for graphene’s practical application, three-dimensional graphene macro-scale foams (GF) with controllable microscopic structure has attracted wide attentions. GF is a solid, open-cell foam, which is usually made by chemical vapor deposition on a metal foam, followed by removal of the metal foam. Researcher have reported the potential application of GF as a biocompatible and conductive scaffold for neural stem cells,\cite{36} oils removal materials,\cite{37} gas detection device\cite{38} and energy storage devices,\cite{39} etc. GF is mechanically robust and thus greatly simplifies the experimental measurement for electrical and thermal properties. Its continuously and covalently bonded
structure makes it possible to overcome the interface thermal resistance for applications as thermal interface materials.[27] Pettes et al. investigated the effects of processing conditions on thermal conductivity of GF.[27] They obtained $\kappa$ directly by measuring the electrical resistance during electrical heating. It was found that $\kappa$ follows a quadratic correlation with temperature at low temperature and has a peak of $250$–$650$ W mK$^{-1}$ at about $150$ K. This work revealed the different dominant phonon scattering mechanisms at low temperature to near RT for GF. The low effective $\kappa$ was attributed to the very low volume fraction and high porosity. Lin et al. studied the thermal diffusivity of GF samples at RT using the transient electro-thermal (TET) technique. The intrinsic $\kappa$ of the two-layer graphene insides GF was originally determined without measuring the porosity of the GF sample, which highly improved the accuracy of thermal characterization of graphene from GF experiments.[15]

3-D graphene aerogel (GA) has flexible shape, strong mechanical strength, lightweight, high porosity and excellent durability. The assembling of GA is generally through the formation of physical cross-links between graphene sheets using sol–gel chemistry. Sol–gel chemistry involves the reduction of graphene oxide to form a highly cross-linked hydrogel, which can then be freeze-dried or supercritical-CO$_2$-dried to form a graphene aerogel.[40] The porous attributes of GA can be regulated by adjusting the size and shape of the primary nanoparticles[40] as well as the reduction agent and reaction conditions. Extensive attention has been received and remarkable progress has been made for GA’s applications in electrochemical devices,[40, 41] environmental treatment [42, 43] and energy storage,[44] etc. Li et al. demonstrated that their GA synthesized by chemical reduction with ethylenediamine (EDA) is a highly efficient and recyclable absorbent for organic liquids;[45] Xu et al. measured the reversible magnetic field-induced strain and strain-dependent electrical resistance of GA
decorated with Fe$_3$O$_4$ nanoparticles, proving it has potential applications as an ultralight magnetic elastomer.[46] Zhang et al. presents the fabrication and characterization of three-dimensional (3D) GA–polydimethylsiloxane (PDMS) composites. Their outstanding electrical, thermal and mechanical properties propose potential applications in stretchable electronic devices, ultra-large strain sensors, thermal interface materials, hydrophobic anti-icing films, and energy absorption and viscoelastic damping devices.[47]

Graphene paper (GP) is a bulk material with anisotropic thermal transport capability. Although the thermal transport of GP is expected to be limited by the abundant pore structure and small flake size, the reported $\kappa$ ($\geq 1000$ W m$^{-1}$ K$^{-1}$ at RT)[48] and electrical conductivity ($\sim 1.57 \times 10^5$ S·m$^{-1}$)[49] of GP is much higher than those of other graphene-based bulk materials. These results indicate that the boundary scattering in GP does not strongly impact the phonon propagation in GP due to the extremely low defects density, highly ordered structure and the large in-plane size. Potential applications of GP in high performance electrode materials,[50] good gas barrier,[51] biocompatible material, Li ion battery anodes,[52-54] and energy storage devices[55, 56] have been reported. In general, large freestanding graphene paper is assembled through flow-directed vacuum filtration process of an aqueous graphene oxide dispersion[57], followed by reduction process such as chemical reduction, electrochemical reduction, thermal reduction, ion implantation, flame treatment, or flash light induced reduction.[58] Among the various reduction methods for fabricating GP, thermal reduction of graphene oxide films in ultra-high vacuum was reported particularly effective.[59]

Recently Xin et al. reported the fabrication of a highly ordered graphene paper by using direct electro-spray deposition of graphene films integrated with a continuous roll-to-roll process.[49] Subsequent thermal annealing was applied to remove functional groups and structural defects.
It was reported that 2200 °C is the optimized temperature for thermal annealing, after which the thermal and electrical conductivity could reach 1238.3 W m⁻¹ K⁻¹ and 1.57×10⁵ S m⁻¹ respectively at RT.[49] Song et al. investigated the structural evolution of the thermally reduced graphene oxide film (r-GO), and correlated the different annealing temperatures with κ and mechanical performances of r-GO. When the temperature reached 1200 °C, the r-GOF had an ultrahigh κ of 1043.5 W m⁻¹ K⁻¹. 1000 °C was found to be a critical temperature in enhancing κ.[48]

CNTs have exceptionally high young’s modulus (Y = 1.8 TPa)[60] and tensile strength,[61] high electronic mobility,[62] and high thermal conductivity.[63] Chemical vapor deposition (CVD) is a dominant method for high-volume CNT production. CNTs often form bundles. Past work has shown that CNT arranged in regular arrays of bundles is a promising candidate for devices requiring high-intensity electron beams from field emission sources.[64] SWCNT bundle interconnects showed significant advantages over Cu in terms of performance, power dissipation, as well as thermal management/reliability.[65] Although very high thermal conductivity values of individual CNTs in the order of 3000 W/ m·K at room temperature (RT) were reported,[66-68] thermal conductivity of CNT bundles are much lower due to existence of defects and impurities, tube-to-tube thermal contact resistance, and low density of CNT bundles.[69] Bauer et al. measured the thermal conductivity of vertically aligned CNT arrays to be only 49-79 W/ m·K.[70] Other works reported even lower values (<25 W/ m·K).[69, 71] There is considerable room for improvement of thermal conductivity by reducing defects and impurities in CNT bundles.
1.4 Scope of Present Work

In this work, a novel physical term, thermal reffusivity is used for characterizing phonon scattering intensities and mechanisms in carbon-nanostructures. The thermal reffusivity model and its application are introduced in detail in chapter 2. Different nanostructured carbon materials including graphene foam, graphene aerogel and large-area graphene paper are studied in detail to interpret their unique properties and to address the challenges and topics described in section 1.2.

Specifically, in chapter 3, the thermal diffusivity of GF is investigated from RT to 17 K. Using Scheuetz’s model, the intrinsic thermal diffusivity of graphene is determined accurately. The thermal reffusivity model is introduced and applied to subtract the defect and boundary scattering effect of GF, which ultimately leads to the intrinsic thermal conductivity of graphene in GF materials. The thermal conductivity data of pyrolytic graphite is also studied for calculating the intrinsic thermal conductivity and compared with that of GF.

In chapter 4, based on Hu et al.’s method, a modified synthesizing method is used for fabricating ultra-light graphene aerogel materials. A record-low thermal conductivity value under vacuum is reported, which makes it a very promising material for extreme thermal insulation. The thermal diffusivity and electrical resistivity profiles are studied and discussed in detail to understand the physical principles for the ultra-low thermal conductivity.

In chapter 5, for the high purity graphene paper material, a very interesting phenomenon is observed: as the temperature decrease from RT to about 245 K, there is a sudden jump of $\kappa$ from $\sim$500 W m$^{-1}$ K$^{-1}$ to 2000 W m$^{-1}$ K$^{-1}$. For comparison, the $\kappa$ of partly reduced graphene paper (PRGP) and graphene oxide paper (GOP) are also measured and studied. The results indicate that the thermal diffusivity and conductivity jump only occurs to
the high purity graphene paper. By conducting a comparison study with PRGP, GOP and pyrolytic graphite on phonon scattering mechanisms, the whole physical pictures for the thermal conductivity switch-on is illustrated clearly.

In chapter 6, the current-induced thermal annealing effect on improving the structure and thermal conductivity of CNTs bundles materials are investigated. TET technique is combined with the large current annealing to subsequently study the thermal diffusivity and thermal conductivity evolution under different current and different annealing temperatures. The localized thermal conductivity enhancement as a function of localized annealing temperature is evaluated by numerical calculation. The intrinsic thermal conductivity of graphite walls within the CNT bundles material is also reported. This work provides comprehensive details and reference for the future design of thermal annealing process to purify CNTs.
CHAPTER 2  THE THERMAL REFFUSIVITY AND PHONON SCATTERING

THEORY

The new physical term $\alpha^{-1}$ called thermal reffusivity (denoted as $\Theta$) is introduced to characterize the phonon scattering intensity in different materials, which is firstly defined and used by Xu et al. [72]. Just like electrical resistivity, thermal reffusivity is an intrinsic property of a material, which is solely determined by the phonon scattering inside materials. From the free electron model, electrical resistivity is expressed as the sum of phonon-phonon scattering and impurities scattering: $\rho = m/ne^2\tau = \rho_L + \rho_i$, where $\rho_L$ is the resistivity caused by the thermal phonons and $\rho_i$ is the resistivity sourced from the static defects scattering. For the same purpose, the thermal reffusivity is defined to characterize the phonon scattering for the thermal behavior. From single relaxation time approximation, a classical model for phonon thermal conductivity can be expressed as: $\kappa = \rho c_p v^2\tau/3$. Here, $v$ is phonon velocity, which rarely changes with temperature. $\tau$ is the relaxation time for scattering. The reciprocal of $\kappa$ cannot fully describe the phonon scattering since $\rho c_p$ also changes with temperature. Thus, the thermal reffusivity is defined as the reciprocal of thermal diffusivity to take out the specific heat effect. The above equation can thus be expressed in terms of thermal reffusivity as: $\Theta = \alpha^{-1} = 3/v^2\tau$. The relaxation time is inversely proportional to phonon scattering intensity. Therefore, thermal reffusivity directly reflects the phonon scattering intensity. As will be discussed below, $\Theta$ also has two parts: one induced by phonon-phonon scattering, and the other part by static phonon scattering by defects. Just like electrical resistivity, the variation of $\Theta$ versus temperature can be used to identify the residual value at the 0 K limit to evaluate the defect in the material. For metals, the heat capacity of electrons can be approximated as
\[ C = \gamma T \], where \( C \) is the heat capacity per unit volume, \( \gamma \) is a constant. Therefore, for metals, the thermal conductivity becomes \( \kappa = \gamma T v l / 3 \). The thermal reffusivity for metals can be defined by \( \Theta = T / \kappa \).

Thermal reffusivity can be used to characterize different scattering mechanisms. The way \( \Theta \) changes with temperature and its residual value at the 0 K limit all can be used to provide unprecedented details of phonon scattering. Also from the \( \Theta \sim T \) curve, the Debye temperature can be determined. It is well-known that ZA phonons with a smaller wavenumber are far more prevalent in the thermal transport of graphene. Therefore, normal scattering (N-scattering) of ZA phonon is strong compared to Umklapp scattering.[73, 74] At near RT, the N-scattering dominates the phonon scattering for mono-layered graphene, multi-layered graphene and graphite of \( \mu \)m size especially at low temperatures (10 K ~300 K). The phonon scattering mechanisms in graphene mainly include N-scattering, phonon-defects scattering and phonon-boundary scattering. According to Matthiessen's rule, it is generally a good approximation to linearly add all the scattering effect for the overall scattering effect:

\[
\frac{1}{\tau} = \frac{1}{\tau_c} + \frac{1}{\tau_{\text{defects}}} + \frac{1}{\tau_{\text{boundary}}} \quad (1)
\]

For N-scattering, lattice elastic vibration weakens as the temperature decreases, resulting in the reduced N-scattering and increased relaxation time \( \tau_n \). Thus, as temperature approaches 0 K, the overall reversed relaxation time ( \( 1/\tau_c \) ) slowly reaches to \( 1/\tau_{\text{defects}} + 1/\tau_{\text{boundary}} \). Thus \( \Theta \) decreases to a constant: \( \Theta(T \rightarrow 0) = 3/[v^2(\tau_{\text{defect}} + \tau_{\text{boundary}})] \), which correspondingly reflects the defect and boundary scattering effects in the thermal reffusivity. It is defined as the residual thermal reffusivity ( \( \Theta_0 \)). For rare-defect crystallite
materials, with no defects and boundary scattering existing, $\Theta$ is expected to be zero at the $0$ K limit. To demonstrate this theory, some near-perfect materials in our previous work is studied, such as silicon, germanium, NaCl and NaF. When the temperature goes down to 0 K, their $\Theta$ truly decreases to zero just as the theory predicts.[72] The residual thermal reffusivity can be used to quantitatively characterize the defect level of materials.

From solid state physics, the phonon population of N-scattering follows a behavior of $e^{-\theta/2T}$ at low temperatures[75], where $\theta$ is the Debye temperature of graphene. Our experiments are conducted at temperatures much lower than $\theta$ (around 2000 K[76]). Combined with the residual thermal reffusivity theory, the model for thermal reffusivity is expressed as $\Theta = \Theta_0 + C \times e^{-\theta/2T}$, where $C$ is a constant. With the knowledge of $\Theta_0$, the mean free path of phonon ($l_s$) induced by boundary and defect scattering can be estimated. $l_s$ represents the average distance that phonon travels between two scatterings. When temperature approaches 0 K, N-scattering gradually vanishes, the remaining scattering mechanisms are primarily boundary and defect scattering. When temperature approaches absolute zero, the residual thermal reffusivity can be written as $\Theta_0 = 3/n^2(\tau_{\text{defect}} + \tau_{\text{boundary}}) = 3/n l_s$ under single relaxation time approximation.

On the other hand, for some 3D structures that is built by assembling graphene based building blocks, the building blocks would be weakly inter-connected. Under this circumstances, the thermal transport is largely influenced by its inner thermal contact resistance. A model for heat transfer can be expressed as: $l_f / \kappa_{\text{eff}} = l_f / \kappa_c + R$, where $l_f$ is the average building block size, $\kappa_{\text{eff}}$ is the effective thermal conductivity, and $\kappa_c$ is the thermal conductivity within one building block, which includes the grain boundary thermal resistance. $R$ is the interfacial thermal contact resistance between neighboring blocks. Multiplying the
specific heat $\rho c_p$ of the 3D material at both sides, the equation in terms of thermal diffusivity can be expressed as

$$\alpha_{eff}^{-1} = R \rho c_p/l_f + \alpha_c^{-1},$$

where $\alpha_{eff}$ is the effective thermal diffusivity and $\alpha_c$ is the intrinsic thermal diffusivity. Combining the above thermal diffusivity equation, an expression can be deduced for the thermal contact conductance at interfaces:

$$R = A / \rho c_p v,$$

where $A$ is a constant. When the thermal contact resistance at interface is very large: $R \gg l_f / \kappa_c$, the equation can be simplified as

$$\alpha_{eff} = Avl_f,$$

in which the phonon velocity $v$ and $l_f$ are weakly temperature dependent.
CHAPTER 3 IDEAL THERMAL CONDUCTIVITY OF GRAPHENE FOAM

This chapter investigates the thermal diffusivity of graphene foam samples varying with temperature from RT to 17.0 K. Using the Schuetz’s model, the intrinsic thermal diffusivity of graphene is determined accurately. A novel method is presented to subtract the defects scattering effects and obtain the ideal thermal conductivity of graphene. Using the concept of thermal reffusivity, the defects effect and the Debye temperature of graphene are identified. Finally, the ideal thermal conductivity of graphene at the temperature range of 33K to RT is presented. The results are discussed and further interpreted by comparing with other works. This chapter begins with the characterization of samples in Section 2.1. In Section 2.2, TET and cryogenic experiment set-up are introduced. The thermal properties results are reported in Section 2.3, followed by structure and physics analysis.

3.1 Sample Characterization

The graphene foam (purchased from Advanced Chemical Supplier Material Company) is synthesized by the chemical vapor deposition (CVD) method. Typically, porous nickel foam is utilized as a 3D scaffold template. In brief, CH$_4$ vapor provides the source for the formation of carbon network by decomposition at 1000 °C under ambient pressure. A thin layer of PMMA is drop-coated on the graphene surface to protect graphene structure. Then the nickel is etched away by dissolving in HCl solution at 80 °C for 3 hours. Finally, the PMMA is removed using hot acetone so as to get the resulting free-standing graphene foams. The detailed procedure for the sample synthesis can be found in reference.[77]

The 3D porous foam-like structure of GF can be seen clearly under scanning electron microscope (SEM). Figure 3.1.1 (a) and (b) shows the images of GF samples from low to high
magnification, from which the seamlessly connected 3D network can be observed. Graphene flakes are interconnected strongly with each other, forming the scaffold with pores size ranging from tens to hundreds of micrometers. Under high resolution, the cell walls are constructed by thin graphene flakes overlapping, curving, and bonding to each other. The graphene flakes are almost transparent under SEM, indicating the extremely small thickness of graphene. Figure 3.1.1 (c) presents the Raman Spectrum of the GF sample. The Raman spectrum is acquired by excitation using a 532 nm laser with an integration time of 10 s. The ratio of integrated intensity of G band to that of 2D band ($I_G/I_{2D}$) is 0.63, indicating there are about 4 layers of graphene in our GF sample.[78] The crystals structure is examined by X-ray Diffraction (XRD) analysis. Figure 3.1.1 (d) displays the XRD spectrum of the GF sample. The fitting result reveals a pronounced peak at 26.6°, yielding the interlayer spacing of 3.35 Å, which is very close to the reported value 3.4 nm for bilayer and three-layer graphene.[79]

X-ray photoelectron spectroscopy (XPS) is conducted to determine the elemental composition and functionalized groups on the GF surface. The result shows that the GF is mainly composed of Carbon (89%), Oxygen (8.43%), Nitrogen (0.43%), and Silicon (2.14%). Figure 3.1.1 (e) shows the C 1s spectrum of GF, two pronounced peaks can be observed under X-ray photoelectron spectroscopy. The primary peak (284.8 eV) corresponds to the sp³-hydridized carbon bond, while the smaller peak presents the C-O bond.[80, 81] The N 1S is presented in Fig. 3.1.1 (f). There is only one obvious peak observed, indicating the presence of small amount of NH-C=O functional group on the surface of GF samples.[82]
Figure 3.1 SEM, Raman and XRD spectra images of the GF sample studied in this work. (a) and (b): SEM images of GF cellular structure and wall structure respectively. (c): Raman spectrum of the GF sample. Raman condition: CW laser at 532 nm wavelength, 100× lens, and 10s integration time. \( I_G/I_{2D} \) is the ratio of integrated intensity of G band to that of 2D band. The value of \( I_G/I_{2D} \) indicates the GF is composed of about 4-layer graphene. (d): XRD spectrum of the GF sample. The fitting result reveals a pronounced peak at 26.6°, yielding an interlayer spacing of 3.35 Å. (e) and (f): X-ray photoelectron spectra of GF. (e) the C1s spectrum, indicating different bonds for carbon atoms in the sample. (f) the N1s spectrum, suggesting the presence of NH-C=O functional group at the surface of the samples.
3.2 Experimental Details of TET Technique and Cryogenic System

The thermal diffusivity of GF samples at different temperatures are measured to study how the thermal diffusivity varies with decreasing temperature. A Janis closed cycle refrigerator (CCR) system is employed to provide a stable and reliable environmental temperature from of 295 K to 10 K. The transient electro-thermal (TET) technique developed by our laboratory is used in the experiment. The TET technique has been proven as an accurate and reliable approach to measuring thermal diffusivity of various solid materials, including conductive, semi-conductive or nonconductive materials. The thermal diffusivity of different materials, such as micro-scale polyester fibers,[83] micro/nanoscale thin films composed of anatase TiO$_2$ nanofibers,[84] single-wall carbon nanotubes,[85] DNA fibers,[72] and silkworm silks,[86] etc. were measured successfully using the TET technique. The obtained results have high accuracy with less than 5% difference compared to the values in references.

Figure 3.2.1 (a) shows the schematic of the TET experiment. TET measurements are conducted every 25 K at environmental temperature from 295 K to 100 K. Figure 3.2.1 (b) is a microscope image of the GF sample (sample 1) suspended between two gold-coated silicon electrodes. Denser data points (every 5-20 K) are collected at low temperatures (< 100 K) to have a clearer view of low temperature effects. Details for the physical model of TET can be found in our previous paper.[85]
Figure 3.2.1 (a) Schematic of the experiment setup and data collecting for the TET technique. The whole sample base is mounted on the cold head of the CCR system. A current source supplies the step current and an oscilloscope records the voltage evolution for the GF sample. (b): Microscope image of the GF sample (sample 1) suspended between two gold-coated silicon electrodes. (c): The raw voltage against time data collected by the oscilloscope for sample 1 at environmental temperature of 195 K. The inset demonstrates the linear relationship between resistance and temperature for sample 1 from 295 K to 10 K. (d): Theoretical fitting of the normalized temperature rise for sample 1 at different environmental temperatures: 295 K, 195 K, 10 K. Dots represent the experimental data, and solid lines show the fitting result.

For the suspended samples, the one dimensional heat transfer model in the length direction is reasonable. Heat convection and gas conduction are neglected considering the very low air pressure (<0.5 mTorr) in the chamber. The average normalized temperature rise, which is defined as $T^* = [T(t) - T_0]/[T(t \rightarrow \infty) - T_0]$, is given as:
\[ T^* = \frac{48}{\pi^4} \sum_{m=1}^{\infty} \frac{1 - (-1)^m}{m^2} \frac{1 - \exp[-m^3 \pi^2 \alpha_{\text{measure}} t / L^2]}{m^2}, \]  

where \( \alpha_{\text{measure}} = (1-f) \alpha \) is the measured thermal diffusivity, \( \alpha \) is the real thermal diffusivity of the sample, \( f \) is a type of Biot number which represents the heat loss from the surfaces of the sample by radiation. The temperature evolution of the sample results in the voltage change of the sample: \( T^* = (V_{\text{sample}} - V_0) / (V_{\infty} - V_0) \), with \( V_0 \) and \( V_{\infty} \) are the voltage of the sample before and after the heating respectively. Hence, by measuring the voltage evolution, the normalized temperature profile is obtained. Here \( f \) can be defined as \(-8\varepsilon \sigma T_0^3 L^2 / D \pi^2 \kappa \). Thus, the measured thermal diffusivity becomes:

\[ \alpha_{\text{measure}} = \alpha + \frac{1}{\rho c_p} \frac{8\varepsilon \sigma \bar{T}^3}{D} \frac{L^2}{\pi^2}. \]  

\( \rho c_p \) is the volumetric specific heat; \( \varepsilon_r \) is the emissivity; \( \sigma \) is the Stephen-Boltzmann constant; \( \bar{T} \) is the average temperature during the joule heating; \( L \) and \( D \) are the length and thickness of the sample respectively. From this equation, if other parameters are kept constant, the measured thermal diffusivity of a sample is linearly proportional to \( L^2 \). TET experiments are repeated to the same sample at two or three different lengths (Table 1).

TET measurements are conducted at every 25 K of environmental temperature from 295 K to 100 K. Denser data points are collected in low temperatures (< 100 K) to have a clearer view of low temperature effects. After that, the sample is taken out and cut shorter for the next experiment. Experiments are repeated to the same sample with three different lengths. The measured samples are detailed at Table 1. The voltage evolution \( V_{\text{exp}} \) is recorded by an oscilloscope (Tektronix DPO 3052 Digital Phosphor Oscilloscope). As a zero-gap semiconductor, graphene’s resistance is inversely proportional to its increasing temperature,
which should be linearly reflected in the decreasing voltage in our TET measurement. The inset in Fig. 3.2.1 (c) shows the resistance against temperature profile for sample 1 from 295 K to 10 K, which confirms the linear $R$-$T$ relationship. A linear fitting can be used to describe the $R$-$T$ relationship: $R = 26.85 - 0.0196 \times T$. Figure 3.2.1 (c) shows one of the voltage evolutions (sample 1 at 195 K). The voltage before electrical heating is 1.104 V. Upon the step current, voltage begins to decrease and finally reaches a steady voltage at about 1.091 V, resulting in the voltage change of 1.18%. Given the step current for this measurement is 47.2 mA, the resistance can be calculated as 23.39 $\Omega$ and 23.11 $\Omega$ before and after the heating respectively. Based on the linear $R$-$T$ relationship of sample 1, the temperature increase is determined as 14.29 K.

The recorded experimental $V$-$t$ data is theoretically fitted by using different trial values of the thermal diffusivity subsequently. By using Eq. (2) in Supplementary Material and MATLAB programming, the experimental data is fitted by comparing with the theoretical curve with different trial value of measured thermal diffusivity ($\alpha_{\text{measure}}$). Applying the least square fitting technique, the value giving the best fit of $V_{\text{exp}}$ is taken as $\alpha_{\text{measure}}$. The $\alpha_{\text{measure}}$ represents the thermal diffusivity during the joule heating process. The corresponding real temperature can be approximated by the average of the environmental temperature ($T_0$) and the stable temperature of the sample ($T_1$). Here, the real temperature ($T$) is taken as $195 + 14.29/2 \approx 202$ K. To determine the uncertainty of the fittings, different trail values are also used for the fitting. It is found that when the trial values are changed by $\pm10\%$, the fitting curve obviously deviates from the experimental data. Thus, the fitting uncertainty is estimated as 10%, but the real error should be much smaller since we measure each value of thermal diffusivity for 30 times and take the average value as the final thermal diffusivity. In this example, $\alpha_{\text{measure}}$ is
determined as $2.38 \times 10^{-4} \text{m}^2/\text{s}$ at the real temperature of 202 K. The normalized temperature rise can be obtained by $T^* = [V(t) - V_0] / [V(t \rightarrow \infty) - V_0]$. Figure 3.2.1 (d) shows the normalized temperature rise for sample 1 at different environmental temperatures: 295 K, 195 K, and 10 K. As illustrated in the figure, the time for reaching the stability becomes shorter and shorter as $T_0$ decreases from 295 K to 10 K, indicating the measured thermal diffusivity is increasing with the decreasing temperature.

### 3.3 Results and Discussion

3.3.1 Thermal diffusivity of graphene foam

The result for $\alpha_{\text{measure}}$ of the three samples against real temperature $T = (T_0 + T_1)/2$ is summarized in Fig. 3.3.1. Here, $\alpha_{\text{measure}}$ is still a combination of the real thermal diffusivity ($\alpha_{\text{real}}$) and radiation effect. The GF samples are cut from an equal-thickness GF film. From table 1, the widths of the three samples are almost equal with an error less than 0.8%. The lengths and widths are measured with INFINITY ANALYZE under the microscope with a high accuracy. We can express $\alpha_{\text{measure}}$ as: $\alpha_{\text{measure}} = \alpha + 8 \varepsilon \sigma T_0^3 L^2 / \rho c_p D \pi^2$. Assuming uniform density, emissivity and $\alpha_{\text{real}}$ for the three samples, which is reasonable considering they are the sample with different lengths, the radiation effect should be linearly related to its length square $L^2$. We plot the $\alpha_{\text{measure}} - L^2$ of the three samples at each temperature (see Fig. 3.3.1 inset for example). $\alpha_{\text{real}}$ is then obtained by linear fitting and extrapolating to the point of the $L^2 = 0$. The real thermal diffusivity is also plotted in Fig. 3.3.1.
The measured thermal diffusivity $\alpha_{\text{real}}$ against temperature $T$ for the three GF samples and the resulting real thermal diffusivity of GF ($\alpha_{\text{real}}$). $\alpha_{\text{real}}$ follows a linear increase with the decreasing temperature from 299 K to 104 K. Under 104 K, $\alpha_{\text{real}}$ tends to be stable with a slight decrease from 43 K to 17 K. The top right inset is the measured thermal diffusivity against length square ($L^2$) for the three GF samples at temperature of 54 K, to show one of the fitting process for determining the real thermal diffusivity of the sample. Triangles are for the experimental data, and the solid line represents the linear fitting.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample_1</th>
<th>Sample_2</th>
<th>Sample_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (mm)</td>
<td>5.14</td>
<td>3.74</td>
<td>1.01</td>
</tr>
<tr>
<td>Width (mm)</td>
<td>1.37</td>
<td>1.38</td>
<td>1.37</td>
</tr>
</tbody>
</table>

$\alpha_{\text{real}}$ shows an increasing behavior as $T$ goes down from 299 K to 104 K. Under 104 K, $\alpha_{\text{real}}$ tends to be stable with a slight decrease from 43 K to 17 K. From the Wiedemann-Franz law, the contribution of electrons transport to the thermal conductivity of graphene is negligible. The thermal behavior of graphene is governed by propagating of phonons in graphene lattice. Thermal transport ability of graphene is limited by phonon scattering in
several mechanisms, mainly including Umklapp phonon-phonon scattering (U-scattering), phonon-defects scattering and phonon-boundary scattering. Only phonons with wave vectors \( (k_p) \) in the order of \( G/2 \) (\( G \) is the reciprocal lattice vector of the first Brillouin zone) participate in the U-scattering by collision. At near RT, phonon energy is so high that almost all phonons possess high enough \( k_p \) to participate in the thermal transferring. Thus U-scattering dominates the scattering process at near RT. As \( T \) goes down, lattice elastic vibrations in graphene weakens and phonon population decreases. The U-scattering weakens correspondently, which results in the increasing thermal diffusivity. At low temperatures (lower than 104 K), however, U-scattering becomes so weak that the defects and boundary scattering whose intensity is independent of the temperature begins to dominate. Thus, at the low temperature (from 104 K to 17 K), \( \alpha_{real} \) tends to be stable, controlled by defects and boundary scattering.

For the slight decrease at temperatures below 43 K, the reason has not been fully understood. It might be part of the intrinsic properties of the GF materials because we also found this ‘dropping’ thermal diffusivity in the data of pyrolytic graphite.[87] The surface area \( A_s \) contributing to the heat radiation could be much larger than \( 2(W + D)L \) due to the high porosity of the GF samples. Besides, for the three GF samples, larger ‘dropping’ of \( \alpha_{measure} \) is observed for the longer samples than the shorter one. Therefore, the radiation could have a little effect to this “dropping” behavior.

The intrinsic thermal diffusivity of graphene can be obtained using the thermal diffusivity of GF. Based on the model of Schuetz et al.[88] a correlation has been demonstrated reliable for GF by Lin H et al.[89] as \( \alpha_g = 3\alpha_{GF} \). In this equation, \( \alpha_g \) is the intrinsic thermal diffusivity of graphene, \( \alpha_{GF} \) is the thermal diffusivity of graphene foam. Using this equation, the thermal diffusivity of graphene can be calculated accurately without knowing the porosity.
of graphene foam. The uncertainty for measuring volume fraction of graphene foam is therefore avoided. This provides a simple and effective way for calculate the thermal diffusivity of solid phase.

3.3.2 Thermal reffusivity model for determining the defect levels

Figure 3.3.2 (b) shows the profile of intrinsic thermal reffusivity of graphene varying with temperature. Clearly, $\Theta$ decreases with temperature from 299 K to 100 K. When $T$ is below 100 K, $\Theta$ gradually becomes stable and comes to $\Theta_0$. To compensate for the data fluctuation at low temperatures and reduce the error, the experimental data is fitted by a model of phonon-scattering. From solid state physics, the phonon population of U-scattering follows a behavior of $e^{-\theta/2T}$ at low temperatures[75], where $\theta$ is the Debye temperature of graphene. Our experiments are conducted at temperatures much lower than $\theta$ (around 2000 K[76]). Combined with the residual thermal reffusivity theory, the model for thermal reffusivity is expressed as $\Theta = \Theta_0 + C \times e^{-\theta/2T}$, where $C$ is a constant. Using OriginPro, the nonlinear curve fitting based on this equation for GF is $\Theta = 1878 + 1.03 \times 10^5 \times e^{-906.66T}$. $\Theta_0$ is accordingly determined as 1878 s/m$^2$, and $\theta$ is 1813 ±48 K. For our graphene foam sample, the residual thermal reffusivity $\Theta_0 = 1878$ s/m$^2$, taking about 27.18% of the RT reffusivity. The fitting is also plotted in Fig. 3.3.2 (b) with the experimental data. The fitting line agrees excellently with the data, demonstrating the U-scattering effect in the thermal transport.
Figure 3.3.2 The intrinsic thermal diffusivity of graphene changes with temperature. (b) Thermal diffusivity of graphene compared with (c) the thermal diffusivity of other literature values for pyrolytic graphite.[87, 90, 91] The solid symbols are the experiment data, and the solid lines show the theoretical fitting of the data. As temperature approaches zero, the intersection point of the fitting line and vertical axis is taken as the residual thermal diffusivity ($\Theta_0$).

Our resulting Debye temperature is 1813 K. Although many theoretical analysis suggested that the flexural acoustic (ZA) phonons provides the dominant contribution to the thermal transfer in graphene,[27] our value is very close to the averaged $\Theta$ (=1911 K) of the three acoustic modes in graphene, which is 2840 K for longitudinal mode (LA), 1775 K for
transverse mode (TA) and 1120 K for ZA.[27] This could result from the effect of the functional groups and other elements in GF as observed in XPS, which interrupt the phonons propagation and increase the energy coupling among ZA, LA and TA modes.

To further demonstrate our residual thermal reffusivity theory in graphene, we calculate the $\Theta$ evolution using some experimental data of pyrolytic graphite in literatures[87, 90, 91] and fit these data using our thermal reffusivity model $\Theta = \Theta_0 + C \times e^{-\Theta_0 T}$. The results are presented in Fig. 3.3.2 (b) for comparison. As seen from Fig. 3.3.2 (b), the model gives excellent fittings for the three data groups. All the three groups of $\Theta$ experience the same decreasing pattern as the temperature goes down. Finally they reaches each $\Theta_0$ value, which is determined by the different defects level in their samples. For the data from Ho et al.[90], Hooker et al. and Slack et al.[87], the resulting residual thermal reffusivity $\Theta_0$ are 43.28, 84.70 and 112.14 s/m² respectively. Considering their $\Theta$ at room temperature are 795.36 s/m², 881.82 s/m² and 799.98 s/m² respectively, the residual $\Theta_0$ only takes about 5%, 9.6% and 14% of the whole reffusivity at room temperature.). These results indicate the highly oriented graphene layers and low defect structure in those pyrolytic graphite samples, Debye temperatures are estimated as 1349 K, 1381 K and 1133 K respectively. Their estimated Debye temperatures are very close to the value of the ZA mode (1120 K), reflecting the dominance of the ZA mode phonon in heat conduction.

With the knowledge of $\Theta_0$, the mean free path of phonon ($l_s$) induced by boundary and defect scattering can be estimated. $l_s$ represents the average distance that phonon travels between two scatterings. When temperature approaches 0 K, U-scattering gradually vanishes, the remaining scattering mechanisms are primarily boundary and defect scattering. When temperature approaches absolute zero, the residual thermal reffusivity can be written as
\[ \Theta_0 = 3/v^2(\tau_{\text{defect}} + \tau_{\text{boundary}}) = 3/vl_s \] under single relaxation time approximation. To calculate phonon velocity, the phonon dispersion relation of graphite by Wirtz et al. [92] is used. Phonon velocity is estimated as 9171 m/s, which is the average of the three branches: out-of-plane acoustic (ZA), longitudinal acoustic (LA), and transverse acoustic (TA). As a result, \( l_s \) from our data is estimated as 166 nm, which should be smaller than the crystallite sizes of GF. For some rare-defect materials, such as silicon and NaCl, the point defect scattering can be rather small. Their crystallite sizes can be estimated by \( l_s \) precisely using this method. For the pyrolytic graphite sample, the corresponding mean free path from defect and boundary scattering are determined as 7.56 um, 3.86 um, and 2.92 um for the data from Ho et al., Hooker et al. and Slack et al. which is close to the reported a-direction crystallite size of pyrolytic graphite [93]. These result further indicates the low defect level in the pyrolytic graphite samples.

3.3.3 Ideal thermal conductivity of graphene

By subtracting \( \Theta_0 \) from \( \Theta \), the ideal thermal diffusivity is obtained by
\[ \alpha_{\text{ideal}} = 1/(\Theta - \Theta_0) \]. To reduce the error of data, we use the fitting data as \( \Theta \). Using \( \alpha_{\text{ideal}} \) and the specific heat capacity of graphene, the ideal thermal conductivity of graphene can be determined as \( \kappa_{\text{ideal}} = \rho c_p \alpha_{\text{ideal}} \), in which \( \rho c_p \) is the volumetric specific heat of graphene. The literature thermal conductivity of graphene ranges from dozens to thousands of WmK\(^{-1}\) due to the different defects levels in each graphene sample. While by using our method, the defects effect can be identified by \( \Theta_0 \). Figure 3.3.3 (a) shows the obtained ideal thermal diffusivity of graphene. \( \alpha_{\text{ideal}} \) clearly has a \( e^{\alpha l_s/2T} \) dependence, suggesting the dominating Umklapp phonon scattering mechanism.
Figure 3.3.3 (a) The ideal thermal diffusivity of graphene. (b) The experimental data for specific heat of graphite [94]. (c) The ideal thermal conductivity of graphene ($\kappa_{\text{ideal}}$) against temperature compared with that we obtained from other literature data of pyrolytic graphite.[87, 90, 91] The data inside the orange rectangle (below 80 K) is less reliable due to the error of $\alpha_G$ at low temperatures and the undecided difference of specific heat between graphene and graphite.

By multiplying $\rho c_p$, we are able to calculate $\kappa_{\text{ideal}}$. As far as we know, there has not been any experimental data for the specific heat of graphene at low temperatures. In the
temperature range of 10 K to 300 K, the specific heat of graphite is normally taken as that of graphene. Figure 3.3.3 (b) presents the measured heat capacity of graphite by Desorbo, et al.,[94] which is used here to calculate $\kappa_{\text{ideal}}$. Figure 3.3.3 (c) shows $\kappa_{\text{ideal}}$ varying with temperature. At RT, $\kappa_{\text{ideal}}$ is about 300 W mK$^{-1}$. This value is much smaller than the previous reported thermal conductivity of 1500-5000 W mK$^{-1}$ for suspended graphene.[6] The difference might result from the curvatures and folds of graphene planes inside the GF sample as seen in SEM images, which largely increases the phonons scattering. In addition, there are other chemical elements (N, O, H and Si) and residual functional group on the surface of the GF samples from the XPS results. For our GF, oxygen takes about 8.43% in the sample. It has been reported by Mu et al. that oxygen coverage of 5% reduced the graphene thermal conductivity by 90%.[95] These extra atoms inevitably distort the order of the lattice, so as to interrupts the phonons propagation in graphene planes and even impedes the neighboring planes. As the temperature goes down, $\kappa_{\text{ideal}}$ increases all the way to 17 K, which further confirms the absence of defect scattering effect. For the literature reported thermal conductivity profiles of graphene, their peaks occur at temperature from 100 K to near RT. The peak position is determined by the defects level in graphene samples. It has been suggested that as the perfection of the graphite samples is improved, the peak of thermal conductivity shifts from RT to about 80 K.[96] In our result, since the defects effect has been completely subtracted, $\alpha_{\text{ideal}}$ increases all the way as expected. Numerous studies suggest that the specific heat of graphite follows the Debye $T^3$ law at very low temperature (<10 K), and transforms to $\sim T^2$ in the intermediate temperature range (10-100 K). The thermal diffusivity of graphene has a temperature dependence as $\alpha_{\text{ideal}} \sim e^{\theta_{\text{D}} T}$. Therefore, the resulting thermal conductivity should
present a behavior of $\kappa_{\text{ideal}} \sim T^2 \times e^{\theta/2T}$, where $\theta=1813$ K in our work. As the temperature goes down from 300 K to 10 K, $e^{1813/2T}$ increases faster than the decreasing of $T^2$. Accordingly, $\kappa_{\text{ideal}}$ increases with the decreasing temperature all the way. The ideal thermal conductivity of pyrolytic graphite is also calculated from the literature data using our model. It can be seen from Fig. 3.3.3 (c) that $\kappa_{\text{ideal}}$ of the three pyrolytic graphite follow the same pattern as the temperature goes down.

Our $\kappa_{\text{ideal}}$ value is smaller than that of pyrolytic graphite at near RT (100 K to 299 K); while it exceeds the value of pyrolytic graphite below 100 K. This demonstrates the superior thermal conductivity of graphene than pyrolytic graphite. As the temperature goes down, $\kappa_{\text{ideal}}$ increases rapidly and goes beyond $10^5$ WmK$^{-1}$ below 80 K based on our calculation. The data below 80 K should be used with less confidence since the specific heat values are taken from graphite experiments, which may be higher than the real specific heat of graphene. [8] In addition, the error of fitted thermal reffusivity is larger at low temperatures due to the data perturbation at low temperatures, which results in the larger error in the value of ideal thermal diffusivity. In this work, the low temperature range is chosen in order to identify the defect level of graphene foam. These results illustrate the phonon scattering mechanism in graphene at low temperatures and shed light on understanding the thermal behavior of graphene-based materials against temperature variation. The ideal thermal conductivity of graphene and the corresponding scattering mechanisms at high temperatures (room temperature to 1000°C) will be further investigated soon once our new high-temperature vacuum stage is ready to use.
CHAPTER 4 INTERFACE-MEDIATED EXTREMELY LOW THERMAL CONDUCTIVITY OF GRAPHENE AEROGEL

In this chapter, we present a modified synthesizing method of graphene aerogel materials (GA) based on Hu et al.’s method. We report a record-low thermal conductivity ($\kappa$) for our ultralight GAs (~4 mg/cm$^3$) under vacuum. The $\kappa$ of our GAs is down to $2 \times 10^{-4}$-4×10$^{-4}$ W·m$^{-1}$·K$^{-1}$ at low temperatures (~40 K) and 4.7×10$^{-3}$-5.9×10$^{-3}$ W·m$^{-1}$·K$^{-1}$ at room temperature (RT), which makes it a very promising material for extreme thermal insulation. In 3.1, the process for synthesizing the GA is presented in detail, followed by the characterization of the GA material. In 2.3, the experimental details for the thermal properties and electrical properties characterization are illustrated. The result and analysis are presented in 2.3, which includes mainly three parts. The mechanism of this extremely low $\kappa$ is explored by studying the temperature variation of GA’s $\kappa$, thermal diffusivity ($\alpha$) and specific heat ($c_p$) from RT to as low as 10.4 K. The uncovered small, yet positive $\partial \alpha/\partial T$ reveals the dominant interface thermal contact resistance in thermal transport. For normal materials with thermal transport sustained by phonon-phonon scattering, $\partial \alpha/\partial T$ always remains negative. The study of $c_p$ suggests highly disordered and amorphous structure of GAs, which also contributes to the ultralow $\kappa$. This makes the GA a very promising thermal insulation material, especially under vacuum conditions (e.g. astronauts areas).
4.1 Sample Synthesizing Method and Material Characterization

4.1.1 Synthesis of graphene aerogel using EDA based chemical reduction

The graphene oxide dispersion in water (purchased from Graphene Supermarket) has the concentration of 5g/L and C/O ratio of about 4. Ethylenediamine (EDA) anhydrous (99.9%) was obtained from Fisher Scientific, and used as received. 4uL reducing agent ethylenediamine (EDA) is diluted with deionized (DI) water (2mL) under magnetic stirring. In this work, the GO solution (5mg/mL × 3mL) is added into the EDA solution drop by drop during the magnetic stirring. After 30 minutes of medium-high speed magnetic stirring, the GO solution is partly reduced and the GO-EDA mixture becomes uniform. Then the mixture is sealed and heated in an oven at 95 °C for 6 hours. The dispersion of GO first becomes brown colloidal and finally transforms into a black hydrogel. During this process, the GO flakes assemble into a macroscopic hydrogel with little stacking. EDA as a reduction agent leads to ring-opening reaction of epoxy groups and functionalization on the surface of graphene oxide. Meanwhile, the graphene oxide is partly reduced by restoring part of the sp² regions.[97] The resulting hydrogel exhibits no volume shrinkage during the heating. After that, the hydrogel is subjected to freeze-drying for 48 hours, so as to completely remove the solvent inside the sample. During the freezing process, cells are made with the formation of ice crystals pushing the r-GO sheets together into cell walls. After freeze-drying, a black aerogel sample is formed. Then the sample is put at the bottom of a long quartz tube, and then flushed with Argon gas for 2 hours to remove air inside the sample completely. After that, the tube is sealed and a microwave heating process (1-5 minutes) is employed. The microwave heating removes a large number of residual functional groups. The conjugation of sp² and the π-π interaction are restored.[97]
The final graphene aerogel sample has metal grey color and good mechanical strength. The GO/EDA ratio and microwave heating time can be varied to make GAs samples with different density and mechanical properties. The volume of the hydrogel is mainly determined by the GO/EDA ratio. Too small or too large ratio will lead to a volume shrinkage after the heating. If the EDA amount is not sufficient to functionalize all of the graphene oxide flakes, the graphene oxide cannot assemble into an integrated hydrogel. If the EDA amount is too large, the pH value of the suspension will be too high to keep the GO colloids stable, which results in a shrinkage of the resulting hydrogel.[97] If we increase the GO and EDA amount but keep a suitable pH value (around 11.5), the resulting GA will be much denser and the mechanical strength improves accordingly. We found that when the GO concentration is less than 1.7 mg/mL, the sample presented some volume shrinkage. Thus the obtained minimum density of the GAs sample is about 2 mg·cm$^{-3}$. Improved mechanical strength of the resulting samples can be achieved by increasing the GO concentration and EDA amount.

4.1.2 Structure characterization

The structure of the GAs is characterized by scanning electron microscope (SEM). The SEM images were taken by using an FEI Quanta 250 field emission SEM with a voltage of 8.00 kV. Under SEM, the self-assembled foam-like network can be seen clearly [Figure 4.1.2 (a)-(b)]. The cell walls of GAs are made up of reduced GO (r-GO) sheets. The thin r-GO sheets fold, curve, twist, and interconnect with adjacent sheets, constituting the framework with pores of tens to hundreds of μm. The Raman Spectra of GAs [Figure 4.1.2 (c)] exhibits two pronounced peaks at about 1348 and 1585 cm$^{-1}$, corresponding to the D band and G band. The G band reflects the sp$^2$ carbon. Its intensity can be used to analyze the level of graphitization
in GAs. The D band sources from the defects and disorder structure in the sp² domains.[98] Our GAs show an \( \frac{I_D}{I_G} \) ratio of 1.14, which is higher than the \( \frac{I_D}{I_G}=1.06 \) for GO. Increased \( \frac{I_D}{I_G} \) is commonly reported for GA synthesized from chemical reduction.[98-100] Although the microwave heating removes most of the residual functional groups from GA, the chemical reduction by EDA brings into a large number of disorder in the sp² domains. As the residual functional groups are removed during chemical reduction, some in plane C=C bond crack and a large number of defects are generated. This is the main reason for the increase of \( \frac{I_D}{I_G} \). Besides, it has been reported that the increased \( \frac{I_D}{I_G} \) is related to the average size of the sp² domains.[101] During the microwave reduction, numerous new graphitic domains with smaller size might be created, which makes the averaged sp² domain size decrease.[99] It is possible that the microwave heating reduction contributes to a small decrease of \( \frac{I_D}{I_G} \), but the overall reduction process still shows an increase of \( \frac{I_D}{I_G} \). This phenomenon has also been reported in Hu et al’s work.[97] The Raman spectrum of GA is obtained using Olympus BX51 universal research Microscopy under 4× lens, with 8 mW laser power, and 5 minutes integration. For comparison, the Raman spectrum of GO flakes (100× lens, 3.0 mW laser power and 60s integration) and the Raman spectrum of GF (100× lens, 0.8 mW laser power and 10s integration) are also presented.
Figure 4.1.1 (a) and (b): SEM images of GAs cellular and wall structure. (c): Raman spectrum. (d): XRD spectrum. (e) X-ray photoelectron spectra of GA. (f) The XPS C1s spectrum, indicating different bonds for carbon atoms in the sample. (g) The XPS N1s spectrum, suggesting the presence of the pyridinic (N1), pyrolic and quaternary nitrogen (N2), and pyridine-N-oxide (N3) at the sample surface. (h) A GA on a dandelion. (i) The compressing test with a 10-gram weight.
Figure 4.1.1 continued

The x-ray diffraction (XRD) is conducted with a Siemens D500 x-ray diffractometer using Cu x-ray tube operated at 45kV and 30mA. XRD patterns of GAs [figure 4.1.2 (d)] shows three major peaks at about 17.590°, 21.345° and 26.376°, yielding an interlayer spacing of 3.395-5.065 Å based on the fitting, which is a little larger than the 3.36 Å from graphite’s (002) plane while much smaller than the 8.32 Å from GO’s 10.6° 2θ peak.[102] The decreased interlayer spacing from GO to GA demonstrates the removal of large amount of the oxygen-containing functional groups of GO. The larger interlayer spacing of GAs than that of graphite indicates the existence of residual functional groups at the surface of GAs, which makes the r-
GO sheets inside GAs different from graphene. As the reduction going on, the peak of GA is expected to shift from peak of graphene oxide at 10.27° to that of graphite at 26.7°.[103, 104] Therefore, the peak at 21.345° is due to the presence of partly reduced graphene oxide. The peak at 21.345° is sharp, indicating that there is a short-range order. The XRD result of graphene foam material is also plotted in figure 4.1.2 (d) for comparison. The peaks of GF are very sharp and have high intensity, which is a typical XRD pattern of well-crystalline graphene; while the peaks of GA are wide and the base line is irregular with large noises. This indicates the large percent of amorphous structure in the GA.

Chemical analysis of GAs is conducted by x-ray photoelectron spectroscopy (XPS) on a PHI55000 XPS with an Al Kα source (1486.6 eV). Specifically, the survey spectra [figure 4.1.2 (e)] were collected from 0 to 1100 eV with a pass energy of 187.85 eV and a step size of 0.8 eV; high-resolution spectra for specific elements were acquired with a pass energy of 58.70 eV and a step size of 0.25 eV. The resulting elemental composition of the GAs is C (82.05%), N (6.99%), O (9.68%), Na (0.56%), and Si (0.71%). Figure 4.1.2 (f) shows the C1s XPS spectrum, which has four obvious peaks by deconvolution, corresponding to the C-C, C-O, and C=O and C(O)OH bond respectively. The C-C bond takes the majority, while other bonds also exist. Figure 4.1.2 (g) presents the deconvoluted N1S spectrum of GAs. The fitting of the spectrum gives the following peaks: the highest peak N1 at 398.5 eV represents the pyridinic nitrogen; N2 at 400.5 eV is attributed to the pyrrolic-type nitrogen; N3 at 403.7 eV corresponds to the oxidized nitrogen.[45, 105] The high porosity endows GAs with an ultralow density (2-6 mg·cm⁻³ depending on the microwave heating time as well as the ratio of GO and EDA), which is comparable with that of air (1.28 kg/m³). Figure 4.1.2 (h) shows one ultralight GA sample standing on a dandelion. The dandelion has very little deformation under the weight of
the sample. The GAs have good mechanical strength and elasticity. Figure 4.1.2 (i) shows the compressibility test. After being removed with a 10-gram weight, the GA sample (density 4 mg/cm$^3$) completely recovers from the deformation. This shows the good elasticity and compressibility of our GA material.

4.2 Thermal Characterization Method

4.2.1 The transient electro-thermal technique

The thermal diffusivity of GAs samples at different temperatures are measured using the transient electro-thermal (TET) technique. A Janis closed cycle refrigerator (CCR) system is utilized to provide stable environmental temperatures from 295 K to 10 K. The GA sample is suspended between two gold-coated silicon electrodes on a thin glass wafer. Two smooth silicon wafers of smaller size are carefully placed on the sample edges and compressed tightly by clips and epoxy resin. In this way, the thermal contact resistance can be reduced to a negligible level. A small amount of silver paste is applied to connect the electrodes to the wirings. The whole stage is then put into a vacuum chamber. For data collecting, a step current is fed through the GAs sample by a current source. An oscilloscope is used to record the resulting voltage-time ($V$-$t$) profile. Figure 4.2.1 (a) shows the schematic of the experiment set-up. The vacuum jacket is pumped to a pressure lower than 0.5 mTorr during the whole measurement to reduce the heat convection to a negligible level.
Figure 4.2.1 (a) The schematic of the experiment set up. (b) The normalized temperature profiles for sample 1-1 at different temperatures: 295 K, 95 K and 10 K. The symbols are experimental data and the lines are the theoretical fittings. (c) The first derivative of electrical resistance against temperature profiles obtained by differentiating $R-T$ curve. Some errors are less than ±2%, so these error bars are not very visible. (d) The measured thermal conductivity of the five GA samples in this work. The inset shows one of the examples for the linear fitting (for group 1 at real temperature of 298.6 K) to obtain its real thermal conductivity.

For each group, a rectangular sample is cut from an equal-thickness film of GA. For group 1, a sample is measured three times with different lengths, denoted as sample 1-1, 1-2 and 1-3 respectively; for group 2, another sample is measured twice, denoted as sample 2-1 and 2-2 respectively.
### Table 2 Details of GA samples characterized

<table>
<thead>
<tr>
<th>Sample index</th>
<th>1-1</th>
<th>1-2</th>
<th>1-3</th>
<th>2-1</th>
<th>2-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Length [mm]</td>
<td>4.90±0.01</td>
<td>3.40±0.02</td>
<td>2.60±0.05</td>
<td>4.90±0.02</td>
<td>2.80±0.01</td>
</tr>
<tr>
<td>Width [mm]</td>
<td>1.70±0.11</td>
<td>1.70±0.09</td>
<td>1.70±0.12</td>
<td>2.02±0.07</td>
<td>2.20±0.05</td>
</tr>
<tr>
<td>Density [mg·cm⁻³]</td>
<td>4.20±0.38</td>
<td>4.20±0.38</td>
<td>4.20±0.38</td>
<td>3.90±0.36</td>
<td>3.90±0.36</td>
</tr>
</tbody>
</table>

The electrical resistivity of GA is not linearly dependent on temperature, as indicated in Figure 4.2.1 (b). But in our TET measurement, the temperature increase of the sample induced by joule heating is very small (ΔT< 6 K). In this very small temperature range, the linear relationship between resistance and temperature can be assumed justifiably. The decreasing resistance profile is linearly reflected in the decreasing voltage during the step current. The recorded experimental V-t data is theoretically fitted by using different trial values of the thermal diffusivity. By using equation (2) and MATLAB programming, the experimental data is fitted by comparing with the theoretical curve with different trial value of measured thermal diffusivity (α_measure). Applying the least square fitting technique, the value giving the best fit of V_exp is taken as α_measure. α_measure represents the thermal diffusivity during the joule heating process. The corresponding real temperature (T) should be the average temperature during the heating process. Figure 4.2.1 (b) shows the normalized temperature profiles for sample 1-1 at different environmental temperatures: 295 K, 95 K, and 10 K. The experiment data agrees very well with the theoretical value calculated from equation (2). As the temperature decreases from 295 K to 10 K, the time to reach the steady state becomes longer and longer, which indicates that the thermal diffusivity is decreasing with the lowered temperature. The profile of the thermal diffusivity against temperature is discussed in the last
section of this work. To determine the uncertainty of the fittings, different trial values are used for the fitting. It is found that when the trial values are changed by ±10%, the fitting curve deviates obviously from the experimental data. Thus the fitting uncertainty is estimated as 10%, but the real error should be much smaller since we measure each value of thermal diffusivity for more than 30 times and take the average value as the final thermal diffusivity.

4.2.2 The steady-state electro-thermal technique

The thermal conductivity ($\kappa_m$) of GAs is measured using the steady-state electro-thermal (SET) technique from RT to 10 K. When temperature of the sample becomes stable, the governing equation for energy balance can be expressed as:

$$\kappa \frac{\partial^2 T(x)}{\partial x^2} + q_0 = 0 \quad (4)$$

in which $\kappa$ is the effective thermal conductivity which includes the radiation effect, $T(x)$ is the temperature at $x$ position, and $q_0 = \dot{I}^2 R_1 / A_c L$ is the joule heating rate per unit volume. $I$ is the current applied to the sample, $R_1$ is the resistance at the steady state, $A_c$ and $L$ are the cross-section area and the length of the sample respectively. Solving the governing equation, the temperature distribution is obtained as $T(x) = -q_0 (x^2 - Lx) / 2\kappa + T_0$. The average temperature along the sample is $\bar{T}(x) = \int_{x=0}^{L} T(x) dx / L = T_o + q_0 L^2 / 12\kappa$. Thus, the average temperature rise is $\Delta T = \dot{I}^2 R_1 L / 12\kappa A_c$. The temperature change reflects in the resistance change as $\Delta T = \Delta R / (dR/dT)$, in which $\Delta R$ is the resistance change before and after the heating. $dR/dT$ is obtained by differentiating the $R-T$ curve. Figure 4.2.1 (c) shows the $dR/dT$ profiles. Combing the two equations, we obtain the effective thermal conductivity as:
\[ \kappa_m = \frac{I^2 R L}{12 A} \cdot \frac{dR}{dT}. \] (5)

The \( \kappa_m \) should represent the thermal conductivity at steady state, thus the real temperature corresponding to \( \kappa_m \) is: \( T_1 = T_0 + \Delta R/ (dR/dT) \). Figure 4.2.1 (d) shows the measured thermal conductivity of the five samples (three in group 1 and two in group 2). The error is calculated by using the error transfer formula of mathematical statistics.

To subtract the radiation effect, each sample is measured 2-3 times to obtain the thermal diffusivity in different lengths. The sample details are summarized in Table 2. For each group of GA, the thickness, width is the same; the emissivity, specific heat and real thermal diffusivity can be taken equal. From equation (3), the radiation effect in the measured thermal diffusivity is proportional to \( L^2 \) (\( L \): sample length). By plotting the measured thermal diffusivity (\( \alpha_m \)) against \( L^2 \) at each temperature and linear fitting to \( L^2 = 0 \), we are able to subtract the radiation effect and identify the real thermal diffusivity (\( \alpha_{\text{real}} \)). This method has been demonstrated in our previous work.[89] The same method is employed to subtract the radiation effect to obtain the real thermal conductivity (\( \kappa \)) of GAs. The inset in figure 4.2.1 (d) shows one of the linear fitting process for obtaining the real thermal conductivity of GA (group 1 at real temperature of 298.6 K).

### 4.3 Results and Discussion

#### 4.3.1 Extremely low thermal conductivity

The real thermal conductivity of GAs is plotted out in Figure 4.3.1 (a). As is seen in the figure, \( \kappa \) for the two groups are extremely low. At RT, \( \kappa \) is \( 4.7 \times 10^{-3} \) and \( 5.9 \times 10^{-3} \) W·m\(^{-1} \)·K\(^{-1} \) for group 2 and group 1 respectively, which is similar to the reported lowest value for silica.
aerogel at moderate vacuum (0.004 W·m\(^{-1}\)·K\(^{-1}\)). This value is much lower than the disordered, layered WSe\(_2\) crystals\([106]\) (0.05 W·m\(^{-1}\)·K\(^{-1}\) at RT); and microcrystalline [6,6]-phenyl C61-butyric acid methyl ester (PCBM) thin films (0.03±0.003 W·m\(^{-1}\)·K\(^{-1}\) at RT).\[107\] They were reported as the lowest thermal conductivity materials for a full dense solid and has been used as a new insulating material in recent years. As temperature goes down, \(\kappa\) quickly decreases and is lower than 10\(^{-3}\) W·m\(^{-1}\)·K\(^{-1}\) at temperatures below 86 K. At temperature of 46 K, the thermal conductivity of the two groups even decreases to 7.15\(\times\)10\(^{-4}\) and 2.20\(\times\)10\(^{-4}\) W·m\(^{-1}\)·K\(^{-1}\) respectively. The reason that the thermal performance in our report is better compared to Wicklein, \(et\ al\)' anisotropic foams \[35\] is due to the air conduction effect. In our work, the thermal characterization is conducted in vacuum environment (air pressure less than 5 mTorr). Using Maxwell’s model\[108\] for effective thermal conductivity of a mixture, the thermal conductivity of our GA with air conduction effect can be estimated around 25.85 mW·m\(^{-1}\)·K\(^{-1}\). Due to the scattering effect of the cell walls, the mean free path of air within pores is much smaller than that in free space (~200 nm). Thus, the real thermal conductivity should be much lower since the thermal conductivity of air within the pores of GA can be reduced dramatically compared to that in free space. Compared to Fan, \(et\ al\)' work,\[34\] their GA material has a much higher density (16-41 mg·cm\(^{-3}\)) than our GA (4 mg·cm\(^{-3}\)). This is the main reason that the thermal conductivity of our GA is lower.
Figure 4.3.1 (a) The thermal conductivity of the two groups of GAs. The inset shows the \( \kappa \) of pyrolytic graphite for comparison. (b) The intrinsic thermal conductivity of GAs by taking out the porosity effect. (c) The specific heat of the two GA samples. The literature data for graphite and amorphous carbon are also plotted for comparison. The data inside the yellow rectangular is less reliable due to the large data fluctuation at very low temperature. (d) The schematic drawing that illustrates the heat transfer process inside GA. At the interfaces of the flakes, intensive interface-mediated phonon scatterings occur.

The trends of \( \kappa \) are very similar for the two groups. From the \( \kappa \)-\( T \) evolution, \( \kappa \) of group 1 decreases from \( 5.9 \times 10^{-3} \) W\( \cdot \)m\(^{-1}\)\( \cdot \)K\(^{-1}\) at 299 K to \( 4.3 \times 10^{-4} \) W\( \cdot \)m\(^{-1}\)\( \cdot \)K\(^{-1}\) at 36 K; \( \kappa \) of group 2 decreases from \( 4.7 \times 10^{-3} \) W\( \cdot \)m\(^{-1}\)\( \cdot \)K\(^{-1}\) at 299 K to \( 2.2 \times 10^{-4} \) W\( \cdot \)m\(^{-1}\)\( \cdot \)K\(^{-1}\) at 46 K. This is an interesting phenomenon since it is completely contrary to the thermal conductivity of
graphite[90] and our previously reported graphene foam (GF)[109]. The inset in figure 4.3.1 (a) shows the thermal conductivity of pyrolytic graphite[90] for comparison. As seen in the inset, $\kappa$ of graphite generally increases from RT to the peak temperature (normally 100 K), and then decreases after the peak. The peak position is mainly determined by the defect level in the graphite sample. As the perfection and order of the samples improve, the peak shifts to a lower temperature.[96] For our GAs samples, the thermal conductivity for the two groups decrease all the way down to 40 K with some data fluctuation at very low temperatures. This indicates the highly disordered structure in the GA samples. The data at temperatures lower than 40 K should be used with less confidence due to the large data fluctuations. $\kappa$ of group 2 is a little smaller than that of group 1, which is reasonable considering the lower density of group 2 (4.2 mg·cm$^{-3}$ and 3.9 mg·cm$^{-3}$ for group 1 and group 2 respectively).

Based on the model of Schuetz et al.[88] a correlation for the thermal conductivity of porous media has been demonstrated reliable as $\kappa_G = 3\kappa_{GA}/\varphi$. Using this equation, the intrinsic thermal conductivity of GAs without the porosity effect ($\kappa_G$) can be estimated. In this equation, $\kappa_{GA}$ is the thermal conductivity of porous graphene aerogels, and $\varphi = \rho_{GA}/\rho_G$ is the volume fraction of the solid phase in the GAs sample. For group 1 and group 2, the density is measured as 4.2 mg·cm$^{-3}$ and 3.9 mg·cm$^{-3}$ respectively. Using density of graphite $\rho = 2200$ mg·cm$^{-3}$, $\varphi$ of two groups of GAs are estimated as 0.0019 and 0.0018. The porosity of the two samples is accordingly 99.81% and 99.82%. The result of $\kappa_G$ is plotted in figure 4.3.1 (b). From our calculation, $\kappa_G$ is 9.3 W·m$^{-1}$·K$^{-1}$ at RT and decreases to 1.4 W·m$^{-1}$·K$^{-1}$ at 10.4 K for group 1; $\kappa_G$ is lower than 8.0 W·m$^{-1}$·K$^{-1}$ for group 2 at temperature from 46 K to 299 K. This calculation proves the very low intrinsic thermal conductivity of the r-GO framework. In addition to the contribution from the high porosity, the low thermal conductivity of the r-GO framework is
also responsible for the ultralow thermal conductivity of GAs. The intrinsic thermal conductivity of the solid phase inside the GAs is two orders of magnitude lower than the ultra-high thermal conductivity of graphene (~5000 W·m⁻¹·K⁻¹). It has been reported that substitution of just 1% of carbon atoms with nitrogen caused 59.2% reduction in thermal conductivity at 300 K. The N dopants significantly increase the phonon scattering in GA and contribute to the ultralow thermal conductivity. However, large residual nitrogen content inside the GA would sacrifice the mechanical strength of GA.

The specific heat \( (c_p) \) against temperature profile provides more hints about the structure of the GA. \( c_p \) at different temperatures is obtained using the measured thermal diffusivity \( \alpha_m \) and measured thermal conductivity \( \kappa_m \) as \( c_p = \frac{\kappa_m}{\rho \alpha_m} \), in which \( \rho \) is the density of the GA sample. Figure 4.3.2 (c) shows the average specific heat from two groups of GAs compared with that of high-purity Acheson graphite,[94] diamond-like carbon films (DLC) and amorphous carbon (AC).[110] As temperature goes down from RT to 45 K, \( c_p \) of GA decrease linearly in both cases. The trends and slopes are both very similar to that of graphite. As temperature goes to zero, the specific heat should go to zero. The pattern at very low temperature is similar to that of organic materials.[111] The data below 45 K goes up a little, which is due to the error resulting from large data fluctuation at very low temperatures. The \( c_p \) of GAs is a little higher than that of graphite.

The difference between the value of GAs and graphite are largely attributed to two factors: the error in the GAs’ density measurement and the difference between the structure of r-GO and that of highly oriented graphite. The unavoidable error when measuring the size of the GA films could result in errors of the density, which makes the specific heat value overestimated. Besides, the XPS result indicates there are many extra atoms including oxygen
and nitrogen and functional groups at the surfaces of GAs, which distort the atomic positions and increase the structure disorder. Thus, the structure of the GAs is different from that of graphite. There have not been any experimental measurements about the specific heat of reduced graphite oxide to our best knowledge. In literatures, \( c_p \) of GO has always been assumed similar to that of graphite\[112\] or amorphous carbon.\[113\] Our \( c_p \) for GAs is very close to the value for DLC and AC. From the XRD spectra, the peaks of GAs are wide and not obvious. This suggests that the GAs are not well-crystallized graphitic material and contains large quantity of amorphous structure. It has been reported that the specific heat of amorphous materials exceeds that of the crystalline form.\[114, 115\] The much more amorphous structure of GAs than the highly ordered Acheson graphite could also contribute to the higher heat capacity of GAs. The different microwave heating time (2 minutes for group 1 and 4 minutes for group 2) leaves the two groups of samples with different amount of nitrogen-containing groups.\[97\] Microwave heating removed more functional groups for group 2, which results in a larger \( c_p \) of group 1 than that of group 2.

4.3.2 Thermal diffusivity and reffusivity of graphene aerogel

Figure 4.3.1 (d) presents the schematic drawing of the heat transfer mechanism inside the GA. Thermal transport inside GA is controlled by phonons transport among r-GO sheets. During the transport, phonons are not only scattered within single flake by phonons, defects and grain boundaries, but also scattered at the interfaces of neighboring r-GO flakes. The r-GO sheets are self-assembled driven by the increasing hydrophobicity and the \( \pi-\pi \) interaction among r-GO sheets during the chemical reduction. The interface between the r-GO sheets is through \( \pi-\pi \) interaction with small bonding areas. The scattering intensity at interfaces can be very high.
To better understand the underlying mechanism for the ultralow thermal conductivity, the thermal diffusivity of GAs at different temperatures is measured and analyzed. Figure 4.3.2 (a) shows the real thermal diffusivity of the two groups of GAs samples. From RT to low temperatures, both \( \alpha \) change with temperature very slowly in a small scale. \( \alpha \) of group 1 decreases from \( 8.46 \times 10^{-7} \) m\(^2\)/s at 297 K to \( 3.0 \times 10^{-7} \) m\(^2\)/s at 10 K; \( \alpha \) of group 2 ranges from \( 1.62 \times 10^{-6} \) m\(^2\)/s at 297 K to \( 8.3 \times 10^{-7} \) m\(^2\)/s at 45 K. The decrease of \( \alpha \) is relatively trivial compared to the previously reported thermal diffusivity change of graphene foam (GF)[109] and pyrolytic graphite[90] [Figure 4.3.2 (a)]. As shown at the bottom panel of figure 4.3.2 (a), \( \alpha \) of GF and graphite follows a quick increasing behavior as temperature goes down, and finally becomes stable. In contrast, both \( \alpha \) of our GAs stay almost constant with a small decrease in the low temperature range. This result uncovers a completely different dominant thermal transport mechanism, distinguishing our GAs from other graphene-based materials. We speculate that the main effect controlling the thermal transport is the thermal contact resistance, rather than the phonon-phonon scattering. From single relaxation time approximation, a classical model for phonon thermal conductivity can be expressed as: \( \kappa = \frac{1}{3 \rho c_p \nu^2 \tau} \). Here, \( \nu \) is the effective and averaged phonon velocity. \( \tau \) is an averaged relaxation time for phonon scatterings, inversely proportional to phonon scattering intensity. This equation can be expressed in terms of thermal reffusivity (inverse of thermal diffusivity) as: \( \alpha^{-1} = \frac{3}{\nu^2 \tau} = \Theta_0 + \frac{3}{\nu^2 \tau_u} \), in which \( \Theta_0 \) is the residual thermal reffusivity (induced by defects), and \( \tau_u \) is the relaxation time from Umklapp scattering.
Figure 4.3.2 (a) The thermal diffusivity of the two groups of GAs compared with that of graphene foam (GF) and pyrolytic graphite. (b) The electrical resistivity against temperature for the five GA samples. The linear $\rho_e - T$ data of graphene foam is also plotted at the bottom panel for comparison.
As temperature goes down, the phonon population participating in the Umklapp scattering drops with the decreasing temperature, resulting in an increased $\tau_u$ correspondingly. As temperature approaches absolute zero, the Umklapp scattering term vanishes, and $\alpha^{-1}$ reaches a constant value $\Theta_0$, which is controlled by the residual defect and boundary scattering. For GF and graphite, the thermal contact resistance at interfaces is relatively small due to their continuous and covalently bonded structure. Umklapp scattering of phonons mainly controls the thermal transport. Thus, their $\alpha$ first increases and then becomes stable when temperature goes down to the 0 K limit. This phenomenon was also observed in other bulk materials, such as DNA, silicon, germanium, NaCl and NaF.\[72\] In contrast, for GAs, the r-GO sheets are self-assembled during the chemical reduction. The contacting areas of one flake with both the medium and neighboring flakes are small. In addition, the connecting mechanism among the neighboring self-assembled r-GO sheets is mainly $\pi-\pi$ interaction, which is a weak electrostatic interaction between aromatic rings. Therefore, the thermal contact resistance at the interfaces between flakes is much larger.

A model for heat transfer in GA can be expressed as: $l_f/\kappa_{eff}=l_f/\kappa_c + R$, where $l_f$ is the average flake size, $\kappa_{eff}$ is the effective thermal conductivity of GA, and $\kappa_c$ is the thermal conductivity within r-Go flake, which includes the grain boundary thermal resistance. $R$ is the interfacial thermal contact resistance between neighboring flakes. Multiplying the specific heat $\rho c_p$ of GAs at both sides, we can express the equation in terms of thermal diffusivity as $\alpha_{eff}^{-1} = R\rho c_p l_f + \alpha_c^{-1}$, where $\alpha_{eff}$ is the effective thermal diffusivity and $\alpha_c$ is the intrinsic thermal diffusivity of r-GO flake. Combining the above thermal diffusivity equation, an expression can be deduced for the thermal contact conductance at interfaces: $R \approx A/\rho c_p\nu$, where $A$ is a constant. When the thermal contact resistance at interface is very large: $R \gg l_f/\kappa_c$, the equation can be
simplified as $\alpha_{eff} = A_v l_f$, in which the phonon velocity $v$ and $l_f$ are weakly temperature dependent. Thus, the thermal diffusivity of GAs stays almost unchanged. The dominating mechanism controlling thermal transport in GAs is the interfacial thermal contact resistance among the flakes.

In spite of the above analysis, there is still a small decrease in the thermal diffusivity of GA with decreased temperature. We ascribe this decrease to the thermal expansion and thermal radiation among the r-GO sheets inside GAs. As shown at the bottom panel of figure 4.3.2 (b), $\rho_e$ of GF is inversely proportional to the temperature as expected,[109] which is the common behavior of graphene based material. $\rho_e$ of GAs is very much different from the electrical resistivity of GF. As plotted in Figure 4.3.2 (b), $\rho_e$ presents a nonlinear increasing behavior and increases exponentially with reduced temperature at low temperatures. The fast increasing electrical resistivity of GAs at low temperatures indicates the worsened contact among the r-GO sheets due to the temperature decrease. The aggravated contact inevitably increases the thermal and electrical contact resistance. The r-GO sheets are self-assembled during the chemical reduction. The connection among sheets is randomly oriented and stress-balanced. While as temperature goes down, the thermal expansion of the r-GO sheets results in thermal strains inside the samples. The expansion deteriorates the contact among r-GO sheets and contributes to the decreasing thermal diffusivity consequently. In addition, the radiation effect inside the pores could also contribute to the decreasing thermal diffusivity of GAs. Pores from tens to hundreds of micrometers are formed within the r-GO framework. Within these pores, thermal radiation occurs among the neighboring r-GO sheets. The radiation irradiance follows a behavior of $j^* = \varepsilon \sigma T^4$. As temperature goes down, the radiation energy flux decreases by $\sim T^4$, so the thermal conductivity contribution from radiation decreases by
$\sim T^3$, which is faster than the specific heat of GAs (linear relation with $T$). This results in that part of effective thermal diffusivity decreases by $\sim T^2$. The evident separation of the two groups’ data further proves the structure difference for the two groups of GAs. $\rho_e$ for samples of group 1 is obviously larger than that of group 2, further indicating the more defected structure of group 1 GAs. Besides, the variation of $\rho_e$ for group 2 at low temperatures is relatively small, which proposes that the contact deterioration has smaller effect to group 2 than group 1. This further demonstrates the different defect levels between the two groups of samples, which we also observe in the thermal conductivity profile.
CHAPTER 5 SWITCH ON THE HIGH THERMAL CONDUCTIVITY OF GRAPHENE PAPER

This chapter reports on the discovery of ultra-high thermal conductivity ($\kappa$) switch-on phenomenon in high purity graphene paper (GP) when its temperature is reduced from room temperature down to 10 K. The $\kappa$ after switch-on (1732 to 3013 W m$^{-1}$ K$^{-1}$) is 4~8 times that before switch-on. The triggering temperature is 245~260 K. The switch-on behavior is attributed to thermal expansion mismatch between pure graphene flakes and impurity-embedded flakes. This is confirmed by switch behavior of the temperature coefficient of resistance. Before switch-on, the interactions between pure graphene flakes and surrounding impurity-embedded flakes efficiently suppress phonon transport in GP. After switch-on, the structure separation frees the pure graphene flakes from the impurity-embedded neighbors, leading to several-fold $\kappa$ increase. The measured $\kappa$ before and after switch-on is consistent with the literature reported $\kappa$ values of supported and the suspended graphene. By conducting comparison studies with pyrolytic graphite, graphene oxide paper and partly reduced graphene paper, the whole physical picture is illustrated clearly. The thermal expansion induced switch-on is feasible only for high purity GP materials. This finding points out a novel way to switch on/off the thermal conductivity of graphene paper based on substrate-phonon scattering.

5.1 Graphene Paper Structure

The graphene paper material was purchased from graphene supermarket and used as received. Figure 5.1.1 shows the morphology and structural characterization of the GP material. Figure 5.1.1 (a) and (b) show the image of GP under a scanning electron microscope (SEM) with 500× magnification. The GP presents a grey color under SEM. The top layer shows
a seamless surface with small ridges. From Fig. 5.1.1 (b), the stacking layered structure can be seen clearly. The top layer can be peeled off, which demonstrates the strong planar and weak interlayer bonding force. The inset in Fig. 5.1.1 (a) presents a contact mode Atomic-force microscopy (AFM) topology image (MicroNano AFM 3000) of GP. The average height variation of surface along the blue line shown in the 0.6×0.6 μm scanning area is about 0.23 nm, which illustrates the high smoothness of GP. The inset in Fig. 5.1.1 (b) is a digit image of GP. As shown in the inset, the GP is grey with metallic luster, which is the typical color of high purity graphene material.[48] The GP is very flexible and can be easily bent and recovers.

The Raman spectra of GP shown in Fig. 5.1.1 (c) exhibits two pronounced peaks at 1581 and 2719 cm\(^{-1}\), corresponding to the G peak and 2D peak. The D peak is invisible while the G peak is very sharp, which indicates the rare defects and the high crystallinity of graphene sheet. In order to identify the number of layers in the graphene sheet, Raman spectra is obtained at 30 different locations on a GP sample. By integrating the G peak and 2D peak, the ratio of the intensity of G peak to 2D peak is estimated as 0.61-0.72, which corresponds to 5-6 layers of graphene.[78] For comparison, the \(I_G/I_{2D}\) of highly oriented pyrolytic graphite (HOPG) is about 0.85.[78] The inset in Fig. 5.1.1 (c) presents the x-ray diffractometer (XRD, Siemens D500 x-ray diffractometer using Cu x-ray tube) of GP. The sharp and distinct peak around 26.6 degrees 2θ corresponds to the (002) plane, from which the interlayer spacing of GP is determined to be 3.35 Å. For pristine natural graphite, the interlayer distance is also 3.35 Å.[116] This result demonstrates that the GP has high purity and excellent ordered structure. The amount of functional groups or other structural impurities is very small.
Figure 5.1.1 Morphology and structure characterization of GP sample. (a) and (b): SEM images. The inset shows an AFM topology image. (c) The Raman spectrum. The inset shows the XRD spectrum. (d) x-ray photoelectron spectra. The inset shows the XPS F 1s spectrum. (e) The XPS C 1s spectrum, indicating different bonds for carbon atoms in GP sample. (f) The XPS O 1s spectrum, suggesting the residual oxygen-containing functional groups.
To further characterize the chemical composition of GP, x-ray photoelectron spectrometer study (XPS) is conducted. Figure 5.1.1 (d) presents the XPS survey of the GP. The resulting elemental composition of the GP is C 1s (98.91%), O 1s (0.66%), and F 1s (0.43%), which indicates that the GP is composed of highly purified graphene films. The inset in Fig. 5.1.1 (d) shows the narrow scan spectrum of F 1s. A prominent peak at 689.5 eV indicates the presence of the C-F bond on the surface of the GP.[117] Figure 5.1.1 (e) is the narrow scan spectra of C 1s. The C 1s spectra main peak can be deconvoluted into mainly four components: C-C at 284.6 eV, C-O at 285.4 eV, C=O at 287.9 eV and π-π* transition at 290.5 eV.[118, 119] The C-C peak is dominant in the C 1s main peak. Figure 5.1.1 (f) shows the deconvoluted narrow scan of O 1s. Two peaks can be fitted into C-O at 531.4 eV and C=O at 532.7 eV. The above analysis concludes that the GP is highly carbonized graphene with very small amount of oxygen (0.66%) and fluorine (0.43%) containing functional groups. The F amount in GP is very small. From literatures review about the synthesis process of GP,[48, 49] we feel that the residual trace of F element originates from the graphene oxide material which is used for the synthesis of the final GP material.

5.2 Switch On: Analyzed Using Thermal Diffusivity and Reffusivity

5.2.1 Thermal diffusivity switch-on observation and physics

Two graphene paper samples are measured using TET from RT to 10 K in this work. The details of the sample are summarized in table 3. Figure 5.2.1 (a) shows the schematic of the experiment set-up. A microscopy image of one of the samples is also presented.
Table 3 Details of the GP, GOP and PRGP samples measured in this work.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>index</th>
<th>Length [mm]</th>
<th>Width [mm]</th>
<th>Thickness [µm]</th>
<th>Density [kg/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP</td>
<td>S1</td>
<td>16.7±0.1</td>
<td>0.28±0.05</td>
<td>28.6±1.0</td>
<td>1623±66</td>
</tr>
<tr>
<td>GP</td>
<td>S2</td>
<td>18.5±0.1</td>
<td>0.20±0.03</td>
<td>28.6±1.0</td>
<td>1623±66</td>
</tr>
<tr>
<td>PRGP</td>
<td>S1</td>
<td>2.3±0.06</td>
<td>1.1±0.06</td>
<td>17.3±2.5</td>
<td>1466±212</td>
</tr>
<tr>
<td>PRGP</td>
<td>S2</td>
<td>1.3±0.07</td>
<td>0.5±0.01</td>
<td>17.3±2.5</td>
<td>1466±212</td>
</tr>
<tr>
<td>PRGP</td>
<td>S3</td>
<td>1.4±0.05</td>
<td>0.2±0.01</td>
<td>17.3±2.5</td>
<td>1466±212</td>
</tr>
<tr>
<td>GOP</td>
<td>NA</td>
<td>1.1±0.01</td>
<td>0.2±0.002</td>
<td>33.6±2.1</td>
<td>1357±117</td>
</tr>
</tbody>
</table>

A. Observation of thermal diffusivity jump

Figure 5.2.1 (b)-(c) shows the V-t raw data and the theoretical fitting of TET measurement of S2 at six different temperatures: 295 K, 245 K, 220 K, 210 K, 195 K and 75 K. During the TET experiment, a current of 160~280 mA is used, so as to make sure the voltage change due to joule heating takes only about 1.3% of the total voltage. The temperature increase of the sample is about 2.6 K at 10 K to about 23.5 K at 295 K. From 295 K to 195 K, the TET signals present a very interesting evolution. At RT, the voltage of the sample presents an increasing behavior with the joule heating and then becomes stable, which is a typical TET signal for materials with a positive TCR. As the temperature goes down to 245 K, a small decreasing part emerges at the beginning of the TET signal, after which the signal increases and becomes stable. From 245 K to 210 K, the decreasing part develops and begins to dominate the entire TET signal. As temperature goes down to 195 K, the TET profile monotonically decreases and then reaches steady state, which is similar to the TET signal of other graphene based materials.[10, 120] These data indicate that from RT to low temperature, the TCR of GP changes from positive to negative. This TCR change will be elaborated by the R-T study below.
Figure 5.2.1 (a) The schematic of four-probe TET experiment and sample set up in the cold jacket of CCR system. Four-probe $I$-$V$ measurement is employed in the experiment to avoid the influence of contact resistance. (b)-(c) The evolution of voltage against time for S2 at different temperatures. As temperature goes down, the profile transforms from pure voltage increasing to pure voltage decreasing pattern.

To fit the TET raw data, two different fitting models are used. The fitting for the monotonically increasing or decreasing TET signals are based on the theoretical model of equation (2) in the experimental detail section and conducted with MATLAB programming.[121] When the increasing part and decreasing part are both observed, a new
A theoretical model is constructed to characterize the new phenomenon. In this model, $\alpha_1$ and $\alpha_2$ are two different thermal diffusivities corresponding to two simultaneous heat transport mechanisms in GP. The terms in the square brackets are the simplified form of equation (2). Therefore, the new model assumes two simultaneous heat transport processes in GP and considers them to be independent. A linear relationship is used for summarizing the contribution of the two-independent heat transport. The physical principle for the model is elaborated in the next section. From Fig. 5.2.1 (b)-(c), the model gives excellent fitting for the $V$-$T$ raw data. The resulting $\alpha_1$ and $\alpha_2$ values are also presented in each temperature. Different trial values of $\alpha$ is used for the fitting. The fitting error is determined to be ±10% or better, which has been studied carefully in our previous work on the TET technique.[89, 122]

B. Thermal diffusivity switch-on: results

The measured thermal diffusivity of the two samples denoted as S1_round1, S1_round2 and S2 is presented in Fig. 5.2.2 (a). Two separate data groups are observed for all the three samples. The lower thermal diffusivity group is denoted as $\alpha_1$, and the higher thermal diffusivity group is denoted as $\alpha_2$. As illustrated above, $\alpha_1$ and $\alpha_2$ are two different thermal diffusivities corresponding to two thermal transport states in GP samples. $\alpha_1$ ($3.68 \times 10^{-4} \sim 5.57 \times 10^{-4}$ m$^2$ s$^{-1}$) is much lower than $\alpha_2$ ($1.92 \times 10^{-3} \sim 6.49 \times 10^{-3}$ m$^2$ s$^{-1}$). Before switch-on, $\alpha_1$ dominates the thermal transport in GP. As temperature goes down, $\alpha_1$ decreases slowly. The jumping of thermal diffusivity from $\alpha_1$ to $\alpha_2$ starts at about 245-260 K for all the three samples.
Figure 5.2.2 (a) The thermal diffusivity of GP. (b) The resistance against temperature profile of GP. (c) The schematic drawing illustrates the reversible structure separation process. (d) The thermal reffusivity of GP after switch-on. (e) The thermal reffusivity of GP before switch-on.
From 245 K to 195 K, there are two different thermal transport phenomena coexisting in GP, corresponding to $\alpha_1$ and $\alpha_2$ in the TET fitting model. The resulting $\alpha_1$ and $\alpha_2$ are both presented in the figure. At a same temperature point, $\alpha_2$ is about 5-8 times higher than $\alpha_1$. After switch-on, the TET signal is pure voltage decreasing. $\alpha_2$ becomes a dominant thermal transport mechanism in GP. From 195 K to 10 K, $\alpha_2$ increases with the decreased temperature rapidly from 260 K to 75 K. Below 75 K, $\alpha_2$ becomes relatively stable. The $\alpha_2$-$T$ profile is very similar to that of GF and graphite.[10] There is a dropping of $\alpha_2$ for S2 at 45 K to 10 K. It might be resulted from loosen connecting between S2 and the electrodes at very low temperatures. Since the sample's resistance is small [as shown Fig. 5.2.2 (b)], a small connection degradation will affect the results. In this section, our focus is the ultra-high thermal diffusivity switch-on. The variation trend of thermal diffusivity against temperature will be analyzed and explained following the thermal reffusivity concept in the next section.

C. Mechanisms of thermal diffusivity jump

For the two thermal transport mechanisms, we ascribe $\alpha_1$ to the graphene flakes subjected to substrate phonon scattering by neighboring flakes and $\alpha_2$ to the suspended portion of graphene flakes. The jump of thermal diffusivity from $\alpha_1$ to $\alpha_2$ is due to the separation of the graphene flakes induced by temperature reduction and TEC mismatch. Figure 5.2.2 (c) shows the schematic of the structure separation in GP due to temperature reduction and thermal expansion mismatch. At high temperatures (295 K-245 K) where the graphene flakes are stacked with small inter-flake distance, the graphene flakes can be regarded as supported graphene on a substrate of neighboring graphene flakes. From XPS analysis, GP consists of about 0.66% O and 0.43% F. Although theses impurities account for a very small proportion
of the chemical composition, they could provide large scattering effect for phonons. The phonon propagation along the in-plane direction is largely impeded by those extra atoms. For pure graphene flake domain, the neighboring flake scattering effect limits \( \alpha_1 \) to a great extent by phonon-substrate interaction.[17, 21, 22]

The pure graphene flakes in GP present a negative thermal expansion coefficient at near RT according to the experiment and numerical calculation.[123] Huang et al. studied the disorder-induced thermal contraction in functionalized graphene. They found that the functionalization suppresses (enhances) the thermal contraction (expansion) of the lattice, due to the increase in the system mass, membrane thickness, and the compressibility of phonons.[124] GP in our work consists of about 0.66% O and 0.43% F. The impurities-embedded flakes in GP are expected to present a less negative or even positive thermal expansion coefficient. As temperature goes down, the discrepancy of thermal expansion between pure graphene and impurity-embedded flakes results in biaxial tensile in impurities-embedded flakes and compressive strain in pure graphene flakes. Although the tensile strain in impurities-embedded flakes could improve the thermal transport a little as indicated in Kuang et al.’s work,[11] the compressive strain in pure graphene flakes reduces \( \kappa \) as reported in literatures.[125, 126] Since the pure graphene flakes play a dominant role in the thermal transport of GP, the overall \( \kappa \) of GP presents a slow decreasing pattern as the thermal strain built up by lowered temperature. The thermal strain builds up as temperature goes down, but without structure separation. Although graphene itself has a negative TCR, the compressive strain in graphene will make its electrical resistance decrease against reduced temperature. This effect is stronger than the intrinsic TCR of graphene, leading to an overall positive TCR. The positive TCR of graphene under strain has been observed and studied in our previous work, in
which the thermal strain due to the thermal expansion mismatch between graphene and PMMA substrate resulted in a positive TCR of graphene. When the thermal expansion mismatch becomes smaller at low temperatures, the effect of intrinsic negative TCR of graphene becomes more significant. As a result, the TCR becomes less positive. When graphene and PMMA separate at low temperature, the TCR went back to negative.[127] The positive TCR of graphene on substrate is also reported in other literatures. Pang et al. reported an increasing positive TCR of polymer/graphene composite thermally treated at 180 °C.[128] Therefore, when strain effect exceeds the intrinsic TCR effect, the TCR of graphene becomes positive. That is why we observed a resistance increase during TET heating, like that at 295 K. This type of overall positive TCR for supported graphene is also observed in our work for few-layered graphene supported on poly (methyl methacrylate) (PMMA) and studied in detail.[127] Therefore, at this state, the TET signal presents a pure voltage-increasing pattern. The thermal diffusivity is entitled $\alpha_1$.

As temperature goes down, curvatures first develop for the graphene flakes. When temperature is further lowered down, the increasing thermal strain causes a significant TEC mismatch among pure graphene flake and the impurity-embedded flakes. The two materials separate, as shown in Fig. 5.2.2 (c). The thermal diffusivity of this state is $\alpha_2$. At this state, since the graphene is strain free, strain-induced electrical resistance change disappears. As a result, the TCR of the sample is more controlled by the intrinsic TCR of graphene, which is negative. Therefore, a decrease of the electrical resistance is observed in TET heating, as is shown in the TET experiments at 195 K and 75 K in Fig. 5.2.1 (c). This kind of high temperature positive TCR transfer to negative TCR at reduced temperatures was also observed for PMMA-supported graphene, and has been explained in detail in our work.[127] The
thermal diffusivity of this state $\alpha_2$ is expected to be much higher than $\alpha_1$ since the graphene flake is not or much less subjected to substrate phonon scattering.

D. Physics behind two-style V-t curve in TET

For the two-style V-t curve (first decreasing, then increasing) in TET experiment at 245 K, 220 K, and 210 K, they can be explained as below. At 245 K, since this temperature is not very low, although the graphene flake separates from the neighboring substrate, this separation is not in large-scale. The free-standing part in graphene flakes still plays a dominant role for phonon propagation at the beginning of thermal transport. Thus, at the beginning of the TET heating, the sample shows a negative TCR, as observed in the figure for the voltage decrease. But after the sample is heating up by the electrical current a little bit, its temperature goes up. Subsequently, the graphene flakes thermally contract, which reverses the already existing structure separation. As a result, the graphene flakes are in contact with the impurity-embedded flakes again. The overall sample's TCR becomes positive again and its thermal diffusivity goes down. That is the reason when we do the TET two-step heat transfer, the voltage decreasing part gives a very high thermal diffusivity ($\alpha_2$), which represents the state of graphene separated from the neighboring flakes. The voltage increasing part gives a lower thermal diffusivity ($\alpha_1$), which represents the state that the graphene flakes are in sound contact with the neighboring flakes. When temperature is reduced further from 245 K, as presented at 220 K, it requires more heating in TET to reverse the structure separation state. Thus, an increased contribution of the voltage decreasing part is observed from 245 K to 220K. This part makes more contribution in the case of 210 K. When temperature is reduced more, the voltage decreasing part dominates all the heat transfer process. As the pure graphene flakes are completely
separated from the impurities-imbedded graphene flakes, the structure-separation cannot be reversed any more during the TET heating cycle. From 195 K to 10 K, the phonon scattering intensity decreases with the decreasing temperature, which is controlled by the phonon population and interface scattering.

Our above analysis is also backed up by the observation of the electrical resistance change against temperature. Figure 5.2.2 (b) shows $R_0$ (electrical resistance before TET heating) against environmental temperature $T_0$. In the region close to RT, although not obvious, $R$ decreases with decreased $T$ slowly. The built-up compressive strain in the graphene flakes induced by temperature reduction decreases its electrical resistance. When the temperature is reduced more, this trend changes to a completely negative TCR relation. Also this TCR is quite constant, featuring an almost linear $R$-$T$ relation, which is very similar to the graphene foam we studied before.[10] The $R$-$T$ curve is also in accordance with the dominating role shifting from $\alpha_1$ to $\alpha_2$ at certain temperatures. GP has an extremely high electrical conductivity of about $4.4 \times 10^4$ S/m at RT. For S2, an evident valley value is observed at around 220 K. From 295 K to 220 K, $R_0$ drops from 3.07 $\Omega$ to 3.043 $\Omega$; from 220 K to 10 K, $R_0$ begins to increase as $T_0$ goes down. The $R_0$-$T_0$ behavior agrees with the increasing and decreasing part of the TET profiles respectively. For S1_round1 and S1_round2, although the $V$-$T$ signals in TET experiment present a positive-to-negative TCR changing behavior, the TCR of $R_0$ does not show any evident valley value. Instead, a changing slope of $R_0$ occurs at 170 K for S1_round1 and at 220 K for S1_round2. These changing points are both in accordance with the switch-on temperature of thermal diffusivity for the two rounds of S1 respectively.

The reason why the valley value is not evident is attributed to the base heating/cooling effect. During TET signal collecting, only the GP sample is heated and the base is kept at a
constant temperature. However, the $R_0-T$ profile is obtained by changing the temperature of the whole environment including the sample base. Under this situation, the electrical contact resistance between GP and electrodes could be affected by the changing temperature, which also contributes to the $R_0$ profile. Since the resistance of GP is very small, even a small contact resistance variation could have large influence over the resistance change. In addition, S1 has a relatively higher thermal diffusivity than that of S2 for the whole temperature range. This indicates that S2 might contain higher density of impurities than that of S1. The triggering temperature of S2 is higher than that of S1. This implies that at the same temperature, S2 is endowed with higher thermal stress which exceeds the VdW force among the flakes and facilitates the flakes separation. Under this situation, the thermal strain effect in resistance of S2 is more evident than that of S1, which results in a clear valley value near the triggering temperature.

5.2.2 Structure evolution revealed by thermal reffusivity

We intend to use the thermal reffusivity theory to study the structure of the GP and compared it with that of graphene foam and graphite which we reported in our previous work.[10]

Figure 5.2.2 (d) shows $\Theta$ of GP after ultra-high thermal transport switch-on. Since the error bars for $\alpha$ are already given in Fig. 5.2.2 (a), the error bars for $\Theta$ are omitted for clarity. $\Theta$ decreases as temperature goes down. As temperature decreases to 95 K, $\Theta$ of the three GP samples becomes stable at around 200 s/m$^2$. For S2, there is a sudden jump of the data at 45 K. It could be resulted from the electrode connecting loose of the sample at very low temperatures. Evidently, the pattern of $\Theta$ for GP after switch-on is similar to that of graphene foam, graphite and most of the crystallite materials.[10, 129] In our previous work, it was
found that for most materials, Θ decreases with decreased temperature and finally reaches a stable residual value, just like the normal electrical resistivity behavior of metals. It is well-known that ZA phonons with a smaller wavenumber are far more prevalent in the thermal transport of graphene. Therefore, normal scattering (N-scattering) of ZA phonon is strong compared to Umklapp scattering.[54, 73, 74] At near RT, the N-scattering dominates the phonon scattering for mono-layered graphene, multi-layered graphene and graphite of μm size especially at low temperatures (10 K ~300 K). As temperature goes down, lattice elastic vibrations weaken and the phonon population drops. The intensity of the N-scattering decreases subsequently, which results in the decreasing thermal reffusivity. At low temperatures, the N-scattering finally diminishes to a negligible level. The residual thermal reffusivity (Θ₀) is determined by the impurities and the defects scattering in the sample.

The three groups of experiment data are fitted using the thermal reffusivity model, which is expressed as .[10] In this model, Θ₀ is induced by the boundary and defects scattering of phonon, and it is assumed to be independent of temperature. θ is the Debye temperature, and C is a constant parameter. By fitting with OriginPro, the resulting Θ₀ is 195 ±20 s/m² by averaging the three GP samples. Using the phonon velocity of 9171 m s⁻¹, the in-plane structure domain size of GP is estimated as µm.

The Debye temperature of GP is determined as 610 ±233 K. Many studies calculated high Debye temperature values for graphene, which is above 1000-2000 K.[59, 130, 131] For the three acoustic modes in graphene, the corresponding Debye temperature is 2840 K for the longitudinal mode (LA), 1775 K for transverse mode (TA) and 1120 K for the flexural acoustic (ZA).[27] Theoretical calculations suggested that ZA phonon dominates the thermal transport in graphene.[21, 27, 132] For few-layered graphene, the out-of-plane acoustic phonons still
dominates the thermal conductivity.[133] From our previous work, the calculated Debye temperature for pyrolytic graphite is very close to that of ZA mode. In this work, the Debye temperature of GP calculated from the thermal reffusivity model is much lower than the literature values. This discrepancy could be attributed to the structure change of GP at low temperatures. From our thermal reffusivity model, one assumption is that the phonon scattering intensity due to impurities and boundaries is independent of temperature. Only under this circumstances, $\Theta_0$ can be considered as a constant. However, GP experiences thermal expansion among flakes which distorts the shape and size of contacting area. The change of the inner structure of GP with temperature results in a large increase of boundary scattering intensity. As a consequence, $\Theta_0$ is overestimated. The higher $\Theta_0$ leads to significant underestimation of $\theta$ from the model. Therefore, our estimate should be taken as a lower bound of the magnitude of the Debye temperature.

Before ultra-high thermal transport switch-on, $\Theta$ of GP decreases slowly with temperature [see Fig. 5.2.2 (e)], which is completely different from the trend of graphite. This phenomenon illustrates that the thermal expansion and lattice strain among the graphene flakes has a major influence on thermal transport near RT (295 K- 170 K). Thermal expansion contributes to thermal resistance, particularly at high temperatures.[134] The compressive thermal strain degrades the thermal contact among graphene flakes. As a result, the phonon scattering intensity increases as the temperature goes down before switch-on.

5.3 Thermal Conductivity: Switch-On

Using specific heat of graphite and the density of the GP, the thermal conductivity of GP is calculated. Although the structure of GP and graphite are different, the difference of the specific heat between them is expected to be small. GP is made of high purity graphene.
There are no experimental data of the specific heat of graphene to our best knowledge. From literatures, the low-temperature specific heat of graphene is expected to be a little higher than that of graphite due to the contribution of low-frequency ZA phonons. Above 100 K, graphene has an identical specific heat as that of the graphite.[8] The computer modeling result of the specific heat of graphene are presented in figure 5.3.1 (a). The interlayer spacing of GP is similar to that of graphite (3.35 Å). The deviation resulted from ZA mode phonons in 5-6 layers’ graphene in GP is expected to be smaller than that of single layered graphene.[135] The specific heat of GP should be similar to that of graphite. Therefore, it is physically reasonable to use the experimental data of graphite as the specific heat of GP. The experimental data of specific heat of graphite[94] and the numerical calculation result of SLG is plotted in Fig. 5.3.1 (a) for comparison purpose. The density measurement is conducted by measuring the weight and volume of a GP sample. Using an analytical balance (Radwag xA 82/220/2X), the weight of the to-be-measured GP sample is 120.92 ± 0.04 mg. The sample dimension is 5.02 cm ×5.19 cm ×28.6 μm. The thickness of the sample is measured using a screw thread micrometer. The measured volume is 74.51 ± 2.51 mm³. Thus, the density of GP is determined as 1623 ± 55 kg/m³.
Figure 5.3.1 (a) The experimental specific heat data of graphite and the calculated specific heat data of single-layered graphene from literature for comparison.[8] This experimental data of graphite is used for calculating the thermal conductivity of GP. (b) The switch-on of the thermal conductivity of two GP samples. At low temperatures, $\kappa$ presents a $T^{1.5}$ trend as shown by the solid black line in the figure. The literatures reported thermal conductivity of graphene is presented in the figure to help the readers better understand the level of our thermal conductivity. The thermal conductivity of our GP should be lower than that of graphene due to the intrinsic structure phonon scattering. The black solid circles, solid square and hollow triangle are the literatures reported $\kappa$ for suspended mechanically exfoliated mono-layered graphene.[20, 136] The black solid upward triangle and downward triangle are literature $\kappa$ of suspended isotopically pure $^{12}$C (0.01% $^{13}$C) graphene and 99.2% $^{13}$C graphene respectively.[7] The orange solid circle present reported $\kappa$ of supported mono-layered graphene.[17, 137] The orange triangles are $\kappa$ of supported three-layered graphene.[50]

Figure 5.3.1 (b) shows the measured thermal conductivity of GP. $\kappa$ of the three samples present similar values and patterns. In the temperature range of about 260 K to 170 K, an
evident jump of $\kappa$ from about 500 W m$^{-1}$ K$^{-1}$ to about 2200 W m$^{-1}$ K$^{-1}$ is observed. From RT to the triggering temperature, $\kappa$ of the three data groups are slowly decreasing from 634 W m$^{-1}$ K$^{-1}$ to 246 W m$^{-1}$ K$^{-1}$. For S1_round1 and S1_round2, switch-on of $\kappa$ starts at 245 K and complete at 170 K and 195 K respectively. For S2, the switch-on occurs at 260 K to 210 K. Upon switch-on, $\kappa$ becomes 4.13-7.95 times the $\kappa$ before switch-on at the same temperature. As temperature continues to goes down, $\kappa$ of the three samples exhibits a rapid reduction. At very low temperatures (45 K to 10 K), $\kappa$ continues to decrease with a reduced rate from 148-372 W m$^{-1}$ K$^{-1}$ at 45 K to 4.4-9.4 W m$^{-1}$ K$^{-1}$ at 10 K. From 10 K to 95 K, $\kappa$ follows a power temperature trend of $T^{1.5}$, as shown in Fig. 5.3.1 (b). This indicates the dominating phonon scattering in GP becomes defects and boundary scattering.[138] To check if the switch-on is a reversible process or not, S1_round2 is conducted as a repeated experiment of S1_round1 using the same sample. From Fig. 5.3.1 (b), the result of round2 mostly coincides with that of round1, which indicates that the switch-on of GP is reversible. The switch-on does not change the structure of GP permanently. When temperature is increased back to RT, the separation among the graphene flakes disappears and the structure returns to the original contacting state. When temperature goes down to 245 K, the mismatch and separation among graphene flakes emerge again. As a result, $\kappa$ jumps from 529W m$^{-1}$ K$^{-1}$ at 270 K to 3013 W m$^{-1}$ K$^{-1}$ at 245 K again. The ending temperature of switch-on process for round2 (195 K) is a little higher than that of round 1 (170 K). It could result from the fact that the preceded separation process makes it easier for the separation of the graphene flakes during the second-round experiment.

Before switch-on, $\kappa$ is measured to be 634-710 W m$^{-1}$ K$^{-1}$ at RT, which is comparable with the literature reported $\kappa$ of supported graphene. $\kappa$ of 150-1250 W m$^{-1}$ K$^{-1}$ was reported for three-layered graphene with different lateral dimensions supported on a SiN$_x$ substrate.[137]
Seol et al. reported the RT thermal conductivity of mono-layered graphene supported on silicon dioxide as 600 W m\(^{-1}\) K\(^{-1}\).\[21\] Cai et al. obtained \(\kappa\) for Au/SiNx membrane supported mono-layered graphene as (370 + 650/-320) W m\(^{-1}\) K\(^{-1}\) at RT.\[17\] Our \(\kappa\) near RT is similar to those reported values of supported graphene at RT, which demonstrates that the thermal transport in GP before switch-on is largely suppressed by contacting with neighboring impurity-embedded graphene flakes. After switch-on, the graphene flakes are free from the neighboring phonon scattering. Under this circumstances, the structure of GP can be regarded as an interwoven with suspended graphene flakes. The resulting \(\kappa\) is expected to be comparable with the high \(\kappa\) value of suspended graphene.\[139\] From Fig. 5.3.1 (b), the thermal behavior of graphene flakes in GP after switch-on is similar to that of reported suspended graphene. For GP, \(\kappa\) of the three samples at 245 K range from 1732 to 3013 W m\(^{-1}\) K\(^{-1}\). From literatures, \(\kappa\) of single-layered suspended graphene is reported to be about 1800-5000 W m\(^{-1}\) K\(^{-1}\) at RT.\[136\] For comparison, \(\kappa\) of graphite is about 1781-1960 W m\(^{-1}\) K\(^{-1}\) from literatures.\[91, 140, 141\] After switch-on, GP has a very high \(\kappa\) similar to that of graphite and smaller than that of the suspended single-layered graphene. This is reasonable considering that the GP is composed of about 5-6 layers of graphene flakes. It has been reported that as the number of layer increases, \(\kappa\) decreases as a result of the inter-layer scattering effect.\[16, 142\] \(\kappa\) of suspended and supported 1 to 3-layered graphene is presented in the figure to help readers have a better understanding of the level and range of our thermal conductivity. The boundary scattering due to abundant pore structure and the small flake size limits the overall in-plane \(\kappa\) of our GP. \(\kappa\) of GP should be lower than that of the single-layered or few layered graphene due to the structure phonon scattering.
The thermal strain caused by temperature decrease results in the mismatch and separation among the neighboring graphene flakes, which is responsible for the $\kappa$ jump. Since the GP is composed of high purity graphene with very little impurities, the in-plane phonon scattering mean relaxing time is very long. The phonon propagation in GP is largely impacted by substrate scattering from neighboring impurities-imbedded flakes. From Raman analysis in the structure section, the backbone of GP is 5–6-layered graphene flakes. Literatures suggested that a top oxide deposition penetrates a characteristic distance of approximately 7 layers into the core layers of graphene at RT.[138] The impact of substrate on thermal transport in few-layered graphene is weaker with the increase of the layer thickness.[143] Wang et al. reported that when the supported 3-layered graphene length is 5.0 μm, $\kappa$ at RT is 1250 W m$^{-1}$ K$^{-1}$.[137] This value is one fold lower than the reported 2300 W m$^{-1}$ K$^{-1}$ for suspended 3-layered graphene of 5 μm width.[16] For our GP, the separation and switch-on results in a 3.13–6.95 times higher $\kappa$. The discrepancy could be resulted from the much smaller planar size of the graphene flakes (≤1.6 μm) in GP than that of graphene in the literature ($L = 5$ μm). Wang et al. found out that the substrate effect is more significant for smaller graphene size.[137] Besides, the substrate effect for GP is from both sides of graphene flakes rather than from the one side only, which amplifies the suppression effect on thermal transport. Jang et al.[138] investigated the impact of the upper oxide deposition on a supported few layered graphene. An extra 38% reduction in $\kappa$ at RT was observed for 4-layered graphene. In addition, the atomic mass and the type of atom of the substrate also play important roles in affecting the thermal transport in graphene. The coupling strength of graphene is expected to be stronger with carbon atoms in the substrate than other lighter or heavier atoms.[127] Although stacking into good layered structure by mechanical compression, there are inter-flake space and openings inside
GP’s density (1623 kg m\(^{-3}\)) is measured to be lower than that of graphite (2200 kg m\(^{-3}\)). Therefore, GP is not actually a material with full density. If we remove the inter-flake space and calculate \(\kappa\) of GP in full density, the \(\kappa\) value could be higher. \(\kappa\) of full density could reach 2348-4084 W m\(^{-1}\) K\(^{-1}\) after switching-on and 859-962 W m\(^{-1}\) K\(^{-1}\) before switching-on. These values are still reasonable by comparing with the reported value of suspended and supported graphene respectively.

The thermal contact resistance among the graphene flakes along the thickness direction and thermal strain in single flake could affect the thermal transport in GP, but the overall switch-on behavior of \(\kappa\) is not influenced by these effects. Kuang et al.’s work demonstrated that the thermal strain in pure graphene flakes may enhance the thermal transport.[11] To estimate the applied strain on the thermal properties of graphene due to TEC mismatch, the previous experimental TEC value of \(-7\times10^{-6}\) K\(^{-1}\) can be used.[144] If we assume that the temperature changes from 300 K to 0 K, the resulting thermal expansion is 0.0021, which is very small. According to the result reported in Kuang et al.’s work,[11] a thermal strain of 0.0021 results in less than 1.4% of \(\kappa\) variation for 3-layered graphene, which is almost negligible. It is indicated in Huang et al’s work that the specific heat of the GP could be affected by the thermal strain. However, the thermal strain in GP is very small in the whole low temperature range in our work. If 0.0021 is used for the upper bound of strain, the corresponding specific heat variation is less than 0.7%. The main features of the result, including the resulting \(\kappa\) jump, are not affected. The thermal contact resistance in the thickness direction is expected to be very small. GP is composed of graphene flakes stacking together by the VdW force. From the XRD result, GP has an interlayer spacing of 3.35 Å which is the same to that of pyrolytic graphite. From literature, \(\kappa\) in the direction perpendicular to layer planes of
graphite is reported to be 5.7 W m$^{-1}$ K$^{-1}$.[141] The contacting and overlapping area among the neighboring flakes are large. To transfer heat from one end to the other, there are multiple routes in the GP sample. Even for one single flake, there can be several flakes interconnecting with it, which reduces the thermal contact resistance effect significantly.

5.4 Comparison Study Against Graphene Oxide and Partly Reduced Graphene Paper

5.4.1 Thermal conductivity comparison

For the observed $\kappa$ switch-on, one indispensable condition is that there are both pure graphene flakes and impurities-imbedded flakes in the sample. These flakes have a different thermal expansion coefficient from the pure graphene flakes. However, graphene-related papers with impurities could not always facilitate structure separation and ultra-high $\kappa$ switch-on. In this section, the $\kappa$ variation against temperature for graphene oxide paper (GOP) and partly reduced graphene paper (PRGP) are studied for comparison. The PRGP and GOP are purchased from Advanced Chemical Supplier (ASC) material and used as received. Figures 5.4.1 (a) and (b) show the measured $\kappa$ of the PRGP and GOP respectively. The steady-state electro-thermal (SET) [120, 145] technique is used for measuring the thermal conductivity. The details of the three PRGP samples and one GOP sample is presented in table 3. The $\kappa$ of PRGP ranges from 0.14 W m$^{-1}$ K$^{-1}$ at 15 K to 9.31 W m$^{-1}$ K$^{-1}$ at 300 K. As temperature goes down, $\kappa$ of all of the four groups decreases in a similar trend. The $\kappa$ value of three PRGP samples are much smaller than that of GP, taking only about 1.2% of the $\kappa$ of GP at RT. No switch-on behavior is observed for $\kappa$ of PRGP. The $\kappa$ of GOP is presented in Fig. 5.4.1 (b). As temperature goes down, $\kappa$ of GOP decreases from 2.15 W m$^{-1}$ K$^{-1}$ at 306 K to 0.73 W m$^{-1}$ K$^{-1}$ at 37 K. The $\kappa$ evolution of GOP constitutes a continuous curve with no switch-on behavior.
Figure 5.4.1 The thermal conductivity of (a) PRGP and (b) GOP. The thermal reffusivity of (c) PRGP and (d) GOP. The measurement uncertainty is about ±10%. The error bar is omitted for clarity purpose.

5.4.2 Thermal reffusivity and in-plane domain size

To interpret the different structure of the PRGP and GOP, the thermal reffusivity of the two materials are measured using TET. Unlike GP, the TET signal for PRGP present pure voltage decreasing patterns for the whole temperature range from 300 K to 10 K, which is also
the case for previous reported graphene foam and graphene aerogel materials.[10, 120] No dual thermal transport modes are observed. For the electrically non-conductive GOP, the TET signal is pure voltage increasing, which is from the Ir coating. Figure 5.4.1 (c) and (d) present the thermal reffusivity profiles of PRGP and GOP respectively. As mentioned above, the error for measurement is about ±10% in TET. The error bar is omitted for clarity. Θ of GOP shows a similar behavior as that of GP. As temperature goes down, Θ slowly reaches the residual Θ at about 5.5×10^5 s/m^2. By thermal reffusivity model fitting, the Debye temperature and Θ₀ is determined as 321±23 K and (5.54±0.16) ×10^5 s/m^2 respectively. Accordingly, the structure domain size is calculated to be 5.9 Å, which is extremely small compared to that of GP (1.68 µm). This result indicates the dense impurities of GOP. The Θ profile of PRGP is very different from that of GP. At relatively high temperatures from 300 K to 121 K, four groups of Θ fluctuate within very narrow limits. Below 121 K, Θ starts to increase rapidly. Θ of S1 increases from 5.5×10^5 s/m^2 to 8.5×10^5 s/m^2 at 25 K, then it drops a little from 25 K to 10 K. Θ of S2 rises from 4.2×10^5 s/m^2 to 7.3×10^5 s/m^2 at 25 K. For S3, a repeated experiment is conducted when the temperature is elevated from 10 K back to 300 K. The resulting data of the first round and the second round are consistent. Θ of S3 changes from around 4×10^5 s/m^2 at 121 K to 5.5×10^5 s/m^2 at 15 K.

5.4.3 Structure study and physics interpretation

The κ and Θ evolution of PRGP and GOP is attributed to the structure of the materials. Figure 5.4.2 shows the structure characterization of the two materials, in anticipation to help interpret the observations in Fig. 5.4.1. Figure 5.4.2 (a) and (b) are the SEM images of PRGP and GOP respectively. Unlike the smooth and uniform surface of the GP, extensive ridges and wrinkles are observed at the surface of the PRGP and GOP. For GOP, more impurities present
under the SEM. Figure 5.4.2 (c) shows the XRD results of the PRGP and GOP. The XRD pattern for PRGP presents a major peak at around 24.15°, yielding an interlayer spacing of 3.68 Å. For comparison, the interlayer spacing of GP and graphite is about 3.35 Å.[116] The larger interlayer spacing of PRGP demonstrates the presence of residual oxygen and functional groups in PRGP. The major peak for GOP is at 10.52°. The interlayer spacing is 8.40 Å, which is consistent with the literature value of 8.32 Å at 10.6° for graphene oxide.[102] Compared with the narrow and distinct peak of GP, the XRD peaks of PRGP and GOP are relatively wider with a lower intensity, revealing that the crystalline structure is not as good as that of GP. PRGP presents an even wider peak with a lower intensity than that of GOP.

Figure 5.4.2 (d) and (e) show the XPS survey of the PRGP and GOP. The result indicates the existence of other chemical bond such as O 1s (25.1%), N 1s (2.50%), Fe 2p (1.98%) and I 3d (1.51%) on the surface of PRGP. For GOP, the chemical bond composition is C 1s (61.76%), O 1s (34.40%), Au 4f (1.13%), F 1s (1.63%) and Fe 2p (1.07%). Figure 5.4.2 (f) shows the Raman spectrum of the PRGP and GOP. Two pronounced peaks at around 1354 cm\(^{-1}\) for D peak and 1593 cm\(^{-1}\) for G peak are observed for PRGP. The GOP exhibits a D peak at around 1352 cm\(^{-1}\) and G peak at around 1588 cm\(^{-1}\). The 2D peak for GOP is almost invisible, and is very small for PRGP. The D peak intensity are very high for both PRGP and GOP, indicating the large amount of defects and impurities in the materials. The \(I_D/I_G\) ratio for PRGP is higher than that of GOP, indicating that the reduction process results in in-plane C=C bonds cracks. A large number of disorders are induced in the sp\(^2\) domains. This is a commonly reported phenomenon for partly reduced graphene materials.[97, 120, 146] With further reduction, the \(I_D/I_G\) ratio could go down again due to the restoring of the sp\(^2\) domains.[147] For comparison, the D peak for GP is invisible, which implies the high quality crystals in GP.
Figure 5.4.2 SEM images of (a) PRGP and (b) GOP. (c) XRD spectrum of PRGP and GOP. XPS survey of (d) PRGP and (e) GOP. (f) The Raman spectrum of PRGP and GOP, indicating the presence of defects and impurities in the samples.
For GOP, the thermal reffusivity pattern reflects the dominant role of N-scattering at near RT and the impurities and defects phonon scattering at low temperatures, which is similar to that of GP. From the above characterization, there are large amount of defects and other impurities atoms on GOP. This is in accordance with the high $\Theta_0$ value of GOP. For PRGP, since part of the oxygen groups have been removed by reduction, the new emerged graphene domains in the sample make the PRGP electrically conductive (conductivity~ $5\times10^3$ S/m). For comparison, the electrical conductivity of GP is about $4.4\times10^4$ S/m, which is about one order of magnitude higher than that of PRGP. The $\kappa$ of GP (~634 W m$^{-1}$ K$^{-1}$) is about 68 times higher than that of PRGP (9.31 W m$^{-1}$ K$^{-1}$) at RT. The large discrepancy is mainly attributed to the oxygen content and the functional groups on the surface of the PRGP. The $\kappa$ and $\Theta$ profiles of the PRGP are very similar to that of the graphene aerogel (GA) which we studied and reported before.[120] The main mechanism controlling the thermal transport is the thermal contact resistance at interfaces. When the thermal contact resistance is very large, the effective $\kappa$ of the sample can be deduced as .[120] In this expression, $A$ is a correlation constant; $v$ is the phonon velocity and $l_f$ is the average flake size of PRGP, which are both insensitive to the temperature change. This is the reason that $\Theta$ of PRGP fluctuates within a very narrow limit from 300 K to 121 K. Under 121 K, the thermal expansion among the partly reduced graphene flakes deteriorates the contact among r-GO sheets and contributes to the increased thermal reffusivity.[120]

The reason why only GP presents the switching-on behavior can be summarized as following. There might be structure separation in PRGP and GOP as well, but the separation has insignificant effect in thermal transport. The phonon propagation in PRGP and GOP is
largely suppressed by the in-plane impurity scattering and the interface scattering at the flakes boundary. For GOP, the highly dense oxygen content and impurities lead to the dominating role of impurities scattering in thermal transport. Besides, the much larger interlayer spacing inhibits the neighboring impurities layers scattering effect to a great extent. For PRGP, although part of the oxygen content has been removed during the reduction process, the residual functional groups on the surface of PRGP flakes results in a weaker inter-flake bonding. The interface thermal contact resistance dominants the thermal transport in PRGP. As a result, the expansion induced separation and the neighboring impurities layers scattering change make relatively insignificant contribution compared to the in-plane scattering and the interface scattering. Therefore, no switch-on behavior can be observed for $\kappa$ and diffusivity of PRGP and GOP. On the other hand, the pure graphene flakes in GP has a very low impurity density. The intensity of impurities scattering and interface scattering are extremely low. The neighboring flakes scattering effect dominates over the point defect scattering and the thermal contact resistance in thermal transport. As a result, the switch-on effect is evidently observable from $\alpha$ and $\kappa$ of GP. The difference in thermal expansion between pure graphene flakes and impurity-embedded flakes plays the most important role in the switch-on in GP.
CHAPTER 6  CURRENT-INDUCED THERMAL ANNEALING ON IMPROVING THE STRUCTURE AND THERMAL CONDUCTIVITY OF CNT BUNDLES

In this work, we demonstrate how this electric current-induced thermal annealing can be combined with the transient electrothermal technique (TET) to study the sequential thermal and electrical properties evolution of CNTs materials during annealing. The TET technique is a fast, simple yet robust method developed in our lab for characterizing thermal properties of solid materials.[148-151] By using a same experimental set-up for annealing and thermal characterization, sample contamination and damage problem can be averted. The annealing effects on improving the electrical and thermal properties of CNT bundles are reported. The mechanisms are analyzed using the thermal reflusivity theory. Raman spectroscopy and scattering electron microscope (SEM) are conducted to investigate the annealing effect on improving the structure of material and reducing impurities. The temperature distribution along the length direction of a single CNT bundle during CITA is evaluated using finite difference modeling. The different annealing levels at different positions of sample is harnessed for studying and comparing the temperature effect, which significantly reduces the deviation from sample quality variation. The resulting improvement of averaged thermal diffusivity and intrinsic thermal conductivity of graphite walls is presented against annealing temperature during CITA process.

6.1 Synthesis and Structure Characterization

The multi-walled carbon nanotube (MWCNT) bundles were synthesized using a ferrocene assisted chemical vapor deposition (CVD) process in quartz tube furnace. The diameter of the bundle is controlled by using a patterned catalyst area. Briefly, ferrocene was
introduced into gas stream by thermal evaporation concurrently with acetylene using a specially constructed source. MWCNT bundles array with about bundle diameter of about 200 μm were harvested from a large area sample for thermal properties measurements. The details of the synthesis process can be found in the literature.[152]

Figure 6.1.1 presents the morphology and structure of a single CNT bundle sample. Figure (a)–(b) are SEM images with different magnification from 500× to 15000×. The CNT bundles sample presents a cylinder-like shape. Hundreds of thousands of CNTs form a bundle by aligning along the axial direction. Under higher magnification, coil-like carbon nanotubes can be seen. The macroscopic CNT morphologies was reported driven by the competing factors of collective growth and spatial constraints.[153] The diameter and wall thickness of individual CNT in the bundle are characterized using transmission electron microscopy (TEM). Figure 6.1.1 (c)-(d) are two of the TEM images of the MWCNTs in the bundle. TEM reveals that the CNT bundles consist of MWCNTs with typical outer diameter from 18 to 25 nm. The wall thickness ranges from 15 to 22 layers. The wall of the MWCNT is not smooth. As indicated with the yellow arrows, amorphous region and defects are observed along the walls of CNTs. Wall thickness also varies along the axial direction.
Figure 6.1.1 Morphology and structure characterization of CNT bundles. (a)-(b) SEM images of the CNT bundles under ×500 and ×15000 magnifications. (c)-(d) TEM images. The yellow arrows indicate the amorphous region. (e) Raman spectrum indicating three pronounced peaks. (f) XRD spectrum. (g) The X-ray photoelectron spectra. In the insets are the deconvoluted spectrums for O 1s and C 1s.

Raman result of CNT bundles is obtained under 20× objective by using 532 nm laser excitation with 6 s integration time (Olympus BX51). The power of laser is 4.98 mW. The result is presented in Fig. 6.1.1 (e). Three pronounced peaks are observed which correspond to the D peak, G peak and 2D peak respectively. The G peak (1583.0 cm\(^{-1}\)) is related to vibrations in sp\(^2\). The D peak at around 1348.1 cm\(^{-1}\) involves the resonantly enhanced scattering of electrons via phonon emission by defects or sidewalls that breaks the basic symmetry of the graphene plane [154], which can be used as an indicative of structural disorder from amorphous carbon and other defects. The integrated intensity ratio between the D band and G band shows a value of ~0.86, which is smaller than the reported value for CVD grown MWCNTs and graphitized MWCNTs.[155] This result indicates the fair quality and structure of the samples. The 2D peak (2689.5 cm\(^{-1}\)) is activated by double resonance processes.[156] which indicates
the long-range order in a sample. Near the G band, there is an additional shoulder peak at about 1618 cm\(^{-1}\), called D' band. The D' band is a unique Raman band for MWCNTs, which also originates from disorder, defects or ion intercalation between the graphitic walls.\[155\] The peaks are sharp, indicating that the CNT bundle has a fair structure and order. These results also reveal the existence of defects in the CNT bundles.

X-ray diffraction (XRD) is performed to obtain detailed structural and phase information about the CNT bundles. Three peaks are observed in the XRD profile presented in Fig. 6.1.1 (f). The strong and sharp (002) peak at around 25.8° corresponds to the inter-planar spacing of 0.34 nm, which is very close to that of pure graphite (0.335 nm). This result indicates that the inter-wall impurities are rare. The other two diffraction peaks at the angles 2\(\theta\) of 42.8° and 53.4° are indexed to the (100) and (004) reflections. The (100) peak gives a crystal size of 27.5 nm.

To further measure the elemental composition and chemical bonds at the surface of the samples, X-ray photoelectron spectroscopy (XPS) spectrum is collected. The resulting atomic concentration of the elements is summarized to be 96.32% C 1s and 3.68% O 1s. The Au 4f signal is from the Au coated steel sample holder, which is used to limit the C and O contamination on the sample holder surface and serves as an internal energy calibration reference. The XPS survey and the three-element narrow scanning are presented in Fig. 6.1.1 (g). The C 1s spectrum is characteristic of a sp\(^2\) type C network. The higher binding energy shoulder peak at ~291 eV is due to \(\pi-\pi^*\) satellite of the sp\(^2\) type C. The O 1s spectrum clearly shows more than one O environment. The low binding energy peak at ~530 eV is due to the metal oxide from signal of the sample holder. The peak at ~532 eV and the peak at ~533 eV is from C-O species and C=O species respectively in the CNT bundles. From these results, it is
conclusive that the quality of the CNT bundles is fair, but there are oxygen-containing C-O and C=O functional groups on the CNT surface.

### 6.2 Thermal Characterization and Annealing Method

Three CNT bundles are annealed by applying large DC currents to them under high vacuum conditions. The three samples are denoted as S1, S2 and S3 respectively. Details of the three samples can be found in Table 4. Each sample is subjected to DC currents whose value is increased from low to high till the sample is burnt broken. The duration for each DC current are set to be 2 s for S1 and S2, and 20 s for S3. The voltage profiles over the samples during current annealing are collected using an oscilloscope. After each annealing, using the same experimental set-up, TET measurement is conducted to measure the in-situ thermal diffusivity. It makes sure that the minimum and optimum current for improving thermal diffusivity can be observed clearly. This method also avoids the errors resulted from the sample to sample quality variation as well as contamination and damage caused by sample transferring process. For comparison, traditional high temperature annealing anneals a group of samples at different temperatures in furnaces followed by thermal characterization. The uncertainty caused by quality variation among samples and samples contamination during transferring process could be very large, and overshadow the annealing effect on structure and physical properties.

<table>
<thead>
<tr>
<th>Index</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
<th>S4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended Length (mm)</td>
<td>2.37± 0.07</td>
<td>2.77± 0.04</td>
<td>2.37± 0.06</td>
<td>3.00± 0.04</td>
</tr>
<tr>
<td>Diameter (um)</td>
<td>280± 12</td>
<td>222± 13</td>
<td>225± 10</td>
<td>211± 8</td>
</tr>
</tbody>
</table>

Table 4 The details of the measured CNT bundle samples
The TET technique is a fast and robust method for measuring thermal diffusivity of various solid materials.[148, 149, 157, 158] Figure 6.2.1 shows details of experiment set-up and principle. Figure 6.2.1 (a) shows a digital camera photo of the MWCNT bundles array, from which individual bundles are obtained. Figure 6.2.1 (b) displays a microscopy image of a suspended CNT bundle sample. In the experiment, the CNT bundle is suspended between two gold coated silicon electrodes and connected using a small amount of silver paste. Figure 6.2.1 (c) shows the schematic of the experimental set-up. The sample is then put in a vacuum chamber, where the air pressure is maintained below 0.5 mTorr. During TET measurement, a step current is fed through sample by a current source to induce a fast joule heating. The voltage profiles are collected using an oscilloscope. Upon heating, the temperature of the sample has a fast increase and then reaches a steady state. The joule heat is transferred by heat conduction along the length direction of the sample and heat radiation. Heat convection can be neglected due to the low air pressure in the chamber. The speed for reaching steady state is determined by the thermal diffusivity of material. Assuming one dimensional heat transfer model, the normalized temperature profile for this transient state can be derived as:[72, 148, 149] in equation (2).

During the small temperature range during joule heating in TET measurement, the temperature coefficient of resistance is reasonably assumed constant. Under this circumstance, the normalized temperature rise can be obtained by normalizing voltage profile. Since CNT bundles have a negative temperature coefficient of resistance, the voltage presents a decreasing and stabilizing pattern. Some normalized temperature profiles of TET of S1 after different currents annealing is presented in Fig. 6.2.1 (d), including data after 50 mA, 434 mA and 1 A
annealing. As the annealing current is increased, the time for temperature to reach steady state becomes shorter and shorter, which reveals an increased thermal diffusivity of S1. The corresponding effective thermal diffusivity is $1.35 \times 10^{-5}$ m$^2$/s after 50 mA annealing, $3.33 \times 10^{-5}$ m$^2$/s after 434 mA annealing, and $4.38 \times 10^{-5}$ m$^2$/s after 1 A annealing.

Figure 6.2.1 Experimental set-up and principle of the transient electro-thermal (TET) technique for in-situ thermal characterization. (a) A digital camera photo of the MWCNT bundles array. (b) A microscopy image of a suspended CNT bundle sample. (c) A schematic of experimental set-up. (d) Selected normalized temperature profiles of TET of S1 after different currents annealing. The dots are raw data and lines are fitting curves from TET model. The corresponding thermal diffusivity values ($\alpha$) are also presented in the figures.
6.3 CITe Results And Discussion

6.3.1 The reduced electrical resistance

The electrical resistance of the samples is calculated using voltage and DC current value \( R = \frac{V}{I_{DC}} \). Figure 6.3.1 shows the resistance profiles of S3 during CITe by currents from 120 mA to 1.05 A. They consist of two stages. The first stage shows a sharp decreasing pattern, while the second stage presents a slowly decreasing behavior. The decrease in the first stage sources from fast joule heating like that in TET measurement. Within the first stage, the temperature of S3 is raised sharply by joule heating. The fast decreasing resistance reflects the temperature change. After the first stage, the sample’s temperature has reached steady or quasity-steady state. In the second stage, as the high density of electrical current continues to anneal the sample, defects which impede the transport of electrons are gradually removed. More electron transport is facilitated. This improved structure results in a slowly decreasing resistance. Therefore, the resistance keeps decreasing slowly. As the annealing current is increased to about 1.05 A, the annealing effect develops into a nearly saturated state. After 1.05 A current annealing, CITe cannot remove any more defects or impurities. As indicated in the second plot in the right figure, the resistance shows a fast decreasing stage due to joule heating (TET), and then stays constant during the second stage. Since there is no structural change during annealing anymore, the resistance becomes constant, which reflects the stable temperature and structure of the sample. The subsequent annealing with current from 1.1 A to 1.25 A results in slowly increasing resistance profiles, which might be caused by damaged inner structure. The resistance profiles indicate that the electrical properties are improved during the current-induced annealing before 1.05 A.
Figure 6.3.1 The resistance profiles of S3 during the large current annealing from 120 mA to 1250 mA. Two-stage evolution is observed.

In addition to the joule heating effect and annealing effect, there is another effect which should be taken into consideration when analyzing the resistance change. When the distance between two adjacent CNTs is sufficiently small, electron tunneling takes place across the connection under large current. This causes a nonlinear $I$-$V$ curve of CNT bundles. For small currents, the energy is not high enough for exciting electrons to overcome the energy barriers at the connection. Therefore, the original resistance measured at the beginning of $I$-$V$ curve of CITA is much lower than that measured from small current. For example, the resistance profiles after 800-1250 mA show an original resistance of 3.9-4.25 Ω. However, the resistance measured by using a small current (46-50 mA) is much higher (> 7 Ω). The resistance profiles measured using small current during TET will be discussed in the next section [Fig. 6.3.2 (a)].
This discrepancy proves the existence of the electron tunneling. Thus, the slowly decreasing behavior of the electrical resistance profiles in the second stage is also a combination effect of permanent structural improvement from annealing and the nonlinear $I-V$ curve under large current. This is an issue that requires further in-depth work.

The in-situ thermal and electrical characterization is conducted by alternation of CITA and TET measurement: a few minutes after each CITA (wait for the samples to cool down), TET measurement is conducted. The small current used for the TET measurement is in the range of 38-52 mA, which causes a ~1% resistance decrease in the samples. Figure 6.3.2 shows the results for the resistance, thermal diffusivity, and thermal reffusivity. The electrical resistance is measured at room temperature after each annealing [Fig. 6.3.2 (a)]. The resistance of the three samples begin to decrease when the heating current is increased to about 100 mA. For S1, it drops from the original value of about 7.4 Ω to the final value of about 6.8 Ω, which is 8% decrease of the original resistance. For S2 and S3, it decreases by 7.6% and 4.4% of their original resistance respectively. Overall, the electrical resistance is not improved significantly by CITA.

As illuminated before, the resistance decrease is due to the healing of structural defects and removing of impurities in CNT bundles. However, the resistance profiles do not follow a monotonic decreasing pattern. Instead, a valley is observed for all the three samples at around 200 mA. S3 presents an extra valley at around 800 mA. These valleys could be attributed to the removal of surface adsorbed content.
Figure 6.3.2 The experimental result of large current annealing effect. (a) The electrical resistance against annealing current and (b) effective thermal diffusivity of CNT bundles against annealing current. (c) The thermal diffusivity and electrical resistance of S4 at low temperatures without annealing.
Previous works reported that annealing reduced the adsorbed oxygen content on the surface of CNTs, which could also weaken the tube-tube contacts such that carriers can now be trapped there.[159] Therefore, a small increasing region of $R_0$ from 200 mA to 400-520 mA is observed. In CNT bundles, there are oxygen-containing C-O and C=O functional groups on the surface. The temperatures required for removing different oxygen groups are different, which causes an extra valley in resistance profile of S3. Another possibility involves the alignment of individual CNTs in the bundles. As the high-density current is applied, some interconnecting tubes between parallel tubes break due to high temperature. This creates different paths for electron propagation. As a summary, the weakened tube-to-tube interfaces, alignment variation, and the improved purity and structure within CNTs contribute cooperatively to the electron transport behavior.

6.3.2 The enhanced effective thermal diffusivity and phonon scattering principle

The effective thermal diffusivity ($\alpha_{\text{eff}}$) after each annealing is summarized in Fig. 6.3.2 (b). $\alpha_{\text{eff}}$ is increased significantly by CITA. The original $\alpha_{\text{eff}}$ of S2 and S3 is about 2.76-2.96×10$^{-5}$ m$^2$/s. For S1, the original $\alpha_{\text{eff}}$ is lower (1.32×10$^{-5}$ m$^2$/s). This indicates that S1 is originally inferior in quality than S2 and S3. Similar to the evolution of electrical resistance, low DC current (lower than 200 mA) has no effect on $\alpha_{\text{eff}}$. $\alpha_{\text{eff}}$ stays constant before 200 mA. After being subjected to 200 mA CITA, $\alpha_{\text{eff}}$ of all the three samples begin to increase. For S2 and S3, $\alpha_{\text{eff}}$ keep increasing with the annealing current till burnt broken. Their $\alpha_{\text{eff}}$ before broken is about 5.80×10$^{-5}$ and 5.20×10$^{-5}$ m$^2$/s respectively, which accounts for 110% and 76% increase over the original thermal diffusivity. For S1, $\alpha_{\text{eff}}$ reaches maximum and becomes relatively stable after being annealed by current higher than 897 mA. The stable value from 897 mA to 1.4 A indicates that the quality of the sample cannot be improved by CITA any
further. This value represents a saturated thermal diffusivity of S1. The upper limit of $\alpha_{\text{eff}}$ of S1 is $4.44 \times 10^{-5}$ m$^2$/s, which is 236% increase over the original value.

Phonons are the main heat carriers in CNTs. During propagation, phonons can be scattered by other phonons, intra-tube defects and impurities, and inter-tube interfaces. There are two reasons for the improved electrical and thermal properties of CNT bundles during annealing. The first one is that CITA process removes impurities and restores structural defects inside individual CNTs, which facilitate electron and phonon propagation.[159, 160] Another mechanism is CITA strengthens tube-to-tube connection, which reduces electrical and thermal contact resistance at interfaces of adjacent CNTs. Previous work indicates that thermal transport in CNT bundles is dominated by tube-to-tube thermal contact resistance.[69, 161] Jin et al. studied the electrical resistivity ($\rho_e$), thermoelectric power and thermal conductivity of annealed CNT bundles at temperature range of 2-300 K. They attributed the thermal annealing effect to the improved crystallinity, which considerably reduced phonon scattering at tube-tube junctions.[161]

To further study the mechanisms responsible for the thermal properties enhancement of our CNT bundles, temperature dependent thermal reffusivity of CNT bundles from 295 K to 45 K are characterized. The thermal reffusivity ($\Theta = 1/\alpha$) is defined as the reciprocal of thermal diffusivity and can be used to directly analyze phonon scattering mechanisms and intensities in different materials.[10, 72, 158] Figure 6.3.2 (c) shows the temperature dependent electrical resistance ($R_0$) and thermal reffusivity of an CNT bundle sample (not annealed). This sample is denoted as S4, whose details can be found in Table 4. $R_0$ shows a linear behavior in the temperature range of 40-295 K.
As temperature goes down, \( \Theta \) decreases from \( 2.70 \times 10^4 \text{ m}^2/\text{s} \) at 295 K to \( 2.02 \times 10^4 \text{ m}^2/\text{s} \) and then reaches a stable value below 170 K. The decreasing part is controlled by Umklapp phonon scattering. As temperature goes down, phonon population reduces, which results in a decreased \( \Theta \). The stable part at low temperature (\( \Theta_0 \)) is determined by interfaces and impurities-induced phonon scattering. This behavior can be characterized using the previous reported residual thermal reffusivity model: \( \Theta = \Theta_0 + C \times e^{-\theta/2T} \), in which \( \theta \) is the Debye temperature and \( C \) is a constant.[10, 72, 158] The experimental \( \Theta \) data is fitted using this model, which gives the fitting result as \( \Theta = 2.03 \times 10^4 + 3.46 \times 10^5 \times e^{-1193/T} \). The fitting curve is also plotted in the figure. From the fitting result, the residual thermal reffusivity (\( \Theta_0 \)) of the CNT bundle is \( 2.03 \times 10^4 \text{ s/m}^2 \), which accounts for 75.2% of the whole thermal reffusivity at RT. This reveals a high intensity of interfaces and impurities-induced phonon scattering in CNT bundles. The Debye temperature is estimated to be 2386 K, which is very close to the literature reported value \( \sim 2500 \text{ K} \) for MWCNTs.[162] It is conclusive that the phonon propagation in CNT bundles is dominated by the interface and impurities-induced phonon scattering even at RT. The CITA process removes impurities and heals defects within CNTs, which reduces the phonon scattering intensity considerably. Therefore, the thermal diffusivity of CNT bundles is enhanced significantly during CITA.

The threshold of electrical resistance and \( \alpha_{\text{eff}} \) change by current are different. The threshold of \( \alpha_{\text{eff}} \) has a delay compared to that of \( R_0 \) at the beginning. Furthermore, no very obvious valleys are observed in the \( \alpha_{\text{eff}} \) profiles. This indicates that \( \alpha_{\text{eff}} \) is less sensitive to the small structure changes at inter-tube interfaces and inner alignment. As discussed above, removing oxygen contents at inter-tube interfaces impedes tunneling of electrons, which is responsible for the valleys in the resistance profiles. On the other hand, tunneling does not
apply to phonons. Phonons are always scattered at inter-tube interfaces. Removing the oxygen contents only reduces the phonon scattering intensity, which facilitates propagation of phonons. Therefore, $\alpha_{\text{eff}}$ is monotonically enhanced by reduced impurities and inter-tube thermal contact resistance.

6.3.3 The unevenly distributed annealing effect along length direction

Three samples S1-S3 are annealed using large electrical current till burnt broken. Figure 6.3.3 (a)-(b) show the morphology of structure after broken. From Fig. 6.3.3 (b), the hollow structure can be seen clearly. A clean and smooth breaking edge near the center point can observed. Instead of a 45° breaking line (caused by tensile break), the breaking lines are almost perpendicular to the axial direction of the sample. This breaking morphology indicates that the breaking is mainly caused by melting under high temperature. For the three samples, the melting occurs under 1.4 A, 1.35 A and 1.25 A for S1, S2 and S3 respectively. The melting temperature will be evaluated and discussed in the next section. From Fig. 6.3.3 (a), the surface of glass substrate is also burnt by heat radiation from sample. The molten CNT bundle sputters a thin layer of carbon film on the surface of the glass substrate. A magnified SEM image of the thin layer of carbon film is displayed as an inset in Fig. 6.3.3 (a). Raman spectroscopy is conducted to find out structure of the carbon film and is also displayed as an inset. The Raman spectrum is acquired under a 50× objective. It exhibits a very broad band centered at around 1558 cm$^{-1}$, which is a characteristic of amorphous carbon.[163] The peak at around 1960 cm$^{-1}$ could be resulted from background reflection of the glass substrate and second-order combined scattering of the two main structures at 550 and 1550 cm$^{-1}$.[164] It is conclusive that the melting of CNT bundles sputters a thin layer of amorphous carbon film on glass substrate.
Figure 6.3.3 The morphology and characterization of the structure after CITA. (a)-(b) The SEM images of the breaking point due to the high temperature annealing and melting under low to high magnifications. The insets in figure (a) is the SEM and Raman signal of the amorphous carbon film sputtered on the glass substrate from the molten CNT bundle. (c) Change of the Raman signal with the distance from the breaking point (DFB). The Lorentz
fitting result of the Raman signals, including (d) the ratio of intensity of the D peak to the G peak. (e) The Raman shift of G peak. (f) The full width at half maximum (FWHM) of G peak.

The temperature distribution along the axial direction of samples during CITA is not uniform: temperature near center point is much higher than that near electrodes. The higher temperature near center point results in a higher level of annealing. Therefore, annealing effect also varies along axial direction. Figure 6.3.3 (c) shows Raman spectroscopy data acquired from different locations along the axial direction of S1. As the position of acquisition is moved from near electrode to the breaking point, the intensity of D peak shows an evident decrease, while intensity of G and 2D peak both present a gradual increase. Analyzed using Lorenzian fitting, the ratio of intensity of D band to that of G band ($I_D/I_G$) is obtained and plotted against the distance from the breaking point (DFB) in Fig. 6.3.3 (d). $I_D/I_G$ changes from 0.75 near electrode to 0.29 near breaking point, which accounts for 2.6 times reduction. This variation points out a dramatically reduced degree of disorder near the breaking point. The Raman shift and full width at half maximum (FWHM) of G peak are also presented in Fig. 6.3.3 (e) and (f). It shows that CITA results in a red-shifted G peak from 1588 cm$^{-1}$ to 1582 cm$^{-1}$. The FWHM of G peak decreases from 53 cm$^{-1}$ to 36.6 cm$^{-1}$, revealing an increased crystallinity from two ends to the breaking point of the sample. The peak is quite weak, so it is omitted for the ease of fitting. The Raman results demonstrate that the effect of CITA on reducing defect and improving crystallinity of CNT bundles decreases along axial direction from near center point to the two ends.
6.4 Thermal Conductivity Evaluation By Numerical Calculation

6.4.1 The averaged and localized annealing effect

It should be noted that the experimentally measured $\alpha_{eff}$ in our TET experiment represents an averaged effect across the whole length of the samples. The annealing effect varies along axial direction as demonstrated in the previous section. In this section, to find out exactly how the localized thermal conductivity ($\kappa$) of CNTs changes with the localized temperature ($T$), finite difference modeling (FDM) is carried out to calculate the $\kappa$ and $T$ evolution along the axial direction during CITA and TET experiments.

Due to the large length to diameter ratio of CNT bundles, only the axial direction heat transfer is considered. Besides, since the temperature distribution is symmetric around the center point along the axial direction, only half of the suspended sample is calculated. The geometries of the half CNT bundle sample and the electrodes are depicted in figure 6.3.3 (c). The system has an initial temperature of 290 K. The length, diameter, and electrical resistance of the sample is set according to the experimental conditions. To calculate the volumetric specific heat of the CNT bundles by, $\kappa$ is measured first using the steady-state electro-thermal (SET) technique.[165, 166]. The resulting $\rho c_p$ before CITA is determined to be $2.1 \times 10^5$ J/m$^3$·K. In the TET experiment, since the temperature increase is in a very small range, the variation of $\rho c_p$ within that small temperature range is negligible. In the CITA simulation, we are only interested in the steady state temperature which is independent of $\rho c_p$. Therefore, the $\rho c_p$ value is reasonably set to be a constant during simulation. Meshes are generated in the length direction with a grid size of 1 $\mu$m.

After CITA, $\kappa$ improvement is different along the length direction. To simplify, we assume $\kappa$ has a linear relationship with the distance from the center point ($l_c$). Near the center
point of the sample, the temperature is the highest, so $\kappa$ has the maximum value. It is denoted as $\kappa_c$. Since the two electrodes have much larger volume compared to sample, the temperature of the electrodes stays constant during the large current annealing. The two ends of sample near electrodes experiences only very small temperature increase, so $\kappa$ of two ends of the sample in the electrodes is assumed unchanged. It is denoted as $\kappa_0$. Therefore, the thermal conductivity is expressed as, in which $L$ is the suspended length of the sample. Here, $\kappa_0$ is the thermal conductivity of sample before annealing. It is measured using steady-state electro-thermal (SET) technique.[165, 166].

There are two steps in the simulation. In the first step, the TET measurement process at RT is simulated. The objective is to find $\kappa_c$. Different $\kappa_c$ values are tried to calculate the evolution of the average temperature ($T_a$) during TET heating. The temperature profile which gives a best fitting of the experimental data is selected. The corresponding $\kappa_c$ value is determined as the thermal conductivity value at the center point. The second step is to simulate the CITA process using the obtained thermal conductivity profile. The purpose is to find the localized temperature distribution over space during CITA. At time equals zero, a large current is fed through the length direction of the sample to induce joule heating. The temperature evolution during the joule heating process is calculated. Since the experiment is conducted in a vacuum environment, heat convection effect is neglected. Only heat conduction, heat radiation with environment, and joule heating is taken into consideration during this process.

In TET measurement, since the temperature increase is quite small ($\Delta T \ll T$) and the sample’s aspect ratio is very large, the radiation effect contributes insignificantly for determining thermal diffusivity (less than 1.5%). Under this situation, error from emissivity is very small in TET measurement at RT. During CITA, because of the very high temperature
induced by joule heating, heat radiation effect becomes one of the most important factors in thermal transport. From literature, the emissivity of SWNTs forest is reported to be 0.98-0.99 across a wide spectral range from UV (200 nm) to far infrared (200 μm).[167] In our simulation, the CNT bundle is treated as a black body (emissivity = 1). This will result in an overestimated radiation effect, which gives an underestimated temperature increase of the sample. However, if we reduce the emissivity by 10%, the temperature increase will rise by ~2.4% according to our calculation. Thus, error from emissivity uncertainty is still very small.

Figure 6.4.1 shows the simulation result, in which figure (a) shows the effective thermal diffusivity ($\alpha_{\text{eff}}$) of the sample as a function of the averaged temperature ($T_a$). $\alpha_{\text{eff}}$ is improved at a very high rate in the temperature range of 546-1093 K for S1, 620-941 K for S2, and 637-783 K for S3. After the fast increasing temperature zone, increase of $\alpha_{\text{eff}}$ slows down and finally becomes relatively stable. $\alpha_{\text{eff}}$ is an averaged value representing the thermal properties of the whole length of samples. To investigate how the localized thermal conductivity is increased by the localized high temperature, the center point of sample is studied in detail. The right $y$ axis in Fig. 6.4.1 (b) presents $\kappa_c$ as a function of the temperature raise at the center point ($\Delta T_c$). $\kappa_c$ shows a similar behavior as the effective thermal diffusivity.
Figure 6.4.1 (a) The effective thermal diffusivity of CNT bundles against the averaged annealing temperature. It shows an averaged effect of annealing. (b) Right y axis: the thermal conductivity of the center point of sample against the annealing temperature at center point. It shows the localized annealing effect at the center point. Left y axis: calculated intrinsic thermal conductivity of graphite walls ($\kappa_{\text{intr}}$) against the localized annealing temperature. The orange rectangular shows the fast annealing zone, within which $\kappa_{\text{intr}}$ has the highest increasing rate with the increased temperature. The green rectangular indicates a saturated annealing state of S1.
For S1, $\kappa_c$ has a fast increase between 303 K and 1497 K and then becomes relatively stable till breaking at 2202 K. For S2 and S3, before breaking, $\kappa_c$ has a fast increase temperature zone and then a slow increase temperature zone. The changing points of the increasing rate are 888 K and 671 K for S2 and S3 respectively. The highest $\kappa_c$ of the three samples are 41.3 W/m K at 2491.8 K, 32.6 W/m K at 2995.7 K, and 28.3 W/m K at 2537.0 K respectively.

6.4.2 The intrinsic thermal diffusivity and conductivity of graphite walls in CNT bundles after annealing

The curvature of CNTs is an important factor when considering its intrinsic thermal properties. CNTs in the samples resemble a coil-like shape. The red line shows part of the shape of one single CNT. During joule heating, heat is transferred following the path of the curve from point A to B. The length of the curvature is much larger than the straight-line distance between A and B. After evaluating several heat transfer paths, the average ratios of the actual heat transfer route over the straight line length in the sample is estimated to be 1.24. The 3D length of the CNTs is larger than that observed in the 2D picture. Taking the radial symmetry property of the CNT bundle into consideration, since , the 3D ratio of the curvatur length of CNTs over the straight line length can be estimated as . From equation (2), the normalized temperature is only a function of $a t / L^2$. Therefore, the ratio of intrinsic thermal diffusivity ($\alpha_{\text{intr}}$) over the effective thermal diffusivity of the center point is $\alpha_{\text{intr}} / \alpha_c = 1.52^2 = 2.31$, in which $\alpha_c$ is calculated by . In fact, heat is conducted through graphite walls in CNT bundles. Thus, $\alpha_{\text{intr}}$ also represents the thermal diffusivity of graphite walls at the center point of CNT bundles.

To find out the intrinsic thermal conductivity of graphite walls ($\kappa_{\text{intr}}$) in CNT bundles, the effect of voidage needs to be taken into consideration. The measured volumetric specific
heat of CNT bundles in our work is about $2.1 \times 10^5$ J/m$^3$ K at RT. For full dense carbon materials, such as graphite, the volumetric specific heat is generally about $1.6 \times 10^6$ J/m$^3$ K.[94] The discrepancy between CNT bundle and other full dense carbon materials is due to the large voidage in the sample. The CNT bundles is a hollow cylinder. Large opening space is observed inside the cylinder walls. In addition, the cylinder wall is composed of individual CNTs aligning themselves together. This assembling pattern leaves void between the neighboring CNTs, which reduces the density of the sample further. Therefore, to calculate $\kappa_{\text{intr}}$, the volumetric specific heat of graphite should be used instead of the measured $\rho C_p$ of CNT bundles. Using the density of graphite (2230 Kg/m$^3$) and specific heat value of graphite (710 J/Kg·K at RT).[94] $\kappa_{\text{intr}}$ can be evaluated as $\kappa_{\text{intr}} = \alpha_{\text{intr}} \times \rho_{\text{graphite}} \times C_p_{\text{graphite}}$. The result against annealing temperature is plotted in Fig. 6.4.1 (b) (left y axis).

$\kappa_{\text{intr}}$ presents a three-stage process as the annealing temperature increases from RT to as high as the melting temperature of CNTs. $\kappa_{\text{intr}}$ of S1 has a fast increasing rate from about 593 K to 928 K. After 928 K annealing, the increasing rate of $\kappa_{\text{intr}}$ is reduced. $\kappa_{\text{intr}}$ finally reaches a saturation value after 1787 K. Increasing annealing current does not improve $\kappa_{\text{intr}}$ any more. For S2 and S3, $\kappa_{\text{intr}}$ first increases quickly and then keeps increasing slowly until broken. There is a changing point of increasing rate at 1178 K and 961 K for S2 and S3 respectively. Before annealing, $\kappa_{\text{intr}}$ is about 39.3 W/m·K for S1, and 98.7 W/m·K for S2 and S3. After annealing, $\kappa_{\text{intr}}$ goes to 753.7 W/m·K, 568.1 W/m·K and 492.1 W/m·K for S1, S2 and S3 respectively. The results indicate that the CITA dramatically increases $\kappa_{\text{intr}}$, which is brought up to 5-19 times higher than that before annealing. However, $\kappa_{\text{intr}}$ after annealing is still not as high as the reported highest value for highly oriented pyrolytic graphite (~2000 W/m·K at RT). The reason is the residual impurities as well as the inter-tube thermal contact resistance which
cannot be removed by CITA. This result provides details for the sequential thermal conductivity enhancement process by CITA. Based on our result, the most efficient temperature range for improving $\kappa_{\text{intr}}$ is approximately 600-1100 K. Within that temperature range, $\kappa_{\text{intr}}$ is enhanced dramatically.

The thermal conductivity improvement result is very promising compared to the previously reported thermal annealing or combined annealing results. Jin et al. reported a 9-time increase in the thermal conductivity at RT for MWCNT bundles after the sample was annealed at 2800 °C in Ar for 4 h. Matsumoto et al. conducted an combined annealing. After optimum (at 800 °C, 150 A cm$^{-2}$ for 1 min) treatment to single-walled CNTS, the resulting electrical and thermal properties presented a 3.1-3.7 times increase. Our results from sole current-induced thermal annealing give a 5-19 times thermal conductivity increase. This result demonstrates the high efficiency of the CITA in improving thermal conductivity of MWCNTs. Applying current can also help prevent undesirable structure changes during direct thermal annealing. Matsumoto et al. attributed the increased thermal and electrical properties of single-walled CNTs during high temperature annealing to the increased wall number, diameter, and crystallinity. The change in wall number and diameter could be undesirable, which can be prevented by applying current to the sample while being thermally treated simultaneously.

CITA has a higher effect on the thermal conductivity of S1 than the other two samples. The reason can be interpreted as following. Before annealing, $\alpha_{\text{eff}}$ of S1 is two-times lower than the other two samples, which demonstrates that the quality of S1 is inferior than S2 and S3. The higher defects and impurities density endows S1 more room to improve. Another reason is the early breaking of S2 and S3. As seen from Fig. 6.4.1 (b), the two samples break
before their thermal conductivity reach a saturation values. Before breaking, $\kappa_{\text{intr}}$ still presents a slowly increasing behavior. The breaking is a consequence of localized overheating due to structure defects. The melting temperature of the three samples are 2491 K, 2996 K, and 2537 K respectively. Literatures reported a very high melting temperature of perfect single-walled CNT to be around 4800 K. However, the existence of defects caused a premelting temperature at around 2600 K.[169] The melting temperature of the three samples are consistent with the literatures value. The difference could be resulted from the different defect density in the sample and the thermal strain effect.
CHAPTER 7  CONCLUSION AND FUTURE WORK

7.1 Conclusion

7.1.1 Conclusion on graphene foam

This work investigated the thermal transport in graphene foam from RT to 17 K using the TET technique. The three-dimensional interconnected foam-like samples basically consists of four-layer graphene. The intrinsic thermal diffusivity (\(\alpha\)) of graphene is accurately determined after subtracting the radiation effect. We identified the defect-induced phonon scattering effects in thermal transport of graphene by fitting the thermal coefficient to the point of T=0 K. Using the residual thermal coefficient (\(\alpha_{\text{res}}\)), we are able to evaluate the Debye temperature and defect-phonon scattering mean free path of graphene. \(\alpha_{\text{res}}\) is found at 1878 s/m\(^2\) for the studied graphene foam, and 43~112 s/m\(^2\) for three highly crystalline graphite materials. This indicates the orders of magnitude higher defect level in the GF. The defect-induced phonon scattering gave a long mean free path of 166 nm. The Debye temperature of graphene was determined at 1813 K, agreeing well with the average of theoretical Debye temperature (1911 K) of TA, ZA, and LA phonons in graphene. By subtracting the residual thermal coefficient, we obtained the ideal thermal diffusivity and conductivity of the studied graphene. The ideal thermal conductivity (\(\kappa_{\text{ideal}}\)) resulted from Umklapp phonon-phonon scattering was found increasing all the way up with decreased temperature. At RT, \(\kappa_{\text{ideal}}\) is around 300 W mK\(^{-1}\). It could go up to greater than \(10^5\) WmK\(^{-1}\) when temperature goes down to 80 K. The ideal thermal conductivity of several reference graphite samples shows the similar trend and comparable results.
7.1.2 Conclusion on graphene aerogel

We synthesized graphene aerogels material with an extremely low thermal conductivity using an improved chemical reduction method. The resulting GAs has a very low density (2-6 mg cm\(^3\)) and good elasticity. By employing the SET technique, we measured the thermal conductivity from RT to as low as 10.4 K for the two groups of GAs (density of 4.2 and 3.9 mg cm\(^3\) respectively). The thermal conductivity of our GA is extremely low (down to 2×10\(^{-4}\) - 4×10\(^{-4}\) W·m\(^{-1}\)·K\(^{-1}\) at low temperatures and 4.7×10\(^{-3}\)-5.9×10\(^{-3}\) W·m\(^{-1}\)·K\(^{-1}\) at RT), which makes it a very promising material for thermal insulation. The thermal diffusivity is further characterized using the TET technique. The thermal diffusivity stays almost constant with a little decrease with the decreased temperature, revealing the dominating effect of thermal contact resistance for sustaining the thermal transport in GAs. The exponentially increasing electrical resistivity (against decreased temperature) indicates the contact among r-GO sheets is worsened as temperature goes down. The specific heat calculated from the experimental data shows a very similar pattern as that of graphite. The value is close to that of amorphous carbon. The results strongly demonstrate the amorphous structure within the GAs, which is also revealed by XRD characterization. The extremely low thermal conductivity uncovered in this work is for GAs of a density around 4 mg cm\(^3\). We predict when the density of GAs is reduced to the level of 0.16 mg cm\(^3\) (lightest reported density for GAs to date), the thermal conductivity of GAs could be significantly reduced down to the order of 10\(^{-4}\) W·m\(^{-1}\)·K\(^{-1}\) at RT, and 10\(^{-6}\)-10\(^{-5}\) W·m\(^{-1}\)·K\(^{-1}\) at temperatures around 10 K. This will make the graphene aerogel an unprecedented insulating material for thermal protection, especially under vacuum conditions (e.g. astronautics areas).
7.1.3 Conclusion on graphene paper

A novel ultra-high thermal conductivity/diffusivity switch-on behavior was discovered for high purity GP when its temperature was reduced to 245-260 K. Upon switch-on, the thermal diffusivity and thermal conductivity of GP had a 4 to 8-fold jump. The ultra-high thermal conductivity switch-on was also observed reversible during a single TET heating process. It suggests that the thermal expansion coefficient difference between pure graphene flakes and surrounding impurities flakes causes separation of the flakes at certain temperatures. When GP flakes are in contacting state, the interaction between pure graphene flakes and surrounding impurities-imbedded flakes efficiently suppress phonon transport in GP. After switching-on, the flakes are free from substrate scattering effect. The physics explanation was also confirmed by the TCR switch behavior during the TET measurement. By conducting repeated experiments, the structure separation was found repeatable. When temperature went back to RT, the flakes went back to the original contacting state. The measured $\kappa$ value of before and after switch-on were consistent with the literature reported $\kappa$ values of supported and suspended graphene respectively. The thermal conductivity, thermal reffusivity profile of graphite, PRGP and GOP were presented and compared to analyze the requirements for the switch-on. No switch-on behavior was observed for PRGP and GOP. The extremely low intensity of the point defect scattering and the small thermal contact resistance in GP results in the strong influence of the neighboring impurity layers scattering in GP. This makes the thermal expansion induced switch-on feasible. This finding points out a novel way to switching on/off the ultra-high thermal conductivity of graphene paper based on substrate-phonon scattering.
7.1.4 Conclusion on CNT bundles

In this work, the sequential process of current-induced thermal annealing on improving the structure, thermal and electrical transport in CVD grown CNT bundles was studied for the first time. By combining a high current annealing in vacuum environment and in-situ TET characterization, the statistical errors from sample-wide structure variation and contamination during sample transfer/preparation process can be averted. The annealing current was increased from tens of mA to as high as 1.4 A till the samples were burnt broken. The electrical resistance reduction and thermal diffusivity improvement of the same samples at different current levels were reported. The annealing resulted in a 4.4%-8% reduction in the electrical resistance, and 76%-236% increase in the effective thermal diffusivity. The low temperature thermal diffusivity and electrical resistance profiles of an unannealed CNT bundle was measured to have a better understanding of the mechanisms of thermal properties enhancement. The CITA process removed impurities and healed defects within CNTs, which reduced the phonon scattering intensity considerably. Raman spectroscopy was used to characterize the structure improvement along the length direction of the bundles, which gives a 61.3% decrease in $I_D/I_G$ at near breaking point compared to near electrodes. This reflects a dramatically reduced degree of disorder. The thermal properties against annealing current were translated into a temperature dependent profile by finite difference modeling. By taking the curvature and void space effect into consideration, the intrinsic thermal conductivity of graphite walls in the bundle was evaluated. CITA resulted in a 5-19 times thermal conductivity increase from about tens of W/ m·K to as high as 753.7 W/ m·K at RT. As the annealing temperature increased from RT to as high as the melting temperature, three stages of the thermal conductivity improvement were observed, which included a fast-increasing region from 600 K to about
1100 K, a slow-increasing region and a saturated region. This work sheds light on the understanding of thermal properties evolution during current induced thermal annealing process.

7.2 Future Work

7.2.1 Scope of future work

The above finished current work lay the foundation for a basic understanding of phonon scattering mechanisms and the nanostructures of carbon materials. Most importantly, a new theory named thermal reffusivity is proposed, improved, and applied in different aspects during the study. A good understanding on the relationship between thermal properties and nanostructures sheds light on the future application study of these new carbon nanostructured materials. The future work will focus on the following two areas: further investigation of the structure and thermal properties relationship, and advanced applications of these new nanostructured carbon materials from thermal science consideration.

7.2.2 Parallel heat transfer in CNT bundles

During the study of the CNT bundles materials, we found an interesting phenomenon. After several rounds of cryogenic experiments, the TET signals began to show a two-staged voltage evolution: a fast decreasing stage and a slow decreasing stage. These two stages correspond to two parallel thermal transport behaviors in the CNT bundles. The unique structure of CNT bundles constitutes the parallel thermal transfer paths. The multi-walled carbon nanotube bundles were synthesized using a ferrocene assisted chemical vapor
deposition (CVD) process in quartz tube furnace. A patterned catalyst film consists of 10 nm Al and 1 nm Fe. At the initial growth stage, the density of the catalyst particles is high, which results in a simultaneous growth of vertically aligned CNTs. As the growth continues, the average speed of the growth front suppresses part of fast growth CNTs. Therefore, fast-growing part of CNTs grow into helical shape CNTs. Figure 7.2.1 (a) shows the schematic of the morphologies and alignment of CNTs in CNT bundles. When heat is conducted from one end of the sample to the other, two parallel heat paths are available. The helical-shape CNTs have much longer length than the straight CNTs. As we estimated in the last chapter, the ratio of the curvature to that of straight length distance is about 1.52. If we estimate the heat resistance at the sample length scale, the effective thermal diffusivity of curved CNTs will be much higher than that of straight CNTs. In addition, the faster growth speed and higher density of catalyst particles inevitably brings in more defects and/or impurities in the curved CNTs. This quality difference also contributes to the lower thermal diffusivity of curved CNTs. In summary, the straight and curved CNTs constitute a parallel heat transport path for phonons. The curved CNTs have much higher thermal resistance. Figure 7.2.1 (b) shows the schematic of the parallel heat transport path.

Figure 7.2.1 (c) shows one of the TET signals after the parallel heat transport paths are developed under low temperature. Due to the existence of the two parallel thermal resistances in CNT bundles, the TET signals are different from other solid materials. Upon joule heating, the voltage of the sample first experiences a quick decrease and then presents a slow decrease. This voltage profile cannot be fitted using the normal TET model with one thermal diffusivity as in equation (2). Instead, a double thermal diffusivity model fits the data excellently.
Figure 7.2.1 (a) A schematic of the root growth mechanism illustrates that the initially straight CNTs develop curved morphologies in latter stages of growth. [153] (b) The schematic of parallel thermal transport path in CNT bundles. (c) One of the TET signals from parallel heat transport in CNT bundles sample.

In the near future, from this parallel heat transport model, two different thermal diffusivity values will be obtained, which correspond to straight and curved CNTs respectively. By taking the thermal transport length ratio into consideration, we will evaluate the intrinsic thermal diffusivity of these two kinds of CNTs. By comparing their thermal diffusivity profile, we will understand the difference in their defect levels and grain sizes. The proportion of the straight CNTs and curved CNTs under different temperatures will be investigated to have a closer look at the structure evolution. In the first round of the cryogenic experiment, there is no parallel heat transport observed. It is after second round of the cryogenic experiment, when the parallel heat transport behavior emerges. The reason for the parallel heat transport path development under low temperature require future investigations and more experiments.
7.2.3 Graphene based super-insulation material

Through the study of the nanostructures and thermal properties of different carbon materials, a basic knowledge and database have been acquired for the design of advanced thermal materials to fulfill different applications scenarios. This will be another future research area.

In the near future, we will take advantage of different carbon nanostructures and combine their unique thermal properties. This makes an advanced super-insulation material possible. Generally, two approaches are now available for obtaining super-insulating materials: by replacing air with vacuum or other low thermal conductivity gas, or by reducing the pore size smaller than mean the mean free path of air. For the first approach, it is very difficult to keep the vacuum or other gas condition within the insulation materials under real situations. A representative material of the second approach is silica aerogel. Silica aerogel has very high porosity. In atmospheric pressure, its $\kappa$ is about $0.03$ W m$^{-1}$ K$^{-1}$. In modest vacuum, its $\kappa$ is about $0.004$ W m$^{-1}$ K$^{-1}$. However, silica aerogel is mechanically rigid and suffers from structural collapse under mechanical compression, which makes it unfit for application as flexible or wearable material. In addition, it is difficult to manufacture silica aerogel in large scale since the synthesis process is very complex.

Graphene aerogel as one of the most promising 3D graphene based materials has very good mechanical elasticity, lightweight, electrical conductive, and extremely low thermal conductivity. These excellent properties make it an outstanding candidate as future super-insulation material. As illustrated in chapter 4, the nanostructure of graphene aerogel features a high porosity and continuous structure consisting of self-assembled graphene flakes. The high porosity and large interface thermal contact resistance result in an extremely low thermal
conductivity. Based on the study in chapter 4, graphene aerogel has a record low thermal conductivity at low temperatures, and comparable thermal conductivity as silica aerogel, which is known as the best insulator so far. What is more, as the lightest material in the world, the density of the graphene aerogel is comparable to air. Even if used in large quantity, GA will not increase the overall weight of the system evidently. The good mechanical elasticity of graphene aerogel also extends its application scope beyond that of silica aerogel.

In addition to the low thermal conductivity, lightweight, and mechanical flexibility, there is another important aspect when design super-insulation material from thermal science consideration. The in-plane thermal conductivity on the surface of the material should be high enough. Under localized heating, for example, when a hot-liquid is splashed onto the surface, heat needs to be quickly dissipated, which requires a surface material with high thermal conductivity. The development of large area graphene paper (GP) materials reveals that it has a very high in-plane thermal conductivity, which reaches a level close to 1400 W m\(^{-1}\) K\(^{-1}\). In addition, it exhibits excellent mechanical stiffness and flexibility with a high tensile strength (13.62 MPa) and Young’s modulus (2.31 GPa).[48] These properties make the GP material an excellent flexible lateral heat spreaders. On the other hand, its thermal conductivity across the thickness direction is quite low, about 10 W m\(^{-1}\) K\(^{-1}\). When used as outside layer of the insulation material, it provides good thermal protection for the cross-plane while quickly spreading the heat in the lateral direction.
Figure 7.2.2 A schematic of the graphene based super-insulation material. The outer layer material will be graphene paper (GP) with high in-plane thermal conductivity and the interior material will be graphene aerogel (GA) with lightweight and extremely low thermal conductivity.

In this future work, the composite material consisting graphene aerogel and graphene paper materials will be designed and synthesized. The thermal insulation properties will be investigated by measuring the cross-plane thermal conductivity from RT to 10 K. The surface thermal dissipating ability will be studied by measuring the in-plane thermal diffusivity and conductivity. The thermal performance for the whole composite material will be tested under steady-state temperature difference conditions and transient localized heating conditions.
REFERENCES


