

Measurement and Modulation of Thermal Transport in One-dimensional Materials with Scanning Electron Microscopy

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**Measurement and Modulation of
Thermal Transport in One-dimensional Materials
with Scanning Electron Microscopy**

by

Dawei Li

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in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

at

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Abstract

The accurate measurement of the thermal transport properties of nanomaterials is crucial for uncovering the microscopic heat transfer mechanisms and guiding the modulation of material performance for applications. Despite the impressive advancements in nanoscale thermal metrology over the past decades, there are still some problems and challenges, including (1) how to eliminate the thermal contact resistance (TCR) error between the sensor and the sample for the resistive contact methods, (2) how to directly evaluate TCR at a single junction between nanostructures, and (3) how to efficiently establish the structure-property relationship for thermal transport at the nanoscale. Besides, the modulation of thermal transport at the nanoscale has long remained challenging. This dissertation aims to address the above issues with scanning electron microscopy (SEM) and focuses on the measurement and modulation of thermal transport in one-dimensional (1D) materials.

First, a method combining the electron beam (EB) heating in SEM with two suspended line-shaped heat flux sensors was developed to eliminate the TCR error at the sample-sensor junction in the thermal conductivity measurement of 1D materials. The two ends of the sample are anchored to the two sensors respectively and the focused EB is utilized as a mobile heating source to heat the 1D sample locally with a high spatial resolution, while the two sensors simultaneously measure the heat fluxes induced by the EB heating and further the thermal resistance ratio of the two sample segments separated by the EB spot is extracted. The spatially resolved thermal resistance distribution can be obtained by moving the nanosized EB heating spot along the sample. The *in situ* thermal resistance mapping along a single cup-stacked carbon nanotube (CNT) was performed using this method, from which the thermal conductivity of the CNT without the TCR error was extracted to be around 40 W/m·K and the TCR at the sample-sensor junction was measured to be 1.35 MK/W.

Second, we developed a method for the *in situ* and real-time measurement of TCR at a single junction between 1D samples in SEM. In this method, the two 1D samples are anchored respectively to a manipulator-based tungsten probe serving as a movable heat sink and a suspended line-shaped sensor. A thermal path from the sensor to the probe is formed and the total thermal resistance of the two samples

in contact can be extracted. Afterward, we separate the two samples and measure their respective thermal resistance in the SEM. Then the TCR is extracted by subtracting the thermal resistance of each sample from the total thermal resistance. Since the movement of two samples can be separately controlled inside the SEM chamber, the contact condition can be dynamically and flexibly adjusted and the high-resolution images of the contact conditions can be *in situ* captured by SEM. Using this method, we measured the TCR between two multi-walled CNTs for 11 contact conditions that could be classified as aligned-contact, cross-contact, and contact-through-contamination conditions. The TCR results were on the order of 10^7 K/W and were studied in combination with the SEM-captured images of the contact morphology.

Third, we developed a method to simultaneously measure the thermal conductivity and observe the internal structure of a 1D sample using scanning transmission electron microscopy (STEM) in the SEM for the structure-property correlation. The two ends of the sample are anchored to a tungsten probe and a suspended line-shaped sensor, respectively. The sensor serves simultaneously as a heater and a resistance thermometer, ensuring highly sensitive thermal measurements. The sensor is fabricated on the edge of the silicon wafer so that the EB can transmit through the 1D sample and that the inner nanostructure of the sample can be observed in real-time. Using this method, we *in situ* measured the thermal conductivity of two cup-stacked CNTs and concurrently observed the internal non-uniform structures. The results indicated that the sample with more structural disorders had a lower thermal conductivity.

In addition, we successfully modulated the thermal transport in cup-stacked CNTs by filling liquid into the samples. We prepared CNTs infused with pure water and LiCl solutions and measured their thermal conductivities with our *in situ* STEM-in-SEM setup. The internal structures of three water-infused CNTs were also observed in real-time. We also measured the temperature dependence of thermal conductivity for a water-infused and a LiCl-solution-infused CNT. The liquid-infused cup-stacked CNTs exhibited higher thermal conductivity ($60\text{-}360$ W/m·K) than the dry samples (about 40 W/m·K). This thermal conductivity enhancement can be attributed to the strengthened interfacial coupling between graphene layers due to the penetration of water molecules or ions into the gaps between graphene cups, which is supported by the molecular dynamics simulation results in the literature.

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1. Introduction

1.1 Carbon nanotube

As one of the representative one-dimensional (1D) materials, carbon nanotubes (CNTs) are seamless cylinders of one or more layers of graphene (called single-walled carbon nanotube, SWCNT, or multi-walled carbon nanotube, MWCNT) shown in Fig. 1.1 [1], with open or closed ends [2]. They were first reported by Iijima [3, 4], and since then their unique properties have been uncovered and extensively studied, including the high mechanical strength [5, 6], exceptional high thermal [7-10] and electrical conductivity [11]. Their excellent properties make them have potential applications including energy conversion and thermal management. For the perfect CNTs, all carbons are bonded in a hexagonal lattice except at their ends, while the mass-produced CNTs will introduce defects such as pentagons, heptagons, and other imperfections in the sidewalls that generally degrade desired properties. Besides, the presently realized mechanical, thermal, and electrical properties of CNT macrostructures such as yarns and sheets remain significantly lower than those of individual CNTs [2]. In addition to the SWCNT and MWCNT, there are also other kinds of CNT, such as cup-stacked CNT. Figure 1.2 shows the transmission electron microscopy (TEM) image [12] and schematic [13] of a cup-stacked CNT, it is composed of a chain of truncated graphene cups stacked together which are tilted a few degrees relative to the longitudinal tube axis [12]. The spacing between the two adjacent graphene cups is around 0.34 nm.

This dissertation focuses on the experimental study of thermal transport in 1D materials. Since the extremely tiny dimension of low-dimensional materials makes it difficult to measure the local temperature and heating rate [9], to accurately characterize their thermal transport properties, a series of nanoscale thermal measurement techniques have been developed. However, the development of new technologies is also accompanied by new problems and challenges.

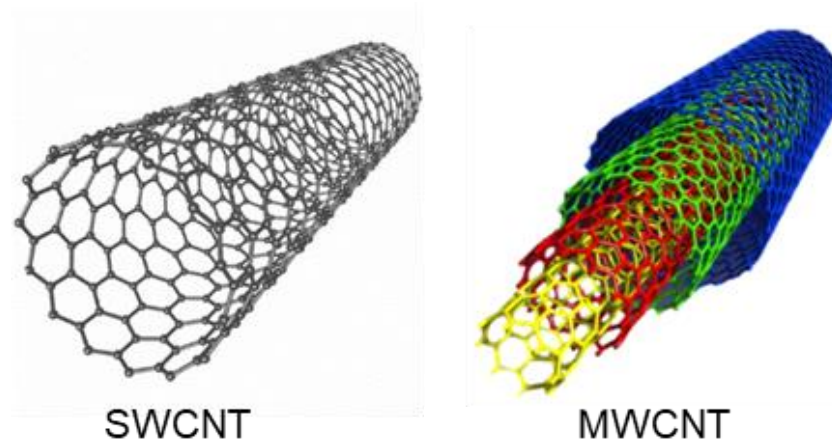
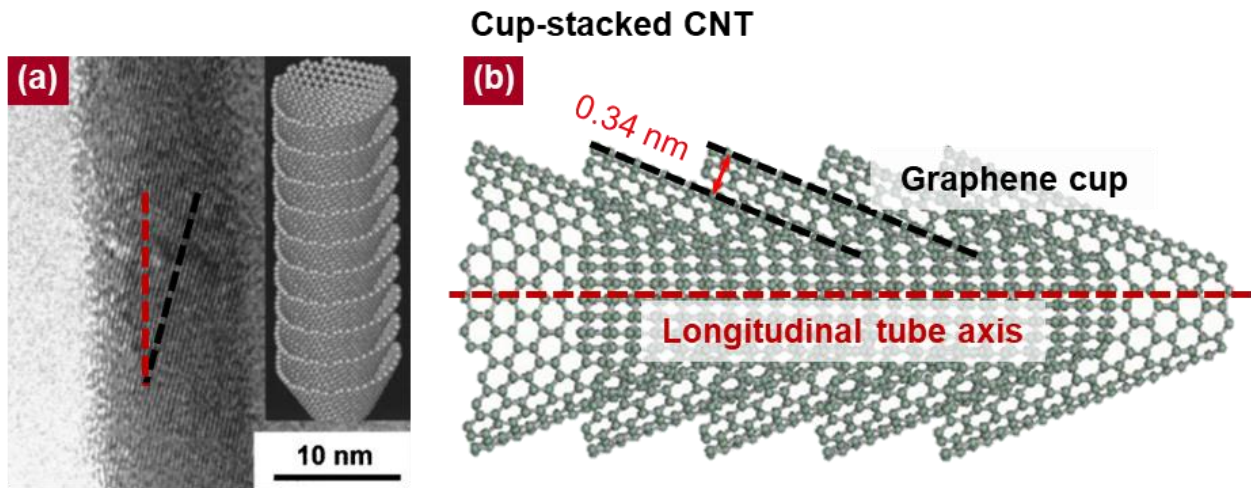


Figure 1.1 Schematic illustrations of SWCNT and MWCNT [1].



M. Endo *et al.*, Appl. Phys. Lett. **80**, 1267 (2002).

K. Takahashi *et al.*, Physica B-Condensed Matter **404**, 2431 (2009).

Figure 1.2 (a) TEM image [12] and (b) schematic [13] of cup-stacked CNT.

1.2 Problems in nanoscale thermal metrology

1.2.1 Inevitable thermal contact resistance error between sensor and sample for the resistive contact methods

The accurate measurement of the thermal transport properties of low-dimensional materials is important for the fundamental understanding of microscopic heat transfer mechanisms and engineering design in a wide range of applications including thermal management and thermoelectrics [2, 14-20].

Figure 1.3 shows several representative experimental methods that have been established for measuring

the thermal conductivity of nanomaterials. In the T-type method [9, 21, 22], there is a suspended metallic nanofilm serving as a heater and resistance thermometer simultaneously, when the sample is transferred to the nanofilm to form a T-type configuration, the temperature distribution along the nanofilm changes from a parabolic profile to a double-parabolic profile since part of the heat leaks out through the sample to the heat sink. The thermal resistance including the sample and the contact between the sample and the nanofilm is extracted from the change in the average temperature rise of the nanofilm before and after the sample transfer. In the thermal bridge device method [7, 8], there are two suspended adjacent SiN_x membranes on long and slender beams made of silicon nitride. Each SiN_x membrane has a serpentine platinum line heater which also serves as a resistance thermometer. After the sample is bridged the two membranes by probe manipulation transfer or suspension droplet deposition and drying or *in situ* growth, the two membranes are denoted as the heating and sensing membranes, respectively. Since the heat flux through the sample and the temperature of each membrane can be measured, the sum thermal resistance of the sample and two contact points can be extracted.

For the electrical self-heating method [10, 23-27], an electrical current is applied to the sample to heat the sample, the electrical resistance of the sample will change by the Joule heating and is monitored by the measurement circuit. Based on the temperature dependence of the electrical resistance of the sample, the thermal conductivity of the sample can be derived. In the basic 3 omega method [26, 28-31], a line heater is driven by a sinusoidal current source at angular frequency ω , which induces a temperature fluctuation at 2ω related to the thermal properties of the heater and/or its surrounding environment. This further perturbs the heater resistance at 2ω , leading to a voltage signal at 3ω [31]. For the Raman optothermal method [32-38], a Raman excitation laser acts as a heater to locally heat the sample and this local temperature rise is determined by using a micro Raman spectrometer as the thermometer based on the temperature dependency of Raman peak position.

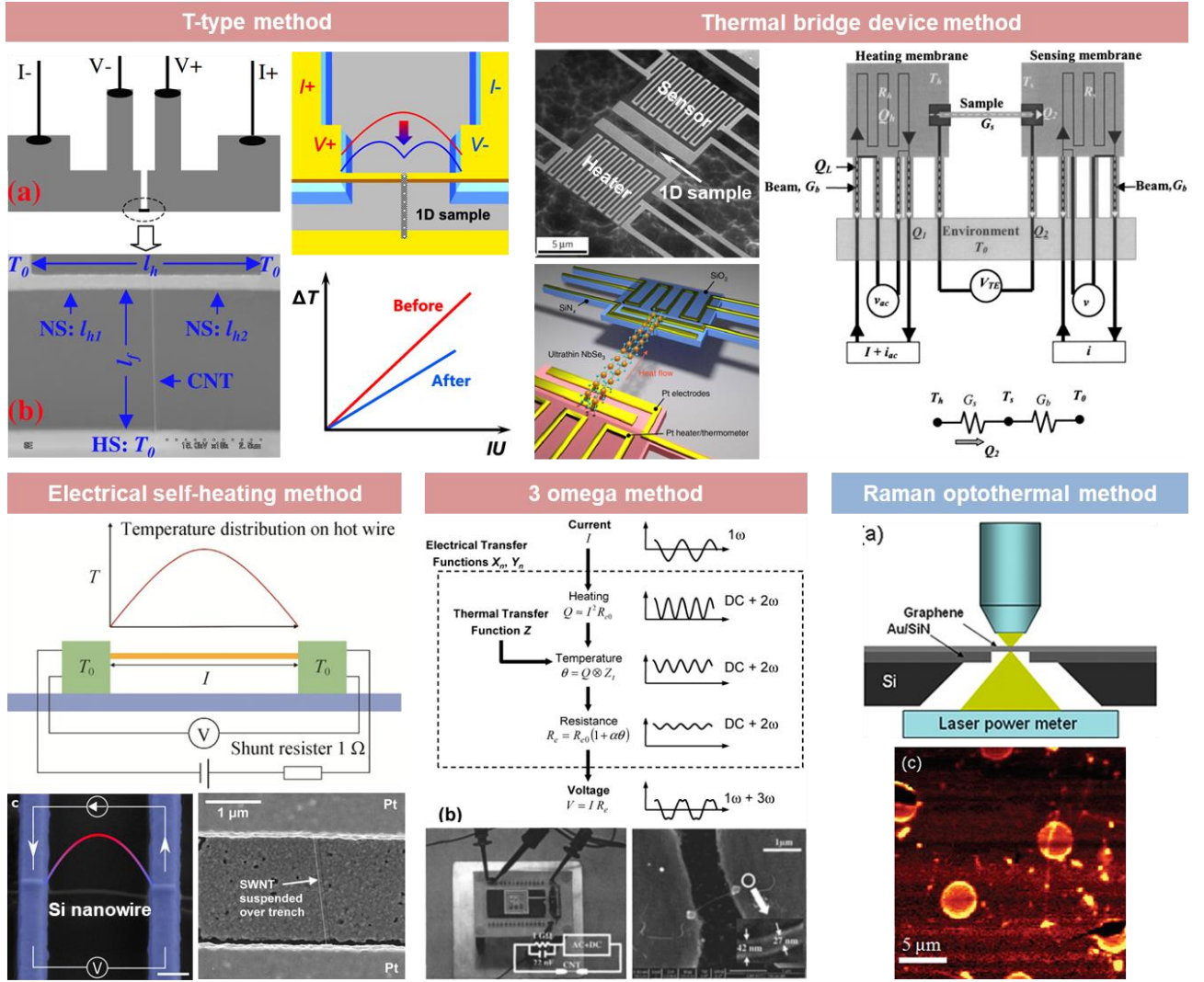


Figure 1.3 Representative experimental methods for measuring the thermal conductivity of low-dimensional materials: T-type method [9], thermal bridge device method [8, 39, 40], electrical self-heating method [10, 24, 26], 3 omega method [29, 30], and Raman optothermal method [33].

The above experimental methods can be divided into resistive contact techniques and non-contact techniques. For the contact methods, the inevitable thermal contact resistance (TCR) between the sample and the sensor can cause large errors and is a long-standing obstacle to the accurate measurement of thermal transport properties of low-dimensional materials [41].

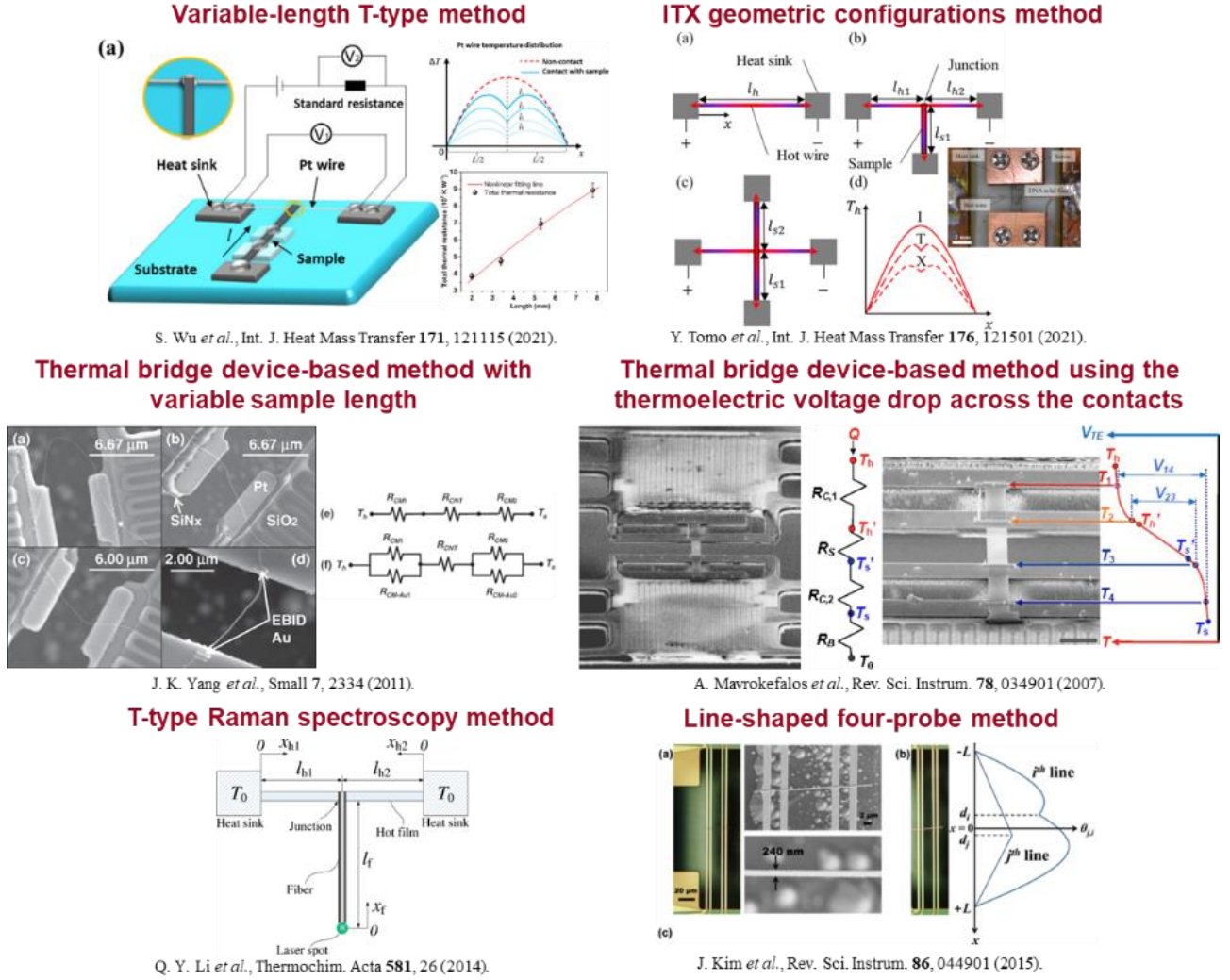


Figure 1.4 Experimental methods used to extract the thermal contact resistance between the sensor and sample [42-47].

Several techniques have been well developed to eliminate the TCR error for millimeter-long microfibers, like changing the sample length or thermal penetration length [42, 43, 46, 48-50] and using the thermoelectric voltage drop across the contacts [47]. As shown in Fig. 1.4, in the variable-length T-type method [42, 48], the contact junction between the Pt wire sensor and the sample keeps unchanged, while the effective length of the sample is shortened by moving the heat sink toward the sensor. Since the much larger contact area between the sample and the heat sink, its thermal contact resistance is negligible. The measured apparent thermal resistance is mainly the thermal resistance of the sample and the TCR between the Pt wire sensor and the sample, and the intercept of the apparent thermal resistance

versus the effective sample length is the TCR between the Pt sensor and the sample. The ITX geometric configurations method [43] adopts a similar strategy. Nevertheless, these techniques are extremely difficult to be applied to nanoscale samples due to the manipulation difficulties. For the thermal bridge device-based method with variable sample length, it should be noted that the apparent thermal resistance is not measured from the same sample and the obtained TCR has a relatively large uncertainty. Despite some endeavors shown in Fig. 1.4 to eliminate the TCR error at the nanoscale [44, 51], eliminating the TCR error for specific nanostructures has remained a critical challenge. Furthermore, the structural non-uniformity in nanomaterials, including interfaces, impurities, and defects, can lead to nonuniform thermal conductivity even in the same sample [52], so there is a desperate desire for thermal property mapping with an ultrahigh spatial resolution.

1.2.2 Difficulty in direct evaluation of thermal contact resistance at a single junction level between nanostructures

The thermal contact resistance at the junctions dominantly impacts the thermal properties of the assembly in practical applications such as bundles, arrays, networks, and composites, while the interface/contact thermal resistance has not been widely discussed [15, 41, 53-58]. As shown in Fig. 1.5, despite a single CNT exhibiting excellent thermal transport properties, CNT random network composites present unexpectedly much lower thermal conductivity, which is attributed to numerous contacts and related thermal resistance in the composites [53]. The temperature mapping image of an electrical heated high-density CNT network also shows some high-temperature spots [54], which demonstrates the terrible heat conduction in the network composite and confirms the dominant effect of the contact.

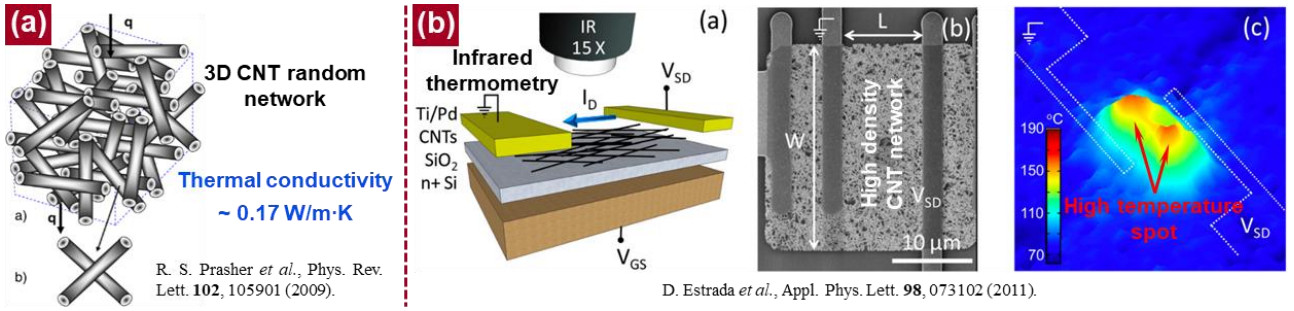


Figure 1.5 (a) The unexpectedly low thermal conductivity of CNT composite network [53]. (b) Temperature mapping image showing the high-temperature spots in a high-density CNT network [54].

In addition, the improvement in the overall thermal conduction of the composites by different strategies is also always inferred to the optimization of the contact [59, 60]. Figure 1.6 shows some studies as examples. Cha *et al.* [60] measured the axial thermal conductivity of SWCNT forests with various volume fractions of SWCNTs. They found that there is an enhancement in the thermal conductivity of the SWCNT forest when the volume fraction is higher than 17%, which they attribute to the increased effective contact area between the SWCNTs by mechanical squeezing. Some SWCNTs which did not serve as a thermal path in the case of lower volume fraction, start to connect with the other SWCNTs when the volume fraction increases. Yang *et al.* [61] reported that the surface functionalization created a rigid covalent between MWCNT and helped form a better effective network for heat flow in the MWCNT composite, which resulted in a significant improvement in the thermal conductivity of the composite. Qiu *et al.* [62] demonstrated that the decoration of Au nanoparticles on the CNT can induce the excitation of low-frequency phonon (LFP) modes in CNTs, which is a strong mechanism to redistribute LFP modes into the interfacial carbon atoms and then activate a resonance with the LFPs of Au nanoparticles and results in more heat transfer across the contact. Wang *et al.* [59] experimentally found that the film of SWCNT coated with boron nitride nanotube (BNNT) exhibited an enhanced sheet thermal conductance compared with the bare SWCNT film, and the enhancement is attributed to the additional thermal conducting path served by the BNNT layer.

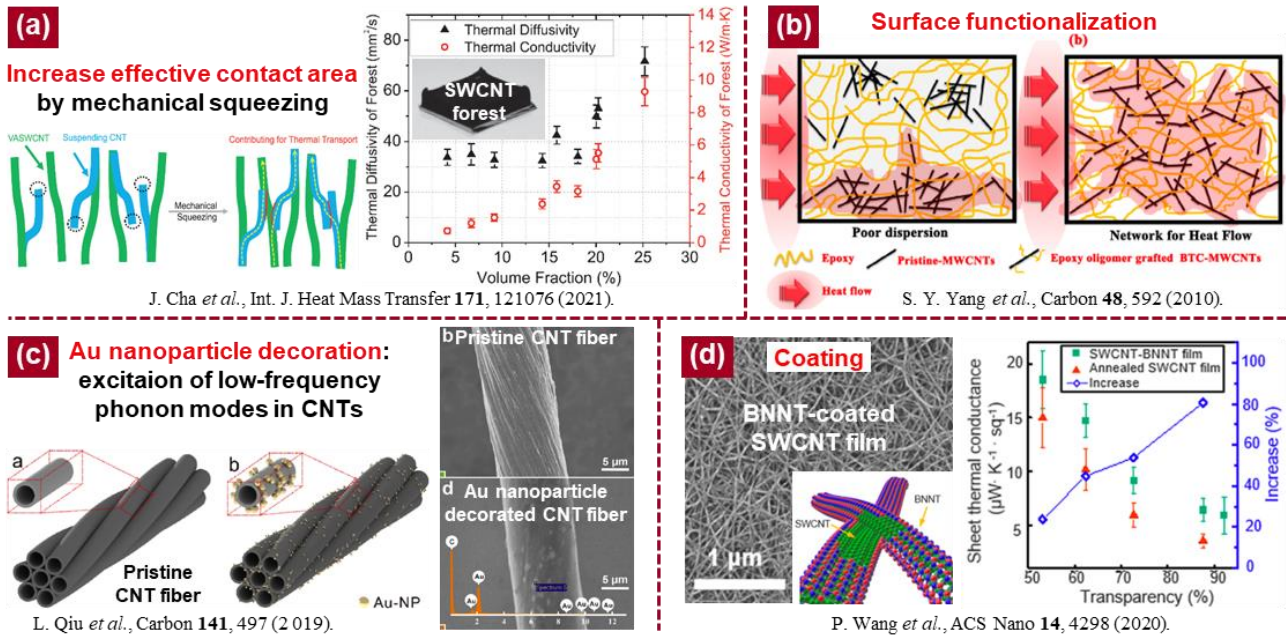


Figure 1.6 Some strategies for optimizing contact inferred from overall heat transfer enhancement: (a) Effective contact area [60], (b) Surface functionalization [61], (c) Surface decoration [62], and (d) Surface coating [59].

From the above introduction, it is learned that the contact conditions are very complex and most studies are focused on and stop at the composite level, which hinders the in-depth understanding and optimization of the TCR. It is meaningful and critical to directly study the TCR at a single junction level between nanostructures, however, its experiment still faces severe challenges [41] since the available experimental method is severely lacking and the tested contact condition is extremely limited.

1.2.3 Separated structural characterization and thermal measurement

The relationship between the nanomaterial structure and its thermophysical properties keeps a captivating subject of both fundamental and applied interest since it can not only uncover the microscopic heat transfer mechanisms but also guide the modulation of the material performance for wide applications [14, 15, 17, 63]. Even though several experimental methods have been exploited and applied to measure the thermophysical properties of nanomaterials and reveal the heat transfer mechanisms, these measurement methods cannot capture the real-time internal structure details of the nanomaterial sample during thermal measurement. Especially for nanowires and nanotubes, usually, the

internal structure of the sample is characterized using transmission electron microscopy before the thermal measurement. However, the thermal conductivity of individual nanomaterials can vary due to the structure variations from sample to sample even if they are from the same batch. Figure 1.7 shows the TEM images of CNTs with defects, amorphous parts, and non-uniform diameter. Furthermore, even the different parts of the same single sample can often exhibit structural variations. Hence the separated structural characterization is not conducive to clarifying the property-structure relationship, it is desperately desired to observe the internal structures along with the thermal measurement to gain insight into the relationship between the structure and the thermophysical properties.

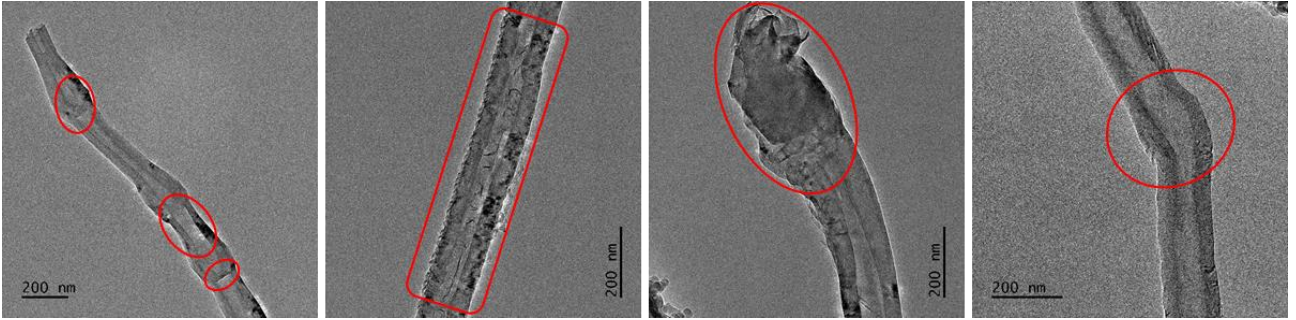


Figure 1.7 TEM images of CNTs with defects, amorphous part, and non-uniform diameter.

In situ TEM with atomic imaging resolution is a powerful technique to study the structure-property relationship in real-time [64, 65]. A series of exciting and impressive efforts have been conducted, however, these endeavors mainly focus on the *in situ* electrical properties measurement in TEM [66-68]. For example, as shown in Fig. 1.8, Hayashi *et al.* performed the *in situ* current-voltage measurements of cup-stacked carbon nanotubes in a TEM, found that the electrical conductivity of the CNT induced by compressive bending strain was reversible, and analyzed the mechanism of enhanced electrical conduction at the compressed side of the CNTs [66]. Zhang *et al.* investigated the electrical properties of segments of tapered InAs nanowires in TEM and analyzed the Joule heating and electromigration mechanism for the breakdown process [67]. A few qualitative *in situ* thermal measurements in TEM as shown in Fig. 1.9 include the observation of anisotropic thermal transport in

a CNT bundle by monitoring the phase change of gold nanoparticles as thermo-markers [69], and visualization of the nanoscale heat conduction pathways with a well-designed nano-thermocouple assembled in TEM [70]. However, these techniques are not suitable for the quantitative thermal conductivity measurement of individual nanomaterials.

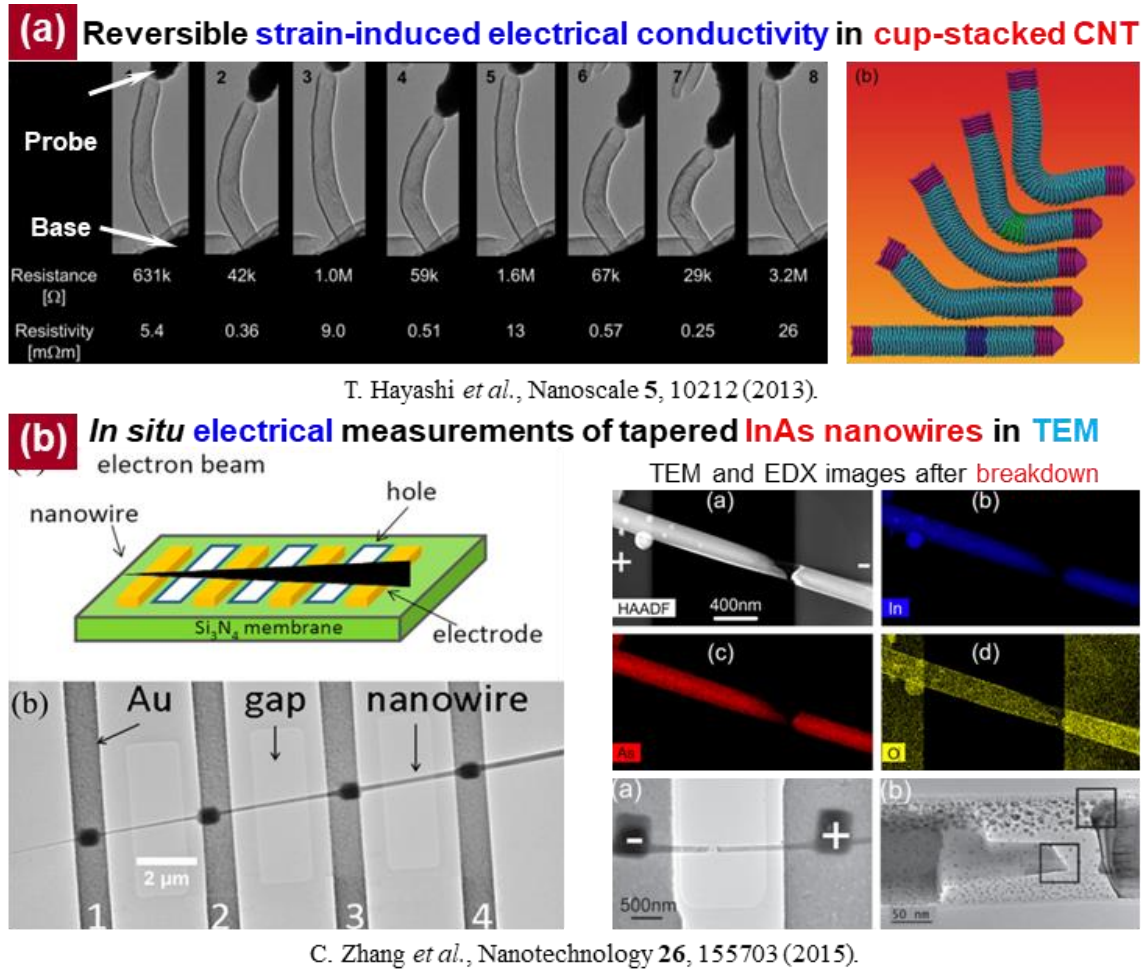


Figure 1.8 *In situ* electrical properties measurement in TEM. (a) Reversible strain-induced electrical conductivity in cup-stacked CNT [66]. (b) Electrical measurements of tapered InAs nanowires in TEM [67].

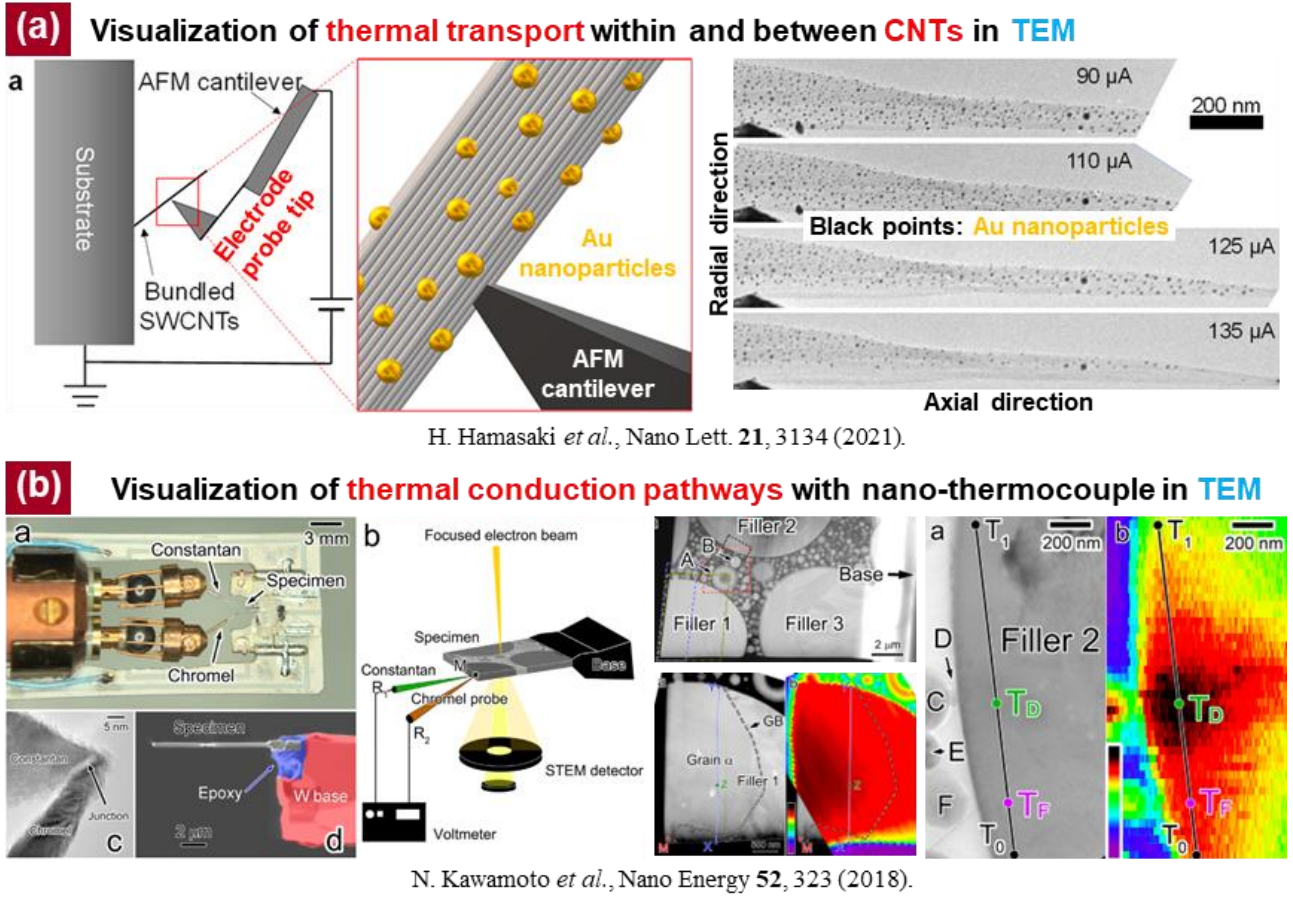


Figure 1.9 Qualitative *in situ* heat conduction visualization experiments in TEM. (a) Visualization of thermal transport within and between CNTs in TEM [69]. (b) Visualization of thermal conduction pathways with nano-thermocouple in TEM [70].

Figure 1.10 shows some endeavors of quantitative thermal measurements in TEM. In 2007, a hot-wire thermal probe for the *in situ* thermal conductivity measurement of 1D materials in TEM was reported [71], but the complicated fabrication of the hot-wire probe, the TEM-related assembly, and the difficult TEM operations have so far brought many challenges in the application of this method. In addition, a MEMS system was integrated into a TEM and used to measure the thermal conductance of a single Si nanojunction *in situ* [72, 73], the design, fabrication, and control of the MEMS system with TEM-related assembly is also complex and difficult. As a result, it is desired to develop an alternative technique.

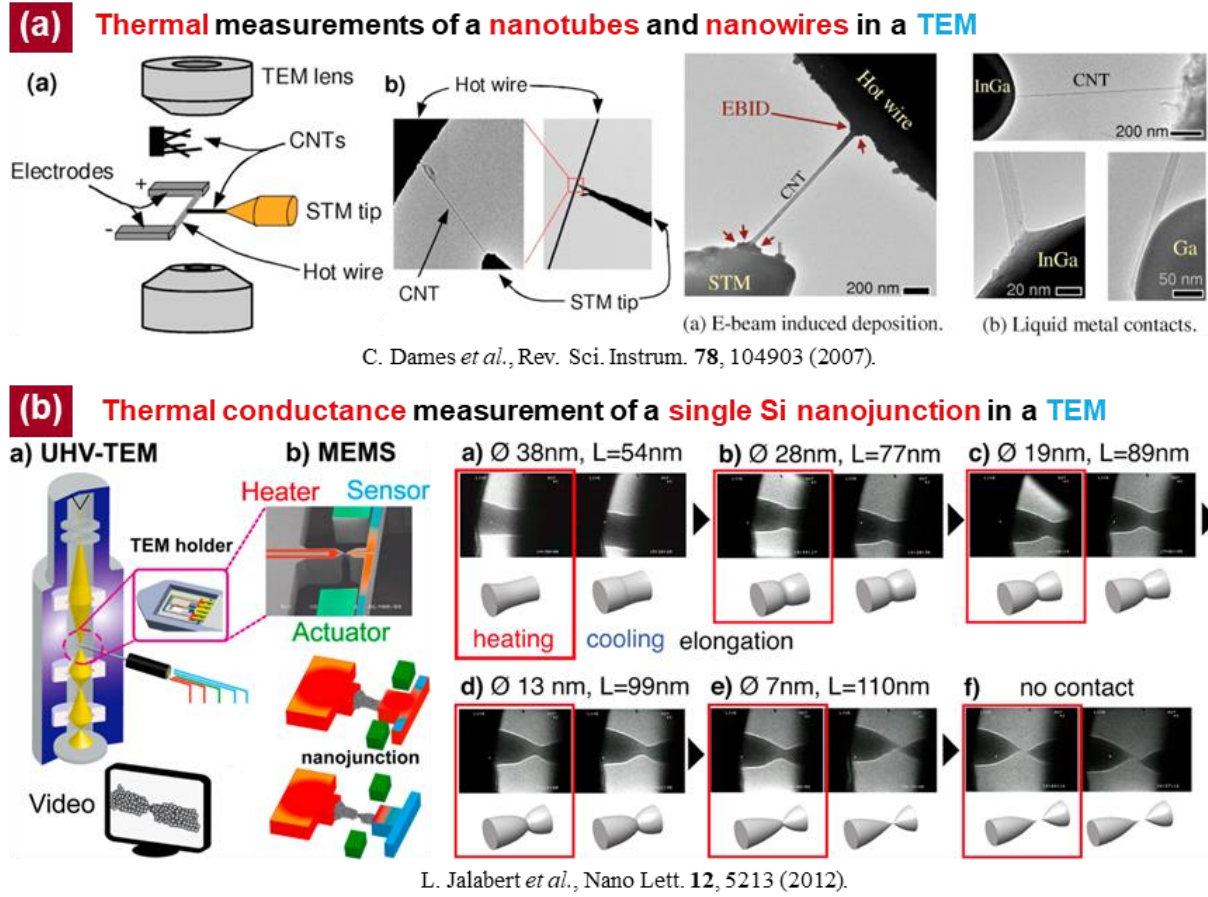


Figure 1.10 Quantitative *in situ* thermal measurements of nanotubes and nanojunction in TEM. (a) Thermal measurements of nanotubes and nanowires in a TEM [71]. (b) Thermal conductance measurement of a single Si nanojunction in a TEM [73].

1.3 Difficulty in the modulation of thermal transport at the nanoscale

Owing to the outstanding and diverse properties and ample potential applications, graphene-based materials have spurred intense research in a variety of fields [2, 32, 74, 75]. The modulation of its thermal transport properties keeps a subject of both fundamental and applied interest since it may lead to a desirable improvement of material performance and uncover the fascinating underlying mechanisms [14, 15, 63, 76]. As shown in Fig. 1.11, several representative experimental endeavors have been made and revealed that the fullerene encapsulation will reduce the thermal conductivity of CNT due to the repulsion between the carbon wall and the confined fullerene [40], the ionic liquid infusion causes a reduction in the thermal conductivity of the cup-stacked CNT [77]. By adjusting the lateral

dimensions, the nanoribbon structure has the capacity to tune the thermal conductivity of graphene as well [25, 78]. The introduction of isotope can regulate the thermal conductivity of graphene [79]. Apart from these, the nanomesh [80] and wrinkle [81] structures have also been suggested to be effective to modulate the thermal conductivity of graphene. The thermal rectification in monolayer graphene and monolayer lateral heterojunction is also experimentally studied and reported [18, 82, 83].

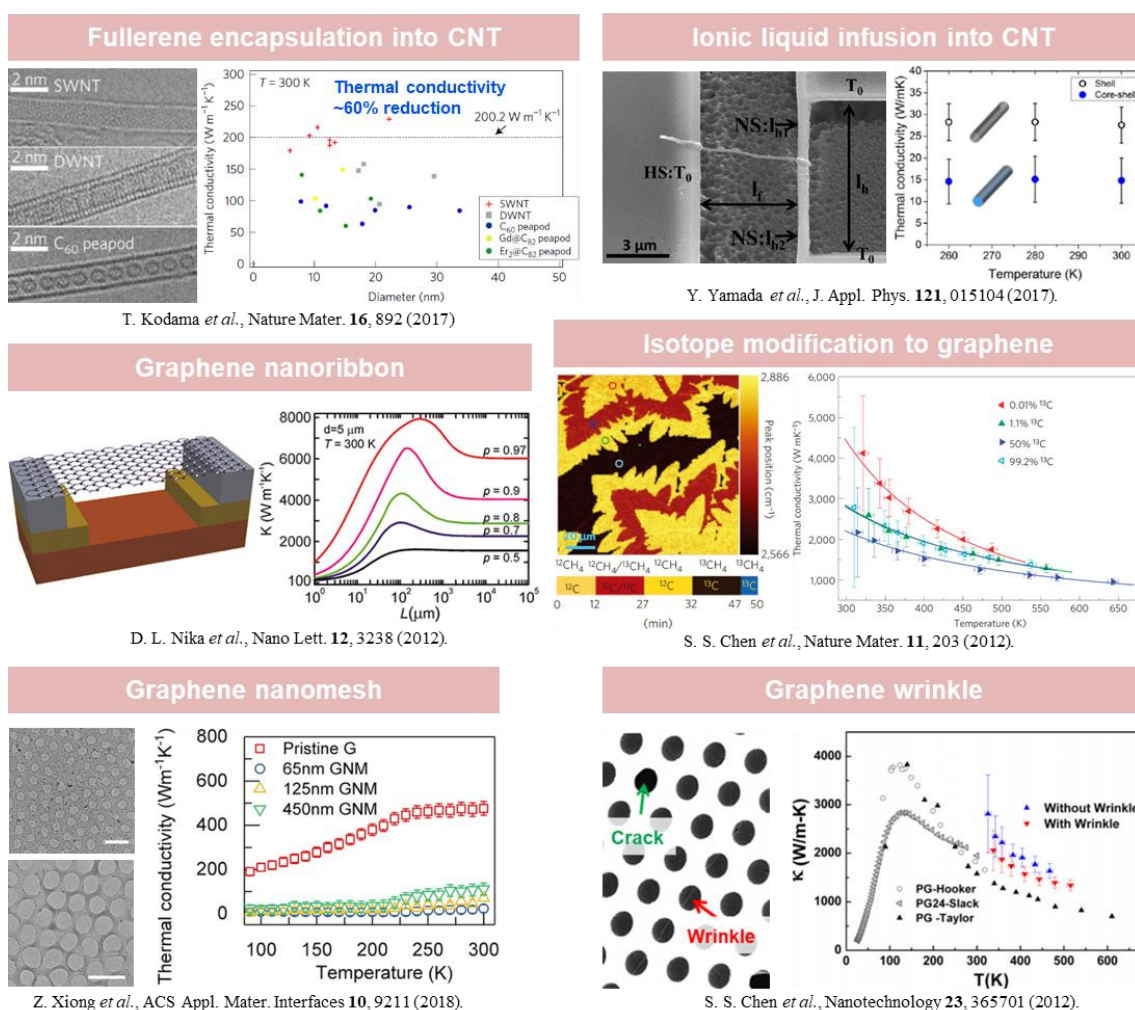


Figure 1.11 Several representative experimental endeavors on the modulation of thermal conductivity of graphene-based materials [40, 77-81].

Recently, some molecular dynamics and experimental studies pointed out that intercalation is a potent approach for modulating heat transfer at the interfaces. For example, as shown in Fig. 1.12, the intercalated water between the graphene and cell membrane displays a layered order and further

mediates the interfacial thermal coupling and promotes thermal dissipation at the interfaces [84]. Attributed to the mismatch in mass density and phonon density of states between the atomically two-dimensional layers, the artificial stacks of monolayer graphene, MoS₂, and WSe₂ have achieved the ultrahigh thermal isolation [85]. The reversible electrochemical lithium intercalation in MoS₂ thin films efficaciously modulates the thermal conductance of MoS₂ and makes it as switchable thermal transistors [86]. Additionally, it is disinterred that the lithium intercalation between the interspacing layers is competent to reversibly regulate the anisotropic thermal conductivity of black phosphorus [87].

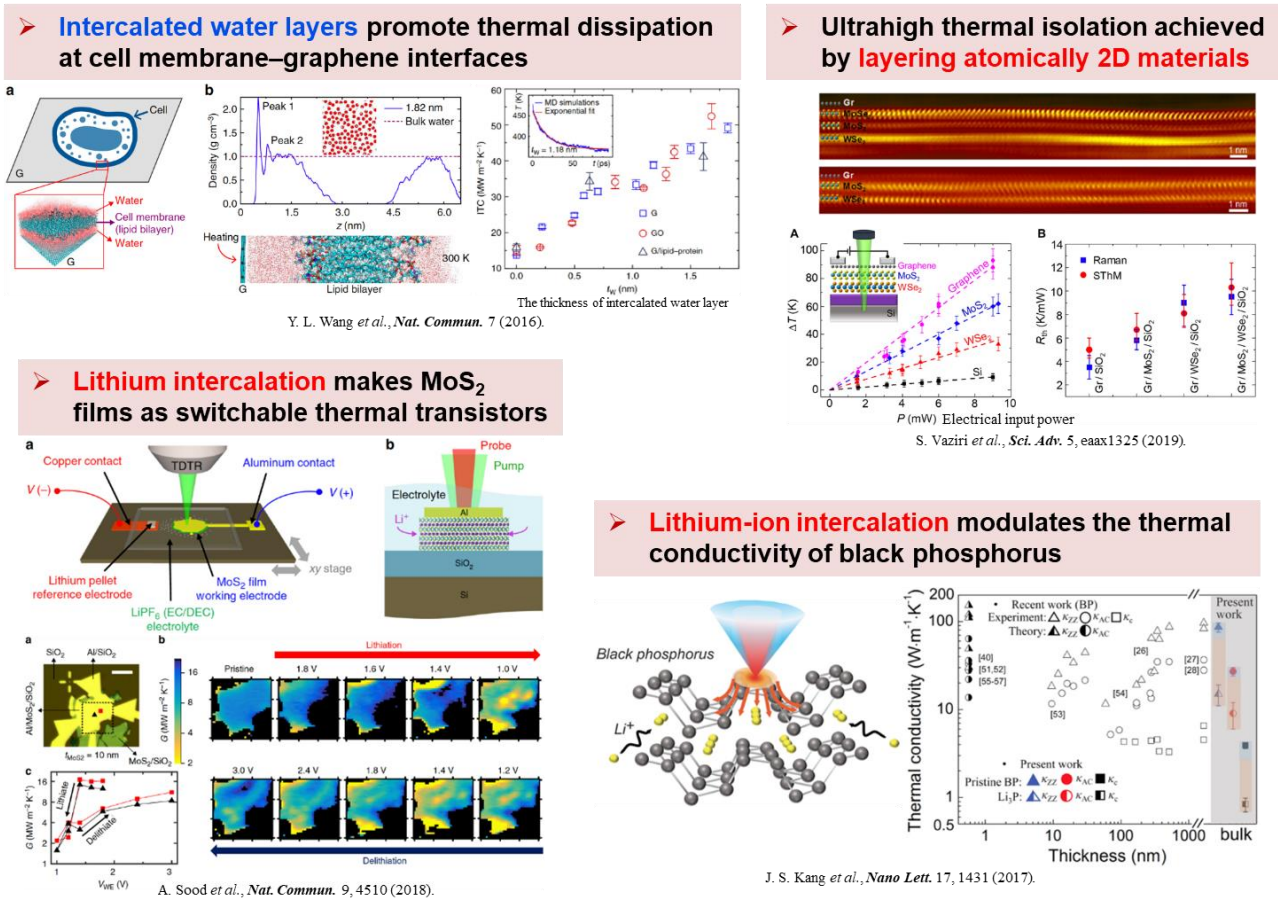


Figure 1.12 Study on the intercalation for modulating the heat transfer at the interfaces [84-87].

So far, the modulation of thermal transport at the nanoscale has long remained challenging. It requires a modulation strategy with a deep understanding of the thermal transport mechanisms. Besides, it is also difficult to successfully fabricate the sample based on the strategy and accurately measure its

thermal transport property.

1.4 Scanning electron microscopy

Electron microscopy has been a revolutionary imaging technology for scientists and engineers, opening up the world of nanoscale materials and enabling the characterization of their unique properties [88]. Electron microscopy is a technique that utilizes the interactions between a focused electron beam and the atoms composing the analyzed sample to generate the high magnification image. Compared to conventional optical microscopy, it has the advantage of breaking the limit of resolution that comes with optical microscopy since electrons can be focused more tightly than light, and allows for a resolution that can reach the atomic level [89].

The two main classes of microscopy are scanning electron microscopy (SEM) and TEM. Figure 1.13 shows the typical layout of a SEM and the interaction of incoming primary electrons (electrons targeted at the sample) with the analyzed sample [88]. In SEM, the images are generated by raster-scanning a focused electron beam over a sample and detecting the signals (secondary electrons, backscattered electrons, and so forth) emitted from the sample. The SEM requires an electron optical system to produce an electron probe, a sample stage to place the sample, the detectors to collect the corresponding signals emitted from the specimen generated by electron-matter interactions, an image display unit, and an operation system to perform various operations [90]. The electron optical system encompasses an electron gun (electron source and accelerating anode), a condenser lens and an objective lens to produce an electron probe, a scanning coil to scan the electron probe, and other components. The inside of the electron optical system and the specimen chamber are kept at vacuum.

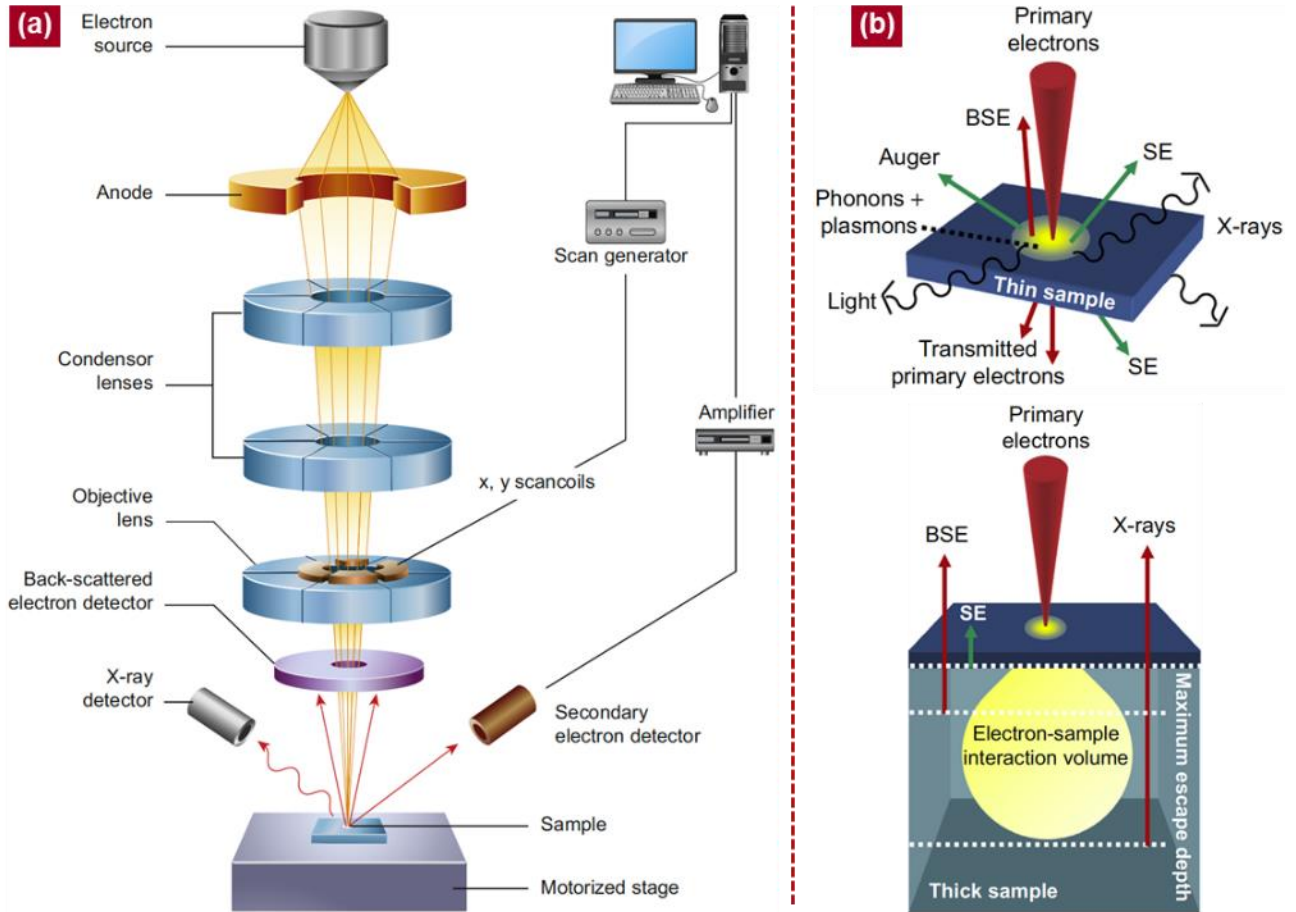


Figure 1.13 Schematic diagram of (a) the main components of a SEM and (b) the interaction of incoming primary electrons with the thin and thick samples [88].

SEM can not only be used to image surface morphology, analyze composition, and investigate crystalline structures. Thanks to its high spatial resolution, the *in situ* experiments in SEM can provide a better understanding of structure-property relationships [91, 92]. Besides, recently, the developments in nanoscale thermal metrology using SEM have also made impressive advancements [93-95].

1.5 Thesis organization

Based on the above introduction, it is learned that despite the great development in nanoscale thermal metrology over the past several decades, there are still some problems and challenges including (1) Inevitable thermal contact resistance error between sensor and sample for the resistive contact methods, (2) Difficulty in the direct evaluation of thermal contact resistance at a single junction level

between nanostructures, and (3) Separated structural characterization and thermal measurement. Besides, (4) the modulation of thermal transport at the nanoscale has long remained challenging. With its high spatial resolution and versatile functions, SEM has a wide range of promising applications in the field of nanoscale thermal metrology, the *in situ* experiments in SEM can also provide a better understanding of structure-property relationships.

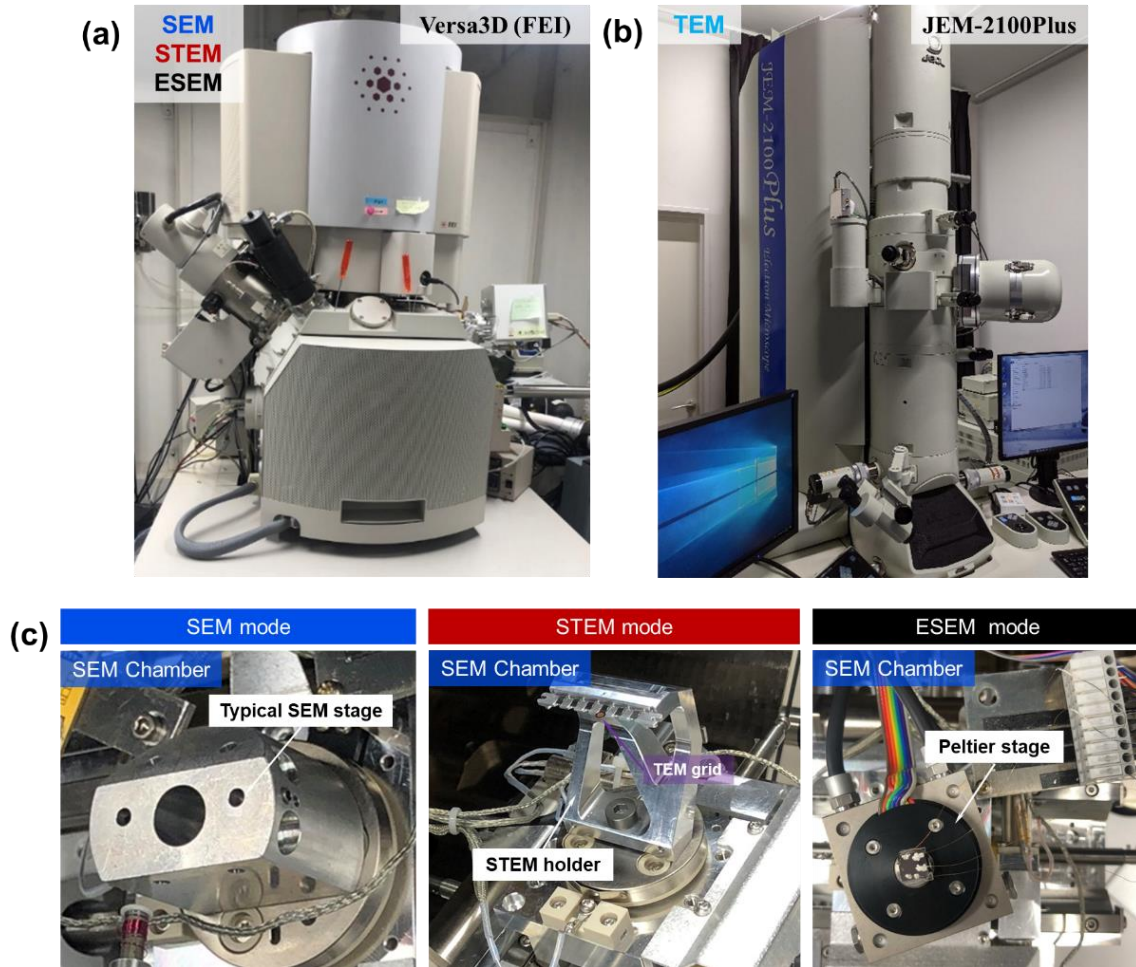


Figure 1.14 Photos of the (a) SEM and (c) TEM used in this study. (c) Different modes of the SEM.

This dissertation aims to address the above issues utilizing the SEM and it is focused on two aspects: measurements and modulation of thermal transport in 1D materials with SEM. Figure 1.14 shows the photos of the SEM (Versa 3D LoVac, FEI) and TEM (JEM-2100Plus, JEOL) used in this study. SEM can be easily switched to SEM mode, scanning transmission electron microscopy (STEM) mode, and

environmental scanning electron microscopy (ESEM) mode by assembling different stages or holders, the detailed introduction of each mode will be given when it is used.

This dissertation is organized into 6 chapters and Fig. 1.15 shows the structure of the thesis. Chapter 1 is an introductory chapter that presents the background and outline of this research. Chapters 2-4 and Chapter 5 introduce the measurements and modulation respectively.

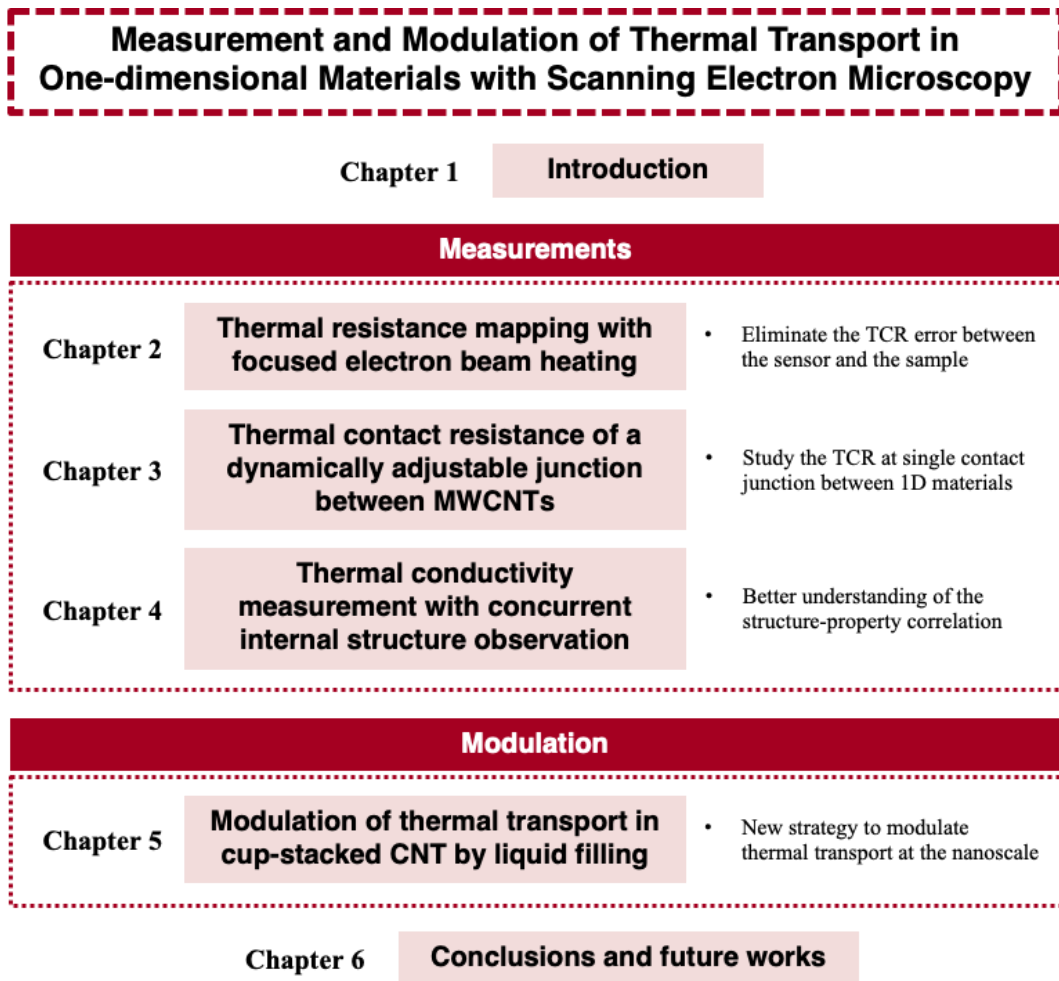


Figure 1.15 Structure of this thesis.

In Chapter 2, to eliminate the TCR error at the sample-sensor junction and obtain the thermal resistance distribution with a high spatial resolution, we developed a method combining the electron beam (EB) heating in SEM with two suspended line-shaped heat flux sensors. The two ends of the 1D sample are anchored to the two sensors respectively and the focused EB is utilized as a mobile heating

source to heat the 1D sample locally, while the two sensors simultaneously measure the heat fluxes induced by the EB heating and further the thermal resistance ratio of the two sample segments separated by the EB spot is extracted. The spatially resolved thermal resistance distribution can be obtained by moving the nanosized EB heating spot along the sample. Using this method, the *in situ* thermal resistance mapping along a single cup-stacked CNT is conducted in the SEM, from which the thermal conductivity of the CNT without the TCR error is extracted and the TCR is measured.

Chapter 3 presents a method for the *in situ* and real-time measurement of TCR at a single junction between two 1D samples in SEM. Since the movement of two samples can be separately controlled inside the SEM chamber, the contact condition can be dynamically and flexibly adjusted, and the high-resolution images of the contact morphology can be *in situ* captured by SEM. Based on this method, we measured the TCR between two MWCNTs for 11 contact conditions that could be classified as aligned-contact, cross-contact, and contact-through-contamination conditions. The TCR results were studied in combination with the SEM-captured images of the contact morphology. It is also found that the TCR significantly increases when the contact passes through contamination.

In Chapter 4, to help clarify the structure-property correlation, an experimental method that allows concurrently the *in situ* thermal conductivity measurement and the real-time internal structure observation of a single 1D material was developed using scanning transmission electron microscopy (STEM) in the SEM. Using this method, we *in situ* measured the thermal conductivity of two cup-stacked CNTs and concurrently observed the internal non-uniform structures. The results indicated that the sample with more structural disorders had a lower thermal conductivity.

Chapter 5 reports the experimental study of modulation of thermal transport in cup-stacked CNT by liquid filling. We prepared CNTs infused with pure water and LiCl solutions and measured their thermal conductivities with our *in situ* STEM-in-SEM setup. The internal structures of three water-infused CNTs were also observed in real-time. We also measured the temperature dependence of thermal conductivity for a water-infused and a LiCl-solution-infused CNT. The liquid-infused cup-stacked

CNTs exhibited higher thermal conductivity (60-360 W/m·K) than the dry samples (about 40 W/m·K). This thermal conductivity enhancement can be attributed to the strengthened interfacial coupling between graphene layers due to the penetration of water molecules or ions into the gaps between graphene cups, which is supported by the molecular dynamics simulation results in the literature.

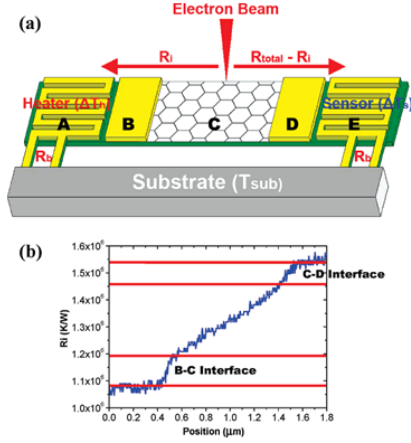
Finally, Chapter 6 summarizes the major contributions of this dissertation and identifies some future works.

2. Thermal resistance mapping with focused electron beam heating

2.1 Introduction

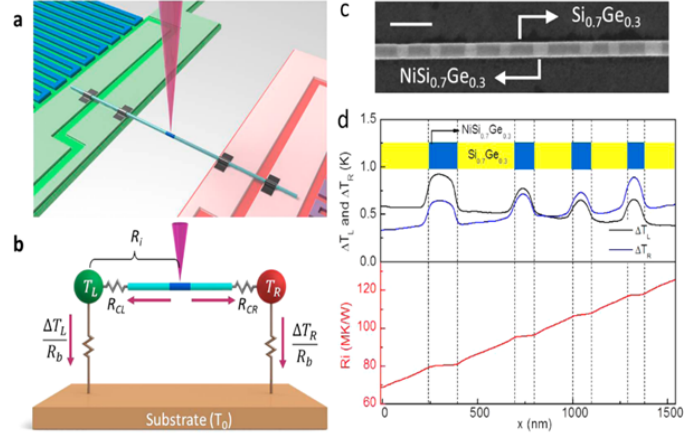
The electron beam (EB) can be focused to a nanosized spot and has been used as a noncontact, mobile heating source with a controllable heating area and nanometer-range spatial resolution [41, 96-101]. As shown in Fig. 2.1, Wang *et. al* [96], Liu *et. al* [98], and Yuan *et. al* [101] combined EB heating with the thermal-bridge device to map the thermal resistance along a SiN_x-supported few-layer graphene, a single nanowire and a SiN_x nanowire respectively. In this technique, the thermal resistance containing the sample and the two contact areas are measured by the typical thermal-bridge device method. Then, when the focused EB with high energy irradiates at and sweeps along the sample, part of the EB energy is converted into heat due to the electron beam-material interactions. Meanwhile, the corresponding heat flows are detected by the sensor islands in the thermal-bridge setup and the thermal resistance ratio of the two sample segments separated by the EB heating spot can be calculated, from which the thermal resistance profiling along the sample with a spatial resolution of nanometers is further obtained. However, the thermal-bridge based method requires complicated nanofabrication processes. Besides, the sensor islands have a relatively large area, which could lead to nonuniform temperature distribution and nonnegligible errors from the radiative heat loss [102]. In addition, the samples in the EB heating experiments have been mainly limited to nanowires and thin film samples, and the applicability of the EB heating technique to a wider range of materials still needs more experimental validation. For example, due to the complicated electron-lattice interactions, it remains a question whether the EB irradiation can generate detectable heat in hollow nanotubes without damaging the sample.

Thermal resistance mapping along a SiN_x -supported few-layer graphene



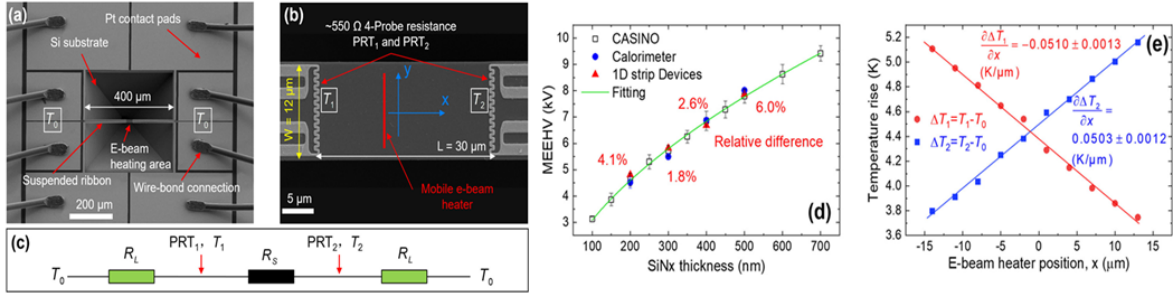
Z. Q. Wang *et al.*, Nano Lett. **11**, 113 (2011).

Profiling nanowire thermal resistance with a spatial resolution of nanometers



D. Liu *et al.*, Nano Lett. **14**, 806 (2014).

In-plane thermal conductivity measurement of SiN_x thin films by utilizing EB heating



P. Y. Yuan *et al.*, Nano Lett. **20**, 3019 (2020).

Figure 2.1 Experimental study of the thermal resistance of nanowire and thin film samples using the electron beam heating technique based on the thermal bridge method [96, 98, 101].

In this chapter, we develop an alternative thermal mapping method that combines focused EB heating in a SEM with two suspended line-shaped metallic heat flux sensors and achieve thermal resistance mapping along a single cup-stacked CNT (GSI Creos Corporation). The cup-stacked CNT has attracted considerable attention due to its unique properties and promising applications [66, 103-107]. In this method, the two ends of a cup-stacked CNT are anchored on two suspended platinum nanofilm sensors, respectively. Compared with the sensor islands in the thermal bridge setup, the line-shaped sensors are easier to fabricate since they have a simpler morphology and do not require the SiN_x supporting beam structures. A focused EB irradiates at and moves along the CNT, the corresponding heat flux is determined by monitoring the average temperature rise of the nanofilm sensor, and then the spatially resolved thermal resistance is obtained, from which the thermal conductivity of the CNT

without the TCR error is extracted to be around 40 W/m·K and the TCR is evaluated. This SEM-based *in situ* thermal measurement method can accelerate high-resolution nanomaterials characterization and the elucidation of nanoscale heat transfer.

2.2 Measurement principle

The measurement principle combines the sample's total thermal resistance and the resistance ratio of the two sample segments divided by the EB heating spot to determine the thermal resistance distribution.

Figure 2.2 shows the schematic and the corresponding equivalent thermal circuit of the total thermal resistance measurement, in which the one-dimensional (1D) sample is anchored at its ends to the two suspended line-shaped platinum nanofilms by electron-beam induced deposition (EBID). Before the 1D sample is transferred to the sensors, the temperature dependence of the electrical resistance and the thermal conductivity of the left and right nanofilm sensors were calibrated with the direct current self-heating method [9, 52]. After the sample transfer, we first drive the heating current in one of the suspended Pt sensors (e.g. the right nanofilm), and the device thermal circuit under this Joule heating is illustrated in Fig. 2.2 where T_{jR} and Q_{jR} are the temperatures at the right junction and the heat flux along the sample respectively. By recording the average temperature rise of the right Pt heater from its electrical resistance change, we can extract the total thermal resistance ($R_{t,tot}$), which involves the thermal resistance of the suspended segment of the 1D sample between the two sensors (R_{1D}) and the TCR at the left (R_{cL}) and right (R_{cR}) junctions, using the following equation based on the T-type method [9, 52, 108],

$$R_{t,tot} = R_{cL} + R_{1D} + R_{cR}$$

$$= \frac{3 \left(\frac{dR_{eR0}}{dT_0} \right) l_{sR1}^2 l_{sR2}^2 - l_{sR1} l_{sR2} \left[\left(\frac{dR_{eR0}}{dT_0} \right) l_{sR}^2 - 12 A_{sR} \lambda_{sR} l_{sR} \left(\frac{dR_{eR}}{dP_s} \right) \right]}{A_{sR} \lambda_{sR} l_{sR} \left[\left(\frac{dR_{eR0}}{dT_0} \right) l_{sR}^2 - 12 A_{sR} \lambda_{sR} l_{sR} \left(\frac{dR_{eR}}{dP_s} \right) \right]} - R_{sL} \quad (2.1)$$

where dR_{eR0}/dT_0 is the slope of the electrical resistance-temperature relationship of the right sensor; dR_{eR}/dP_s is the slope of the relationship between the measured electrical resistance of the right sensor (R_{eR}) and Joule power (P_s) after the 1D sample transfer; A_{sR} , λ_{sR} and l_{sR} are the cross-sectional area, the thermal conductivity, and the length of the right sensor, respectively; l_{sR1} and l_{sR2} are the lengths of the two segments of the right sensor divided by the right junction; R_{sL} is the equivalent thermal resistance of the left sensor which is composed of two sensor segments separated by the left junction in parallel, *i.e.* $R_{sL} = l_{sL1}l_{sL2}/[(l_{sL1}+l_{sL2})A_{sL}\lambda_{sL}]$. A_{sL} , λ_{sL} and l_{sL} are the cross-sectional area, the thermal conductivity, and the length of the left sensor, respectively; l_{sL1} and l_{sL2} are the lengths of the two segments of the left nanofilm divided by the left junction. Likewise, we can also use the left sensor as both a heater and a resistance thermometer, and the L and R in term subscripts in Eq. (2.1) will then be interchanged.

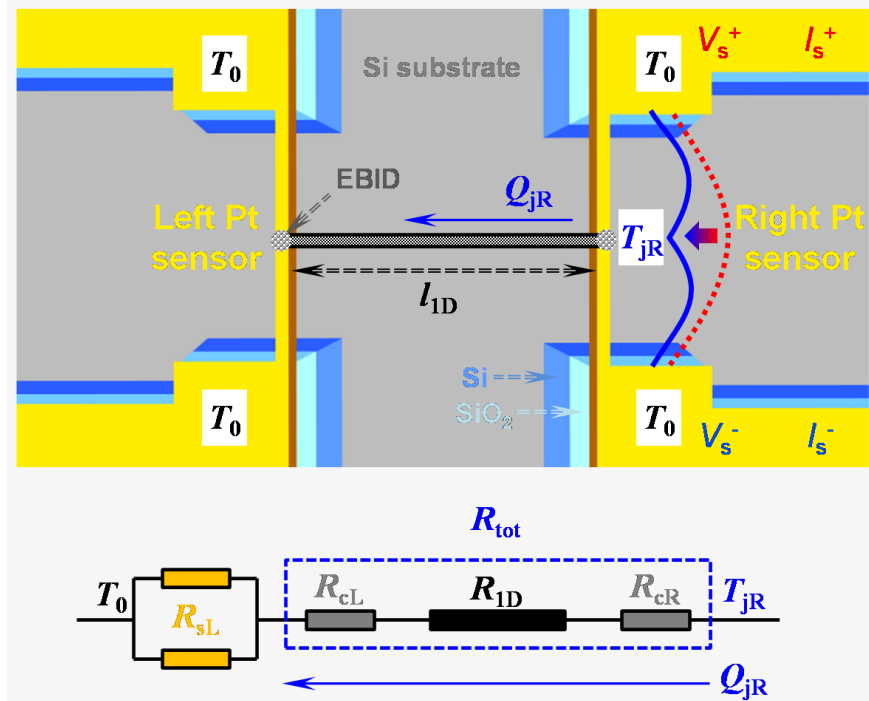


Figure 2.2 Schematic diagram and the corresponding equivalent thermal circuit of the total thermal resistance measurement. After the 1D sample transfer, the temperature distribution along the length of the right sensor changes from a parabolic profile to a double-parabolic profile.

In the next step, we use the focused EB as a local heater and the two suspended Pt lines as heat

flux sensors. Figure 2.3 delineates the schematic diagram and the corresponding equivalent thermal circuit of the device under focused EB heating. When a focused EB acting as a localized heat source is positioned along the 1D sample, part of the EB energy is absorbed by the 1D sample through electron beam-material interactions, which raises the local temperature and causes heat to flow through both sides of the 1D sample to their respective suspended line-shaped sensors and finally to the substrate at a constant temperature of T_0 . The heat conduction in the long and thin 1D sample is one-dimensional and can be analyzed with the thermal resistance circuits. In a typical measurement, the EB is positioned at a distance x along the 1D sample from the left sensor, and the temperature rises of the left and right sensors before and after the EB heating are measured by monitoring their electrical resistance. Since the equivalent thermal resistance of the left and right sensors can be calculated from the calibration results, the heat fluxes flowing through the left and right sensors can be determined by Eqs. (2.2) and (2.3) [109]. At a steady state, the heat flux from the EB heating spot to the heat sink on the left must be equal to the heat flux from the left junction to the heat sink. Likewise, the right-part thermal circuit also has the corresponding relation. Based on the thermal resistance circuit shown in Fig. 2.3, we obtain the following equations,

$$Q_L(x) = \frac{\Delta T_{sL}(x)}{R_{sL}} = \frac{T_{EB}(x) - T_0}{R_L(x) + R_{sL}} = \frac{T_{EB}(x) - T_0}{R_{1DL}(x) + R_{cL} + R_{sL}} \quad (2.2)$$

$$Q_R(x) = \frac{\Delta T_{sR}(x)}{R_{sR}} = \frac{T_{EB}(x) - T_0}{R_R(x) + R_{sR}} = \frac{T_{EB}(x) - T_0}{R_{1DR}(x) + R_{cR} + R_{sR}} \quad (2.3)$$

where $Q_L(x)$ and $Q_R(x)$ are the heat fluxes flowing through the left and right sensors, respectively; $\Delta T_{sL}(x)$ and $\Delta T_{sR}(x)$ are the temperature rises of the left and right sensors caused by EB heating on the 1D sample, respectively; R_{sR} is the equivalent thermal resistance of the right sensor; $T_{EB}(x)$ is the local temperature at the EB heating spot; $R_L(x) = R_{1DL}(x) + R_{cL}$, $R_R(x) = R_{1DR}(x) + R_{cR}$; $R_{1DL}(x)$ and $R_{1DR}(x)$ are the thermal resistances of the 1D sample divided by the EB heating spot. Note that based on the latter assumption, we have $R_{t,tot} = R_{cL} + R_{1D} + R_{cR} = R_L(x) + R_R(x)$. By comparing $Q_L(x)$ and $Q_R(x)$, we can obtain the thermal resistance ratio of the two sample segments and further derive the expression for $R_L(x)$ by

combining the measured total thermal resistance; that is,

$$R_L(x) = \frac{\alpha(x)(R_{sL}/R_{sR})R_{\text{tot}} + \alpha(x)R_{sL} - R_{sL}}{1 + \alpha(x)(R_{sL}/R_{sR})} \quad (2.4)$$

where $\alpha(x) = \Delta T_{sR}(x)/\Delta T_{sL}(x)$.

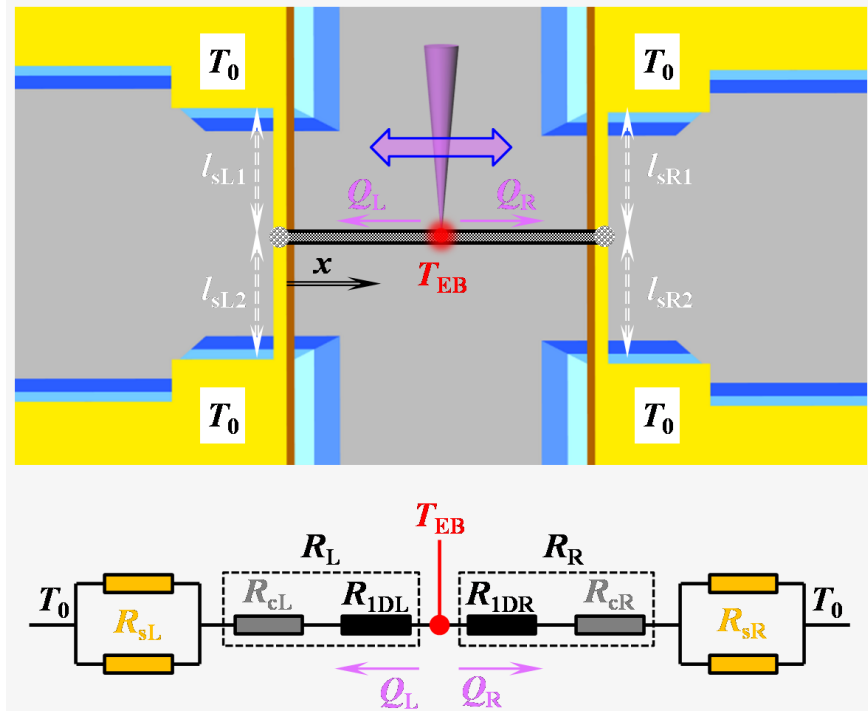


Figure 2.3 Schematic diagram and the corresponding equivalent thermal circuit of the thermal resistance mapping measurement using the focused EB as a localized heat source.

The above measurement principle combines the sample's total thermal resistance and the resistance ratio of the two sample segments to determine the thermal resistance distribution, which is the same as the basic principle in the thermal-bridge-based EB heating method [98]. This principle implies that the sum of the thermal resistance on both sides must always equal the total thermal resistance of the sample, so Eq. (2.4) is not valid if the thermal transport along the 1D sample involves ballistic effects. If the thermal conductivity of the right or left sample segment changes with the length, the sum of the thermal resistances of the two segments will also change with the EB heating position. Therefore, the assumption of diffusive thermal transport is critical for both our method and the thermal-bridge-based EB heating

measurements, which was also emphasized in Ref. [98]. Since $R_L(x)$ is a function of position x , by scanning the EB along the 1D sample from the left to the right sensor and recording the corresponding $\Delta T_{sR}(x)$ and $\Delta T_{sL}(x)$, we can obtain a spatially resolved thermal resistance profile of the 1D sample, from which the thermal conductivity of the sample without the effect of TCR can be obtained and the TCR can be evaluated.

2.3 Experimental procedures

2.3.1 Line-shaped sensor fabrication

In our experiment, the suspended line-shaped Pt sensors were fabricated by a series of MEMS fabrication processes including electron beam lithography, electron beam physical vapor deposition (PVD), and the etching processes [9, 52, 110-113]. The Pt nanofilm sensors also underwent the annealing treatment (180 °C for 8 hours) to improve the grain condition since the size effect reduces the electrical and thermal conductivities of the metallic nanofilms [112-114].

Figure 2.4 and Fig. 2.5 show the schematics of fabrication procedures of the suspended line-shaped Pt sensors and the photos of the used apparatus, respectively.

- (1) Electron beam resist spin coating: The Si substrate is oxidized and covered with a layer of 180 nm thick SiO_2 and then 320 nm thick EB resist is spin-coated on the top.

Apparatus: Mikasa 1H-DX2.

Chemicals and resist spin-coating parameters: ZEP520-A (Zeon Corporation), 5000 rpm for 60 s, resist thickness 320 nm.

- (2) Electron beam lithography: The pattern of the line-shaped Pt sensors is directly drawn on the EB resist using the electron beam lithography, and then the pattern is exposed by immersing the wafer in a developer solution.

Apparatus: Hitachi S-4300SE and Tokyo Technology BEAM DRAW.

Electron beam lithography parameters: Acceleration voltage 20 kV, beam current 1000 pA, dose

time 0.3 μs , and dose 37.5 $\mu\text{C}/\text{cm}^2$.

Chemicals and developing parameters: Developer solution ZED-N50 (Zeon Corporation) and rinse solution ZMD-B (Zeon Corporation) at 26 $^{\circ}\text{C}$ for 3 minutes each.

- (3) Electron beam PVD: Ti layer with a thickness of 8 nm and Pt layer with a thickness of 40 nm are deposited on the SiO_2 substrate using electron PVD. The Ti layer is used for adhesion between Pt and SiO_2 .

Apparatus: Showa Vacuum SEC-12.

Parameters: Electron beam current ~ 0.09 A (Ti), ~ 0.23 A (Pt), and deposition rate 0.9~1.4 $\text{\AA}/\text{s}$ (Ti), 1.0~1.3 $\text{\AA}/\text{s}$ (Pt).

- (4) Lift off of resist: The wafer is immersed in the liquid resist-remover to remove the EB resist remaining on the substrate including the Pt/Ti layer on top of the EB resist and leave only the pattern portion of the line-shaped sensors. Since debris remains after lift-off alone, the wafer is soaked in ethanol and ultrasonic cleaning is performed for about 6 minutes. Then the surface condition of the wafer and the pattern condition of the line-shaped sensors are confirmed by an optical microscope.

Chemicals and parameters: ZDMAC (Zeon Corporation) at 45 $^{\circ}\text{C}$ for 4 minutes.

- (5) SiO_2 etching by buffered hydrogen fluoride (BHF): The SiO_2 layer is etched with BHF to suspend the line-shaped nanofilm sensors from the substrate. The titanium layer is also etched away. During this process, the oxide layer under the Pt thin film other than the nanofilm sensor area is also gradually etched, so be careful about the immersion time in BHF. Also, when transferring from BHF to pure water, to prevent the line-shaped sensors from breaking due to surface tension, a spoon is used to transfer the wafer together with BHF into pure water. After thoroughly washing in pure water, a spoon is used again to transfer the sample into ethanol to replace it with ethanol. This is to prevent the line-shaped sensors from breaking when it is dried outside the pure water. After replacing with ethanol, the wafer is dried on a hot plate heated to 75 $^{\circ}\text{C}$. If washing with pure water is not sufficient, the compound will precipitate during ethanol replacement, so be careful. Then the

condition of the line-shaped sensors is confirmed by an optical microscope. If the nanofilm sensor appears dark in the middle, it is likely bent and touching the substrate.

Chemicals and parameters: Buffered hydrofluoric acid (Daikin BHF63) for 3 minutes at room temperature.

- (6) Si etching by CF_4 plasma: The Si substrate was etched using CF_4 plasma, leaving the Pt sensors suspended above the substrate. An interval of 3 minutes is provided between each etching process to avoid the breaking of the nanofilm sensors due to temperature rise. The etched gap is about 1~2 μm in depth.

Apparatus: Yamato Scientific PR500.

Parameters: CF_4 , power 70 W, flow rate 25 mL/min, 3 minutes $\times$ 3.

- (7) Oxidation by O_2 plasma: The substrate is oxidized by O_2 plasma to increase the insulation of the Si substrate. An interval of 10 minutes is provided between each plasma process. Then the condition and geometric parameters of the line-shaped sensors are checked and characterized by SEM.

Apparatus: Yamato Scientific PR500.

Parameters: O_2 , power 150 W, flow rate 60 mL/min, 30 minutes $\times$ 3.

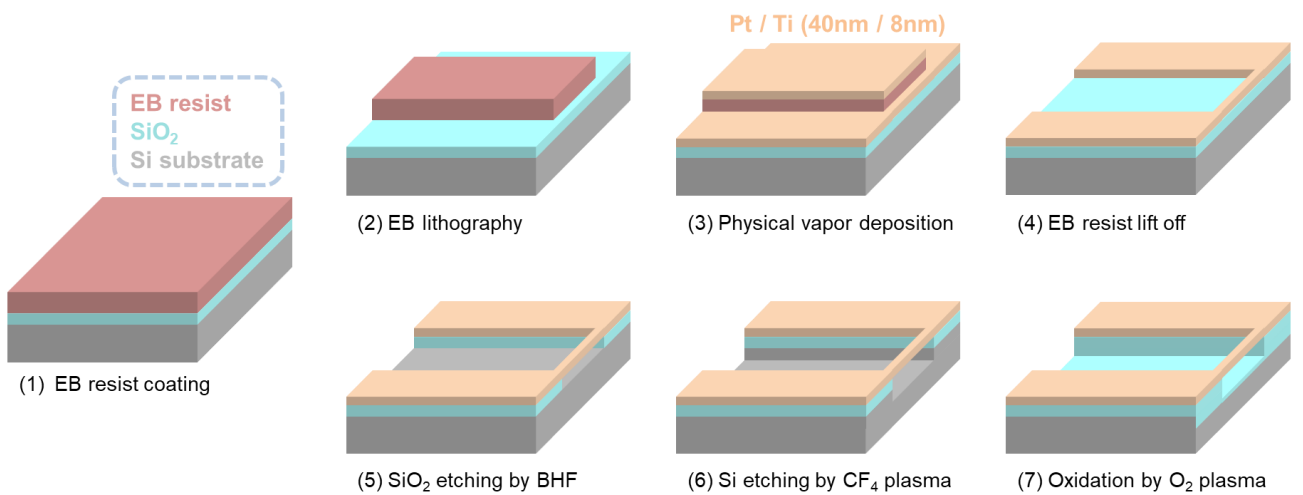


Figure 2.4 Schematic illustration of the fabrication procedures of the suspended line-shaped Pt sensors.



Figure 2.5 Photo of (a) EBL apparatus, (b) PVD apparatus, and (c) Plasma reactor.

Compared with the device used in the thermal-bridge method [8, 96, 98-101], our line-shaped sensors are much easier for fabrication since they have a simpler morphology and do not require the SiN_x supporting beam structures. Figure 2.6 shows the SEM images of the suspended line-shaped Pt sensors. The island between the two sensors is used to distinguish the two sensors. The tilted SEM image evidences that both two sensors are well suspended.

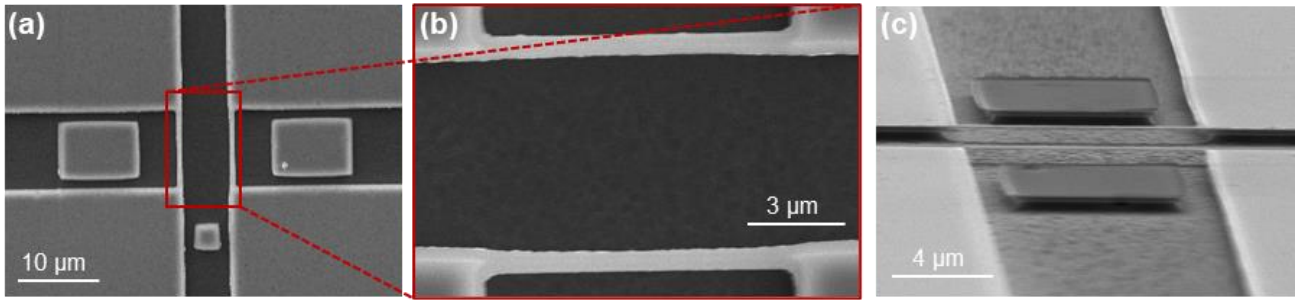


Figure 2.6 SEM images of the suspended line-shaped Pt sensors.

2.3.2 Calibration

Before the CNT transfer, the electrical resistance-temperature relationship and the thermal conductivity of the nanofilm sensors need to be calibrated by the direct current self-heating method [8, 96, 98-101]. Figure 2.7 depicts the physical model diagram of the direct current self-heating method. In this method, the suspended Pt sensor acts as both a heater and a resistance thermometer simultaneously.

Since the suspended nanofilm sensor and the electrodes are integrally fabricated, the effects of contact thermal and electrical resistances on the calibration measurement are avoided.

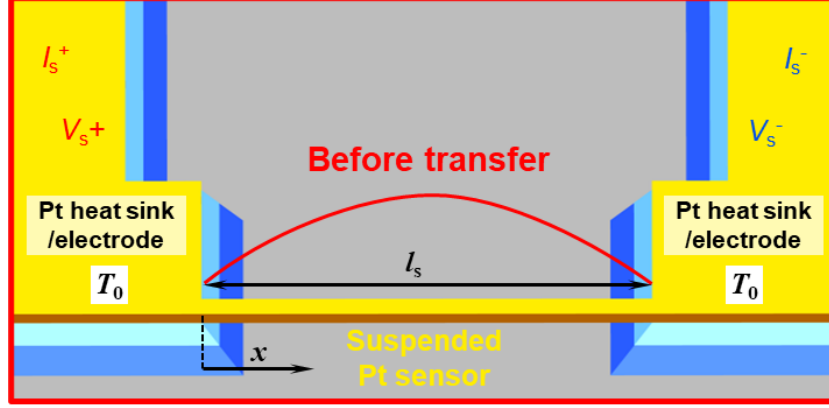


Figure 2.7 Physical model diagram of the direct current self-heating method.

When a constant current is applied to the suspended nanofilm sensor, the temperature of the nanofilm is increased by the Joule heating effect. Since the calibration measurement is conducted under high vacuum ($\sim 1.3 \times 10^{-3}$ Pa) and the average temperature rise of the nanofilm is controlled to be lower than 8 K, meanwhile the quantitative calculation analysis demonstrates that the radiative heat loss is on the order of 10^{-5} μ W, so the effects of heat convection and radiation can be neglected, and the thermal conduction process can be simplified to a one-dimensional steady-state thermal conduction problem. The governing equation for the temperature distribution $T(x)$ along the length of the film is

$$\lambda_s \frac{d^2 T(x)}{dx^2} + S = 0 \quad (2.5)$$

where λ_s is the in-plane thermal conductivity of the nanofilm sensor, and x is the distance from the left end of the nanofilm sensor to the right. S is the calorific value per unit volume of the film.

$$S = \frac{IV}{l_s dw} \quad (2.6)$$

where I and V are the electrical current and voltage applied to the nanofilm sensor, respectively, and l_s , d , and w are the length, thickness, and width of the nanofilm sensor, respectively. Since the electrodes

are well deposited on the substrate and the contact area is large, the electrodes can be regarded as the heat sink and maintain the ambient temperature T_0 . The boundary conditions of the governing equation are:

$$\begin{aligned} T(x=0) &= T_0 \\ T(x=l_s) &= T_0 \end{aligned} \quad (2.7)$$

Solving the above one-dimensional steady-state thermal conduction problem, the temperature distribution along the length of the nanofilm sensor is obtained:

$$T(x) = T_0 + \frac{IV}{2\lambda_s wd}x - \frac{IV}{2\lambda_s l_s wd}x^2 \quad (2.8)$$

By integrating the temperature distribution along the length of the nanofilm sensor, the average temperature rise of the nanofilm sensor ΔT can be obtained,

$$\Delta T = \frac{1}{l_s} \int_0^{l_s} [T(x) - T_0] dx = \frac{l_s}{12\lambda_s wd} IV \quad (2.9)$$

Since the experimentally measured electrical resistance of the nanofilm sensor (R_e) increases linearly with the heating power IV , R_e can be expressed as follows,

$$R_e = R_{e0} + k(IV) \quad (2.10)$$

where R_{e0} and k are the intercept and slope of the Joule heating power dependence of the measured electrical resistance of the nanofilm sensor, respectively. R_{e0} is also the electrical resistance of the sensor without the Joule heating effect at T_0 . By repeating the measurement at different ambient temperatures T_0 , the corresponding R_{e0} can be obtained, and the electrical resistance-temperature relationship of the sensor can be further extracted. The temperature-dependent part of the measured resistance of the sensor can also be expressed as follows,

$$k(IV) = \frac{dR_{e0}}{dT_0} \Delta T \quad (2.11)$$

where dR_{e0}/dT_0 is the slope of the electrical resistance-temperature relationship of the sensor. Therefore, from Eqs. (2.9) and (2.11), the in-plane thermal conductivity of the sensor can be extracted,

$$\lambda_s = \frac{1}{12} \frac{dR_{e0}}{dT_0} \frac{l_s}{kwd} \quad (2.12)$$

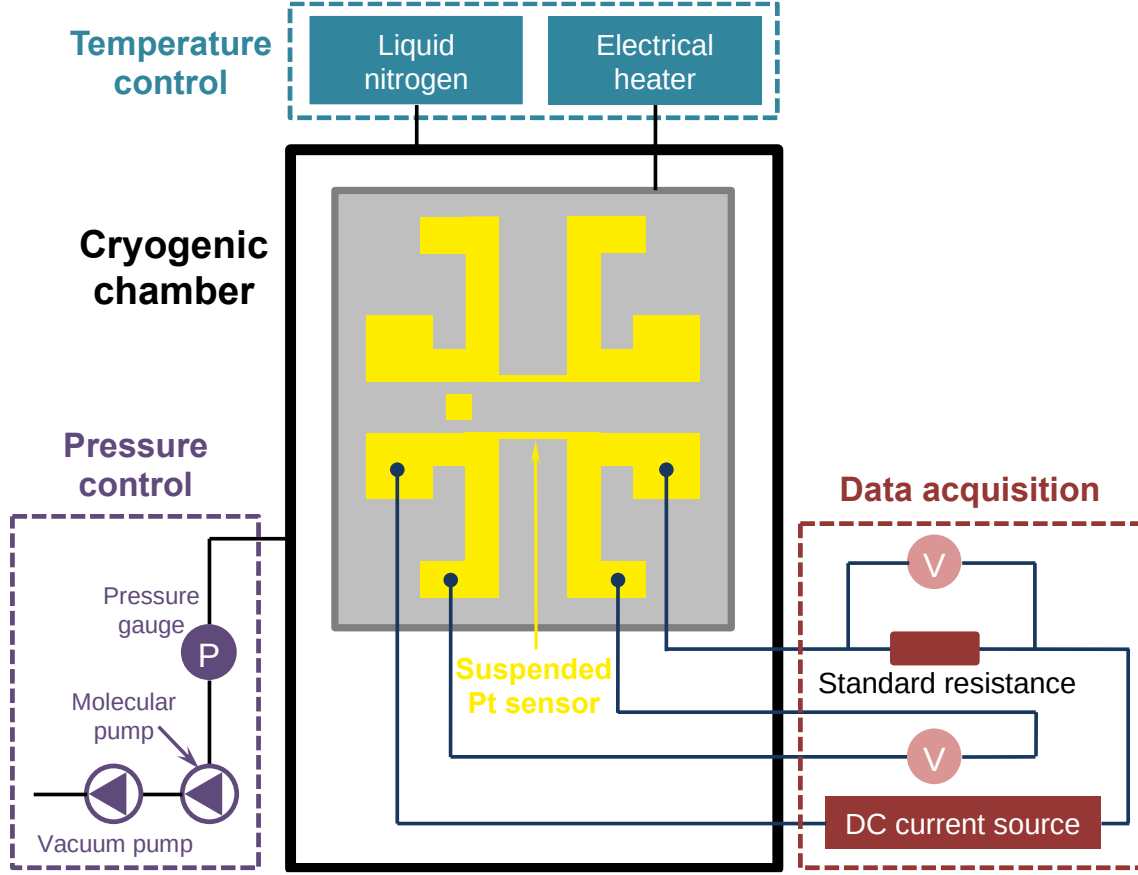


Figure 2.8 Schematic of the experimental apparatus and measurement system for the calibration.

For the actual calibration experiment, Fig. 2.8 illustrates the schematic of the experimental apparatus and measurement system for the calibration. As shown in Fig. 2.9, the chip with line-shaped sensors is mounted on a metal plate in a cryostat (Oxford instruments Optistat CF-V-KT) using carbon tape and wired. The inside of the cryostat is continuously evacuated by a mechanical vacuum pump and a molecular pump to maintain the high vacuum condition. The temperature of the metal plate on which the sensor chip is placed is kept constant by controlling the output of the heater and the flow rate of the liquid nitrogen in the cryostat with a temperature controller. The cryostat can achieve precise temperature control from 77 to 500 K by combining it with liquid nitrogen cooling. In the external

measurement circuit, there is a DC current source (Advantest R6243) and two high-precision digital multimeters (Keithley 2002, 8.5 digits), and a 100 Ω standard resistor (Yokogawa 2792). The DC current source applied a current to the sensor, the voltage across the sensor was measured by a digital multimeter using the four-terminal method, and the current is calculated by measuring the voltage of a standard resistor with a digital multimeter.

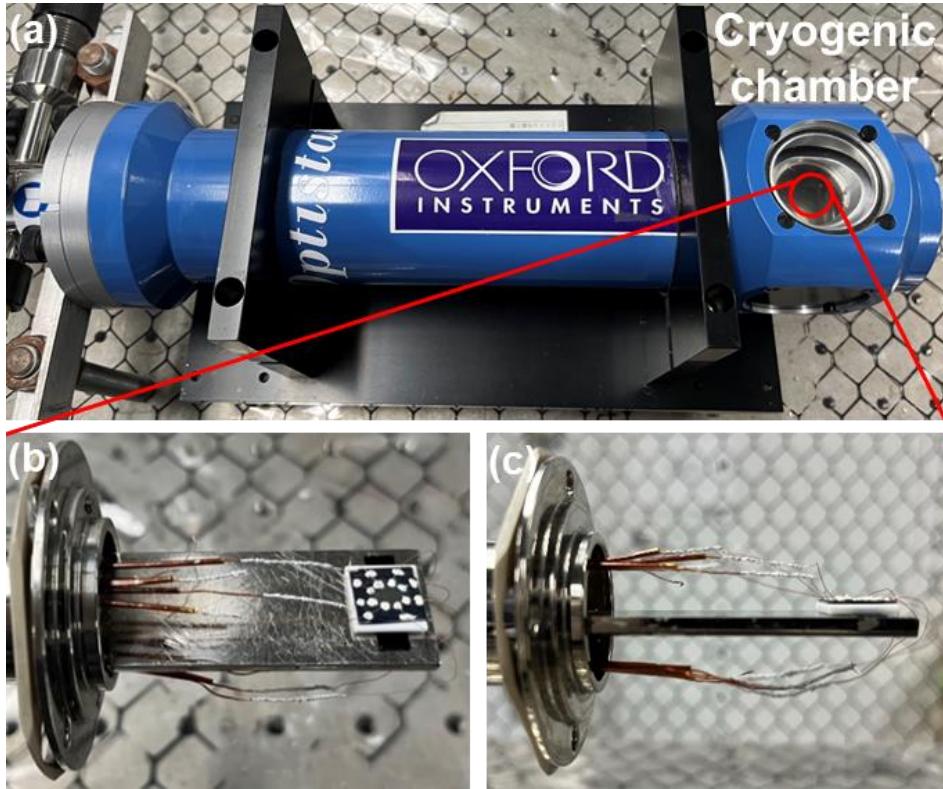


Figure 2.9 Photos of a sensor chip on the metal plate with interconnections.

As shown in Fig. 2.10, the electrical resistance-temperature relationship and the thermal conductivity of the left and right line-shaped sensors were calibrated at 278.15 K, 298.15 K, and 318.15 K. Since the same geometric parameters were used for the fabrication, the left and right sensors show similar electrical and thermal transport properties.

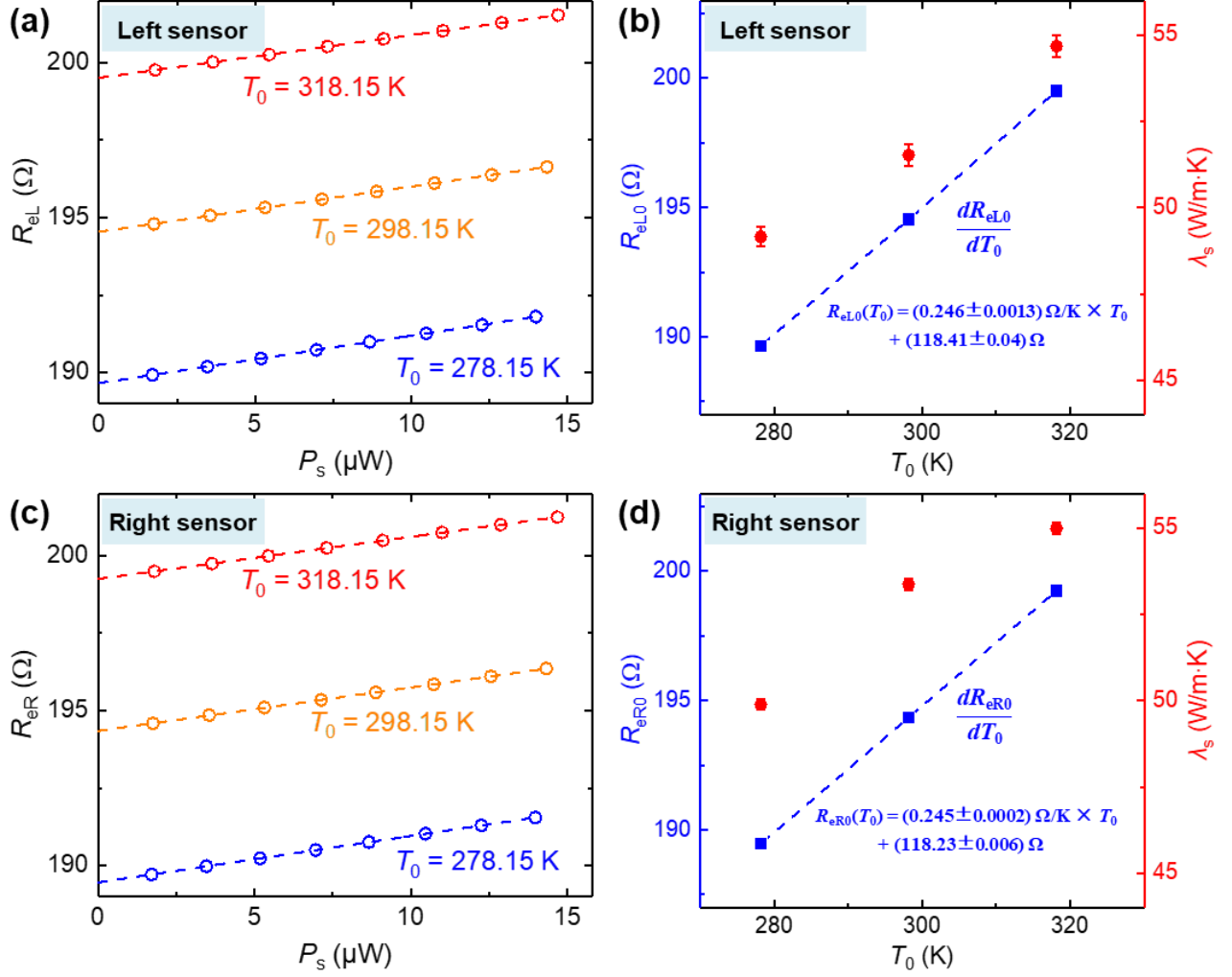


Figure 2.10 The dependence of the electrical resistance of (a) left and (c) right sensors on the Joule heating power at 278.15 K, 298.15 K, and 318.15 K. The calibration results of the electrical resistance and thermal conductivity of (b) left and (d) right nanofilm sensor at 278.15 K, 298.15 K, and 318.15 K before the CNT transfer.

2.3.3 *In situ* thermal resistance mapping experiment

After the calibration measurement, the transmission electron microscopy (TEM) characterized cup-stacked CNT sample is transferred and secured its ends to the two nanofilm sensors by EBID. For the left and right junctions, we used the same EBID parameters which are listed in Table 2.1.

Table 2.1 Parameters for EBID.

EB voltage	10 kV
Working distance	13.0 mm
Tilt angle of SEM platform	35°
Aperture size	50 μm
Spot size	5.0
Pattern	Circle
Application	Ce-dep surface
Outer diameter	600 nm
Inner diameter	0 nm
ScanDirection	Inner To Outer
DwellTime	1.400 ms
Beam	Electron
Time	1 min $\times$ 3 + 30 s

Figure 2.11(a,b) shows the SEM images of the two line-shaped sensors with a transferred cup-stacked CNT sample. The left sensor is 9.570 μm long and 653 nm wide, while the right sensor is 9.580 μm long and 653 nm wide. Their thickness calculated from the time and rate of PVD is 40 nm. The length of the two segments separated by the CNT for the left sensor is 4.849 μm and 4.721 μm respectively, and they are 3.758 μm and 5.822 μm for the right sensor. The length of the CNT between the two sensors (l_{ID}) is 6.152 μm . Since the two sensors have a similar geometry, the island between the two sensors shown in Fig. 2.11(a) is designed to differentiate the sensors. From Fig. 2.11(c), the tilted SEM image after the thermal resistance mapping experiment, we confirm that the CNT has good suspension condition.

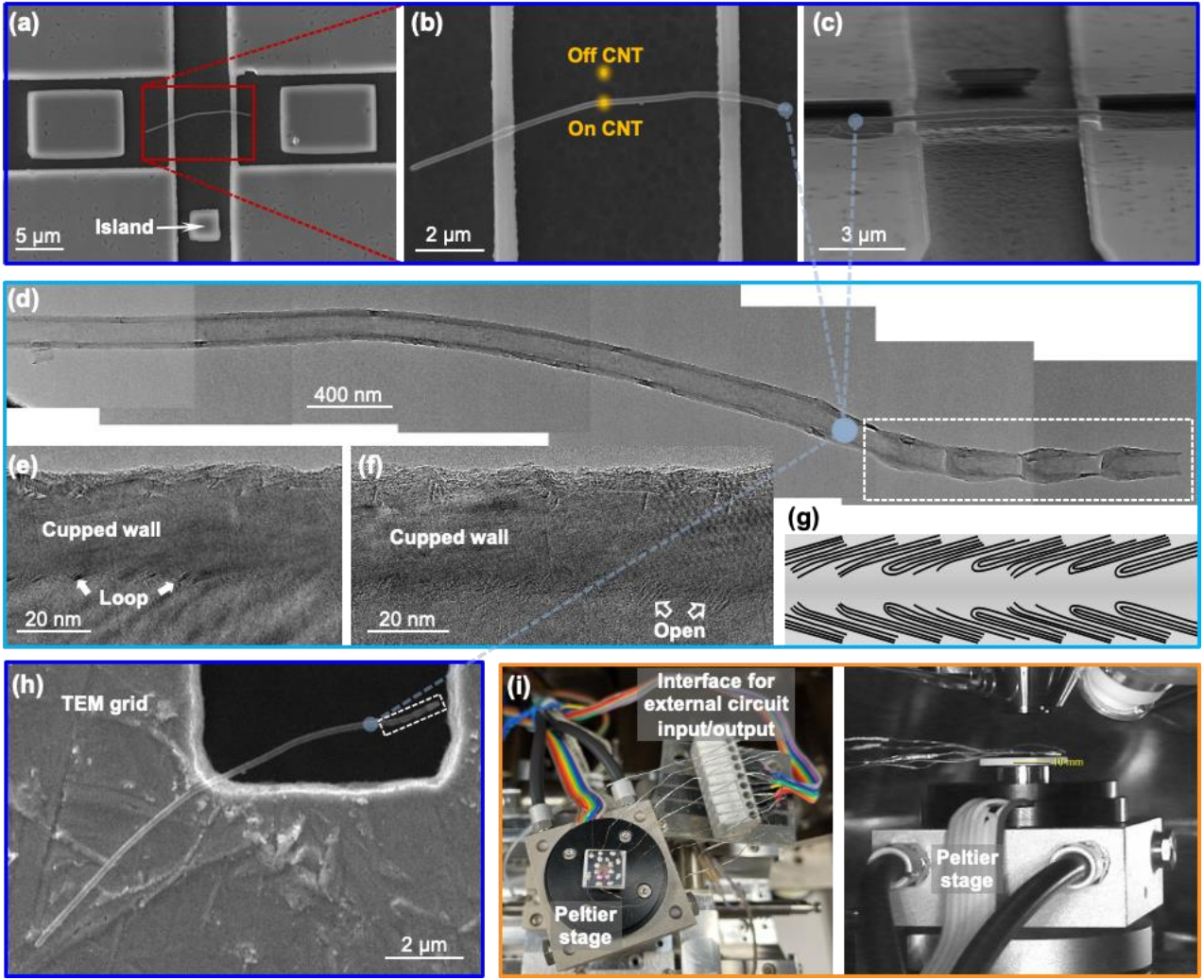


Fig. 2.11 (a-b) SEM images of the two line-shaped sensors with transferred CNT sample. (c) The tilted SEM image after the thermal resistance mapping experiment. (d) TEM image of the tested CNT sample. (e-f) High-resolution TEM images of this CNT sample. (g) Schematic illustration of the cup-stacked CNT which has the open and loop edges of the graphene cups. (h) SEM image of the CNT on the TEM grid before the transfer. (i) Pictures of the experimental setup for the thermal resistance mapping experiment.

Figure 2.11(d) presents the TEM micrograph of this cup-stacked CNT sample, we measured the outer (D_o) and inner (D_i) diameters at 50 different locations along the length, which are 156.5 ± 5.1 nm and 92.8 ± 4.1 nm respectively. As shown in the high-resolution TEM images [Fig. 2.11(e-f)], this CNT has the typical cup-stacked structure illustrated in Fig. 2.11(g) where a chain of truncated graphite cups stacked together and the graphite cups are tilted a few degrees relative to the longitudinal axis [12]. Besides, the open and loop edges of the graphene cups can also be identified. The above TEM images

were acquired on a TEM (JEM-2100Plus, JEOL) with an electron accelerating voltage of 200 kV. Figure 2.11(h) also gives the SEM image of this tested CNT on the TEM grid before the transfer. The light blue dots in Fig. 2.11(b-d,h) indicate the same position of the CNT. The portion of the CNT within the white dashed rectangle in Fig. 2.11(d,h) was attached to the tungsten probe after the transfer, as a result, the section of the CNT for the EB heating experiment has a uniform structure and stable diameters.

Figure 2.11(i) shows the experimental setup for the thermal resistance mapping experiment. The silicon chip was fixed on a Peltier stage which was mounted on the SEM sample platform. The Peltier stage provides an adjustable temperature range from -20 to 50 degrees Celsius. Eight terminals for the test are connected to the interface, which in turn is connected to the external measurement circuit. In the external measurement circuit, there is a DC current source (Advantest R6243) and two high-precision digital multimeters (Keithley 2002, 8.5 digits), of which a digital multimeter and a standard resistor (Yokogawa 2792) are used for detecting the electric current. Since our experiment was carried out in a SEM chamber at high vacuum, heat loss through convection can be neglected. After the temperature of the Peltier stage was stable at 298.15 K, we measured $R_{t,tot}$ by applying electrical current to the left and right sensors respectively. Then, in the thermal resistance mapping experiment, the electron accelerating voltage was 10 kV, and the working distance that can impact the beam current [101] was 7.3 mm. We detected the heating effect of EB by monitoring the electrical resistance of the sensors. First, we positioned the EB at distance x along the 1D sample from the left sensor and then increased the observation magnification to the maximum while the corresponding irradiation area is $100 \times 66 \text{ nm}^2$. Since the CNT sample is not straight, x was corrected afterward. As shown in Fig. 2.11(b), by moving the EB off and on the CNT [115], we indeed observed an increase in the electrical resistance of the sensors, which is attributed to the EB heating effect and was converted into the temperature rise by using the temperature coefficient of resistance. The effect of the offset voltage was eliminated by changing the current direction and averaging the electrical resistance of the sensors. Afterward, we moved EB to the next position and repeated the above measurement. At each EB heating position, we

waited for enough time (longer than 10 s) for the sample to reach the steady state. The steady state was confirmed by monitoring the electrical resistance change of the sensors.

In addition, the feasibility of <Reduced Area> and <Patterning> functions of the SEM for EB heating was also tested. The performance of EB heating is related to many electron beam setup parameters and of course to the EB energy absorption coefficient of the specific sample being measured.

2.4 Results and discussion

After the CNT transfer, we applied the electrical current to the right sensor to extract $R_{t,tot}$. Fig. 2.12 shows the average temperature rise of the left and right sensors before and after the CNT transfer. It is found that the average temperature decreased since part of the heat flux went through the CNT and another sensor to the heat sink, from which we obtained the sum of R_{sR} and $R_{t,tot}$, R_{sL} and $R_{t,tot}$ according to Eq. (2.1). From the above, the slope of the electrical resistance-temperature relationship of the right and left (dR_{eL}/dT_0) sensors are $0.2447 \pm 0.0002 \text{ } \Omega/\text{K}$ and $0.2462 \pm 0.0013 \text{ } \Omega/\text{K}$ respectively, the thermal conductivity of the right and left sensors at 298.15 K are $53.37 \pm 0.16 \text{ W/m}\cdot\text{K}$ and $51.52 \pm 0.30 \text{ W/m}\cdot\text{K}$ respectively, the slope of the relationship between the measured electrical resistance and Joule power for the right and left (dR_{eL}/dP_s) sensors after the CNT transfer are $(1.298 \pm 0.002) \times 10^5 \text{ } \Omega/\text{W}$ and $(1.338 \pm 0.002) \times 10^5 \text{ } \Omega/\text{W}$ respectively. According to Eq. (2.1), we obtained $R_{sL} + R_{t,tot} = 14.3 \pm 1.3 \text{ MK/W}$ and $R_{sR} + R_{t,tot} = 14.1 \pm 2.3 \text{ MK/W}$, since R_{sL} and R_{sR} are calculated as 1.8 and 1.6 MK/W, then we extracted $R_{t,tot}$ as $12.6 \pm 1.3 \text{ MK/W}$ and $12.5 \pm 2.3 \text{ MK/W}$ when the electrical current was applied to the right and left sensors respectively. The uncertainty analysis demonstrates that using the right sensor to measure $R_{t,tot}$ gives a lower uncertainty.

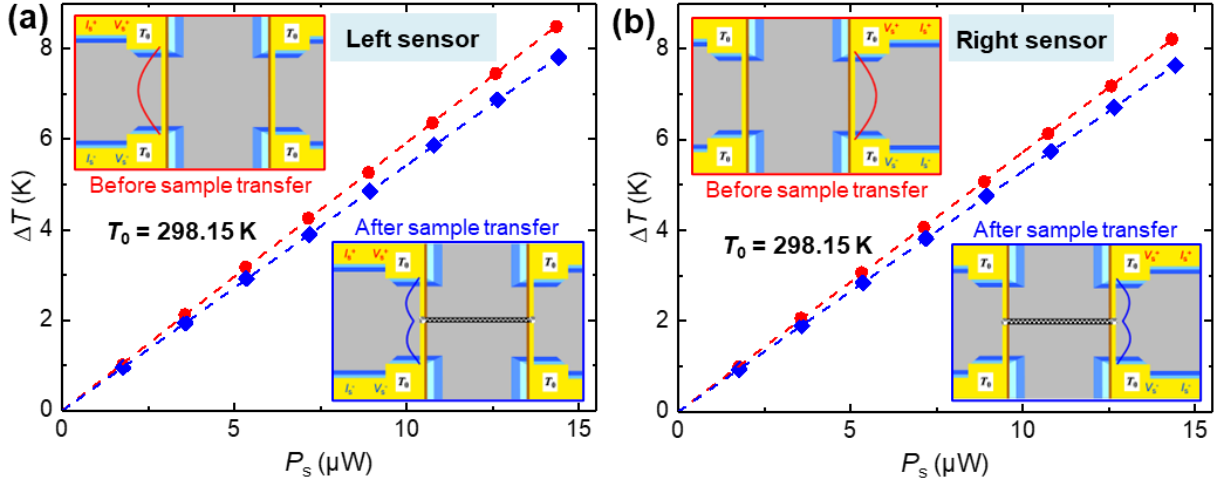


Figure 2.12 The dependence of the change in the average temperature rise of the (a) left and (b) right sensors on the Joule power before and after the CNT transfer at 298.15 K.

Subsequently, the EB heating method described above was used twice to profile the thermal resistance along the CNT. Figure 2.13(a) shows the measured ΔT_{sL} and ΔT_{sR} as a function of x in our two tests. The results of the two tests also exhibit a consistent trend. Table 2.2 lists the experimental results of $\Delta T_{sL}(x)$, $\Delta T_{sR}(x)$, and $\alpha(x)$ in detail. We further calculated R_L and $R_R = R_{t,tot} - R_L$ as a function of x using Eq. (2.4). As shown in Fig. 2.13(b), R_L linearly increases with x , while R_R decreases. Here, the unit of x is μm . By linear fitting, we obtained $R_L(x) = (2.00 \pm 0.30) \text{ MK/W} \cdot \mu\text{m} \times x + (1.35 \pm 0.73) \text{ MK/W}$ and $R_R(x) = (-2.01 \pm 0.30) \text{ MK/W} \cdot \mu\text{m} \times x + (11.02 \pm 0.92) \text{ MK/W}$, respectively. Here the absolute value of the slope is the thermal resistance per unit length of the CNT that excludes the effect of the TCR. Then the shell cross-sectional area of the CNT [$A_{1D} = \pi/4(D_o^2 - D_i^2)$] was used for the thermal conductivity calculation, which is the same as the previous measurements on cup-stacked CNTs [13, 52, 77]. As illustrated in Fig. 2.14, the thermal conductivity of the CNT (λ_{1D}) obtained from the slope of $R_L(x)$ and $R_R(x)$ are $(40.1 \pm 8.5) \text{ W/m} \cdot \text{K}$ and $(40.0 \pm 8.4) \text{ W/m} \cdot \text{K}$ respectively, and the results are slightly higher than the previously reported results without excluding the TCR error [13, 52, 77]. The two rounds of thermal mapping tests in Fig. 2.13(b) showed good repeatability. Note that the previous measurements in [13] did not provide the uncertainty, while the uncertainty reported in [77] could be

underestimated. In Fig. 2.13(b), the intercept of $R_L(x)$ is (1.35 ± 0.73) MK/W, which is the TCR at the left junction and is about one tenth of $R_{t,tot}$. The relatively low TCR demonstrates the good EBID bonding condition and suggests that it can be neglected in this study. As shown in Fig. 2.14, the thermal conductivity without excluding the TCR error is also calculated from $R_{t,tot}$ using the right and left sensors respectively and given for comparison. They are (39.3 ± 6.8) W/m·K and (39.4 ± 8.6) W/m·K, which are close to the results without the TCR error and make the above analysis self-consistent.

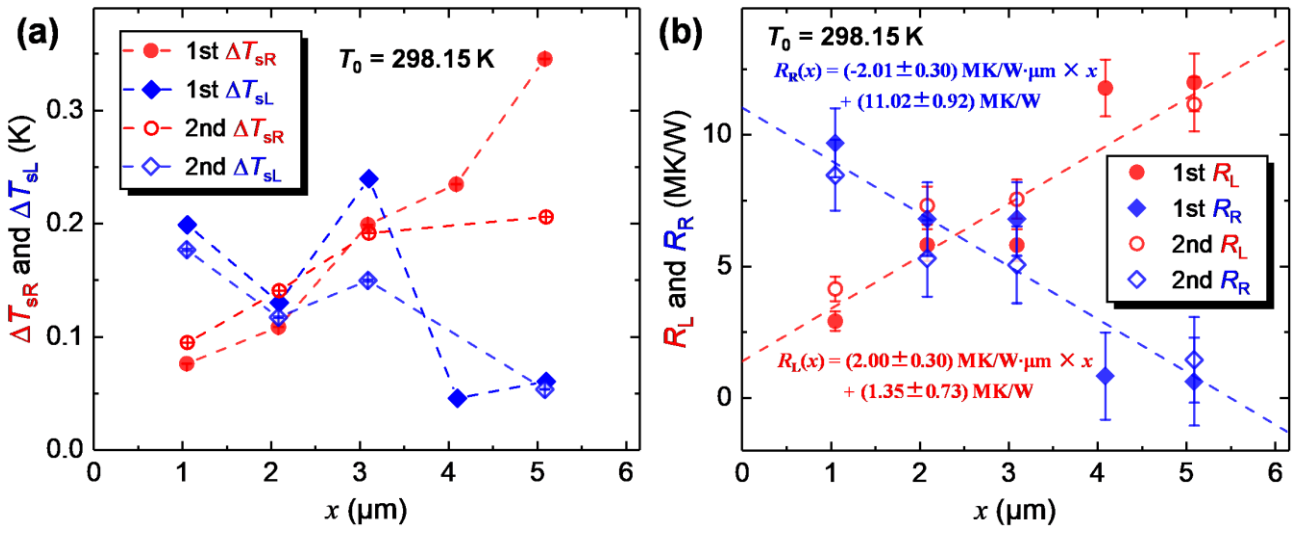


Figure 2.13 (a) The experimentally measured ΔT_{sL} and ΔT_{sR} as a function of x . (b) Experimental results of R_L and R_R as a function of x .

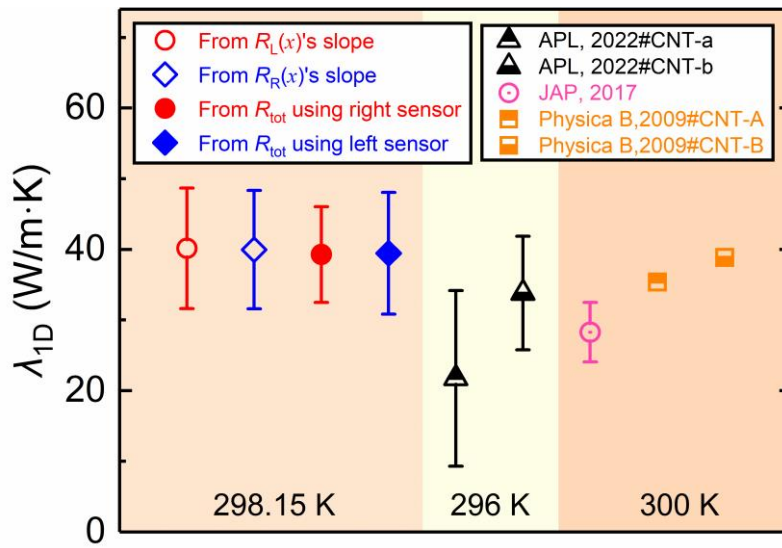


Figure 2.14 Summary of the experimental thermal conductivity results of the cup-stacked CNT plotted with the literature results [13, 52, 77].

Table 2.2 Experimental results of $\Delta T_{sL}(x)$, $\Delta T_{sR}(x)$, and $\alpha(x) = \Delta T_{sR}(x)/\Delta T_{sL}(x)$ as a function of x .

1st EB heating test			
x (μm)	$\Delta T_{sL}(x)$ (K)	$\Delta T_{sR}(x)$ (K)	$\alpha(x) = \Delta T_{sR}(x)/\Delta T_{sL}(x)$
1.054	0.199	0.076	0.380 ± 0.002
2.089	0.130	0.108	0.828 ± 0.004
3.101	0.240	0.198	0.828 ± 0.004
4.098	0.046	0.234	5.113 ± 0.027
5.100	0.061	0.345	5.687 ± 0.030
2nd EB heating test			
x (μm)	$\Delta T_{sL}(x)$ (K)	$\Delta T_{sR}(x)$ (K)	$\alpha(x) = \Delta T_{sR}(x)/\Delta T_{sL}(x)$
1.054	0.176	0.095	0.539 ± 0.003
2.089	0.117	0.141	1.208 ± 0.006
3.101	0.149	0.192	1.286 ± 0.007
5.100	0.053	0.206	3.893 ± 0.020

Note that the thermal resistance profile shown in Fig. 2.13 (b) is not smooth enough and it can be difficult to detect the thermal resistance at an interface or defect in this CNT sample. Unlike the nanowire and SiN_x samples tested by EB heating in the literature [98, 99, 101] based on the thermal-bridge method, the cup-stacked CNT has a much more complex structure than the nanowires and SiN_x , such as the cup-stacked structure, internal hollow structure, crystallization defects, and structural disorders. The lower atomic number of carbon leads to a smaller electron-matter interaction volume [101]. The hollow structure makes the incident electrons tend to transmit through the CNT instead of interacting with carbon atoms. As a result, the EB energy absorption coefficient is considerably low, which makes the temperature rise of the sensors induced by EB heating on the CNT considerably smaller. Moreover, the EB energy absorption is very sensitive to the structural differences along our CNT sample, so the different parts of the cup-stacked CNT have nonuniform EB energy absorption. Figure 2.15 shows the relatively low total EB heating power detected by the two sensors and supports the above analysis, in which $[Q_L(x)+Q_R(x)]$ changes slightly with x and its average value is only around $0.36 \pm 0.09 \mu\text{W}$. This

change in the total heat flux can be attributed to the following reasons: (1) the actual energy and the focusing of the EB can change despite the same setting parameters; (2) different parts of the cup-stacked CNT can have nonuniform EB energy absorption coefficient. This uncertainty depends on the specific test material, so it can also be difficult to probe a very smooth thermal resistance profile in the cup-stacked CNT with the EB-heating technique based on the thermal-bridge device.

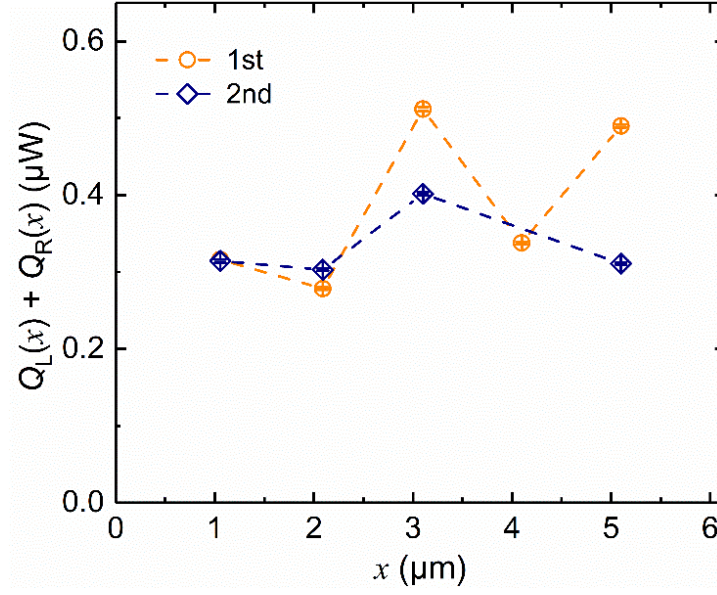


Figure 2.15 Total EB heating power as a function of x for the two tests.

2.5 Uncertainty analysis

After the CNT transfer, we first drive the heating current in the right sensor, and Eq. (2.1) can be written as,

$$R_{\text{tot}} = R_{\text{cL}} + R_{\text{ID}} + R_{\text{cR}} = \frac{A - B + C}{D - E} - R_{\text{sL}} \quad (2.13)$$

where

$$A = 3 \left(\frac{dR_{\text{eR0}}}{dT_0} \right) l_{\text{sR1}}^2 l_{\text{sR2}}^2 \quad (2.14)$$

$$B = \left(\frac{dR_{\text{eR0}}}{dT_0} \right) l_{\text{sR}}^2 l_{\text{sR1}} l_{\text{sR2}} \quad (2.15)$$

$$C=12\left(\frac{dR_{eR}}{dP_s}\right)A_{sR}\lambda_{sR}l_{sR}l_{sR1}l_{sR2} \quad (2.16)$$

$$D=\left(\frac{dR_{eR0}}{dT_0}\right)A_{sR}\lambda_{sR}l_{sR}^3 \quad (2.17)$$

$$E=12\left(\frac{dR_{eR}}{dP_s}\right)A_{sR}^2\lambda_{sR}^2l_{sR}^2 \quad (2.18)$$

$$\frac{1}{R_{sL}}=\frac{\lambda_{sL}A_{sL}}{l_{sL1}}+\frac{\lambda_{sL}A_{sL}}{l_{sL2}} \quad (2.19)$$

In the experiment, we measured l_{sR} , l_{sR1} , l_{sL} , and l_{sL1} from the SEM images, then calculated $l_{sR2} = l_{sR} - l_{sR1}$ and $l_{sL2} = l_{sL} - l_{sL1}$. For $A_{sR} = w_R d_R$ and $A_{sL} = w_L d_L$, where w_R and w_L , d_R and d_L are the width and thickness of the right and left sensors respectively, we measured w_R and w_L from the SEM images and calculated d_R and d_L from the time and rate of PVD. The resolution of the length measurement from SEM images is 0.1 nm and the relative uncertainties of the length and cross-sectional area are less than 0.1%. The uncertainty of λ_{sR} comes from l_{sR} , w_R , d_R , and $(dR_{eR}/dP_s)'$ in the calibration measurement of the right sensor before the CNT transfer. Similarly, the uncertainty of λ_{sL} comes from l_{sL} , w_L , d_L , and $(dR_{eL}/dP_s)'$ in the calibration measurement of the left sensor before the CNT transfer. From Eq. (2.19), R_{sL} is the equivalent thermal resistance of the left sensor which is composed of two sensor segments separated by the left junction in parallel and can be written as $R_{sL} = l_{sL1}l_{sL2}/[(l_{sL1}+l_{sL2})A_{sL}\lambda_{sL}]$. Since the line-shaped sensor was connected to a 100 Ω standard resistor (Yokogawa 2792 Standard Resistor) and the electrical current was measured from the voltage of the standard resistor, and the voltages of the sensor and the standard resistor were measured by 8.5-digit Keithley 2002 Multimeters, the relative uncertainty of voltage and current is about 0.01%. The effect of the offset voltage was eliminated by changing the current direction and averaging the electrical resistance of the sensors. Both dR_{eR}/dP_s and dR_{eR0}/dT_0 are obtained by linear fitting. Based on the propagation of uncertainty, we calculated the relative uncertainties of A , B , C , D , E , R_{sL} , and $R_{t,tot}$. The thermal conductivity of the CNT with the thermal contact resistance error (λ_{ID}') can be calculated as follows,

$$\lambda'_{1D} = \frac{l_{1D}}{R_{\text{tot}} A_{1D}} \quad (2.20)$$

where $l_{1D} = 6.152 \mu\text{m}$ and $A_{1D} = \pi/4(D_o^2 - D_i^2)$ are the length of the CNT between the two sensors and the shell cross-sectional area of the CNT, respectively. l_{1D} is measured from the SEM image. The uncertainty of A_{1D} comes from D_o and D_i which are the outer diameter and inner diameter of CNT, respectively. D_o and D_i were measured by calculating the average values at 50 different locations in the TEM images. Likewise, we can also drive the heating current in the left sensor, and the L and R in term subscripts in Eq. (2.1) will then be interchanged, and the corresponding uncertainty analysis can also be conducted. Table 2.3 shows the uncertainty analysis results. The results reveal that using the right sensor to measure $R_{t,\text{tot}}$ gives a lower uncertainty.

Eq. (2.4) in the main text can be written as,

$$R_L(x) = \frac{F+G-R_{sL}}{1+H} \quad (2.21)$$

where,

$$F = \alpha(x)(R_{sL}/R_{sR})R_{\text{tot}} \quad (2.22)$$

$$G = \alpha(x)R_{sL} \quad (2.23)$$

$$H = \alpha(x)(R_{sL}/R_{sR}) \quad (2.24)$$

where $\alpha(x) = \Delta T_{sR}(x)/\Delta T_{sL}(x)$. Table 2.2 shows the results of $\Delta T_{sR}(x)$, $\Delta T_{sL}(x)$ and α as a function of x . $R_{sR} = l_{sR1}l_{sR2}/[(l_{sR1}+l_{sR2})A_{sR}\lambda_{sR}]$. Note that $R_R = R_{t,\text{tot}} - R_L$, then the uncertainty of $R_L(x)$ and $R_R(x)$ can be calculated based on the propagation of uncertainty. In addition, the slope of the linear fit $[dR_L(x)/dx]$ of the relationship between R_L and x can be obtained, which is the thermal resistance per unit length of the CNT that excludes the effect of the thermal contact resistance. Meanwhile, the intercept is the thermal contact resistance at the left junction (R_{cL}). The thermal conductivity of the CNT without the thermal contact resistance error (λ_{1D}) can be calculated as follows,

$$\lambda_{1D} = \frac{1}{\left[\frac{dR_L(x)}{dx} \right] A_{1D}} \quad (2.25)$$

Likewise, (dR_R/dx) can also be obtained and the corresponding thermal conductivity can be further calculated. Table 2.3 shows the uncertainty analysis results.

Table 2.3 The uncertainty analysis results.

Using the right sensor to extract $R_{t,tot}$ and λ_{1D}'			
Term	Value	Uncertainty	Relative Uncertainty
$(dR_{eR}/dP_s)'$	$1.40 \times 10^5 \Omega/W$	$0.0040 \times 10^5 \Omega/W$	0.29%
dR_{eR0}/dT_0	$0.245 \Omega/K$	$0.0002 \Omega/K$	0.08%
λ_{sR}	$53.37 W/m \cdot K$	$0.16 W/m \cdot K$	0.30%
dR_{eR}/dP_s	$1.30 \times 10^5 \Omega/W$	$0.0016 \times 10^5 \Omega/W$	0.12%
A	$3.51 \times 10^{-22} m^4 \cdot \Omega/K$	$0.003 \times 10^{-22} m^4 \cdot \Omega/K$	0.08%
B	$4.91 \times 10^{-22} m^4 \cdot \Omega/K$	$0.004 \times 10^{-22} m^4 \cdot \Omega/K$	0.08%
C	$4.55 \times 10^{-22} m^4 \cdot \Omega/K$	$0.015 \times 10^{-22} m^4 \cdot \Omega/K$	0.32%
$A-B+C$	$3.15 \times 10^{-22} m^4 \cdot \Omega/K$	$0.015 \times 10^{-22} m^4 \cdot \Omega/K$	0.49%
D	$3.00 \times 10^{-28} m^4 \cdot \Omega \cdot W/K^2$	$0.009 \times 10^{-28} m^4 \cdot \Omega \cdot W/K^2$	0.31%
E	$2.78 \times 10^{-28} m^4 \cdot \Omega \cdot W/K^2$	$0.017 \times 10^{-28} m^4 \cdot \Omega \cdot W/K^2$	0.61%
$D-E$	$2.20 \times 10^{-29} m^4 \cdot \Omega \cdot W/K^2$	$0.193 \times 10^{-29} m^4 \cdot \Omega \cdot W/K^2$	8.78%
$(A-B+C)/(D-E)$	$14.34 MK/W$	$1.26 MK/W$	8.80%
$(dR_{eL}/dP_s)'$	$1.46 \times 10^5 \Omega/W$	$0.0040 \times 10^5 \Omega/W$	0.27%
dR_{eL0}/dT_0	$0.246 \Omega/K$	$0.0013 \Omega/K$	0.52%
λ_{sL}	$51.52 W/m \cdot K$	$0.30 W/m \cdot K$	0.59%
R_{sL}	$1.78 MK/W$	$0.015 MK/W$	0.83%
$R_{t,tot}$	$12.57 MK/W$	$1.26 MK/W$	10.04%
A_{1D}	$1.25 \times 10^{-14} m^2$	$0.19 \times 10^{-14} m^2$	14.86%
λ_{1D}'	$39.27 W/m \cdot K$	$6.78 W/m \cdot K$	17.27%
Using the left sensor to extract $R_{t,tot}$ and λ_{1D}'			
Term	Value	Uncertainty	Relative Uncertainty
$(dR_{eL}/dP_s)'$	$1.46 \times 10^5 \Omega/W$	$0.0040 \times 10^5 \Omega/W$	0.27%
dR_{eL0}/dT_0	$0.246 \Omega/K$	$0.0013 \Omega/K$	0.52%
λ_{sL}	$51.52 W/m \cdot K$	$0.30 W/m \cdot K$	0.59%
dR_{eL}/dP_s	$1.34 \times 10^5 \Omega/W$	$0.0018 \times 10^5 \Omega/W$	0.13%

A	$3.87 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	$0.003 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	0.52%
B	$5.16 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	$0.004 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	0.52%
C	$4.73 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	$0.015 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	0.60%
$A+B+C$	$3.44 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	$0.015 \times 10^{-22} \text{ m}^4 \cdot \Omega / \text{K}$	1.28%
D	$2.90 \times 10^{-28} \text{ m}^4 \cdot \Omega \cdot \text{W} / \text{K}^2$	$0.009 \times 10^{-28} \text{ m}^4 \cdot \Omega \cdot \text{W} / \text{K}^2$	0.79%
E	$2.66 \times 10^{-28} \text{ m}^4 \cdot \Omega \cdot \text{W} / \text{K}^2$	$0.017 \times 10^{-28} \text{ m}^4 \cdot \Omega \cdot \text{W} / \text{K}^2$	1.18%
$D-E$	$2.43 \times 10^{-29} \text{ m}^4 \cdot \Omega \cdot \text{W} / \text{K}^2$	$0.193 \times 10^{-29} \text{ m}^4 \cdot \Omega \cdot \text{W} / \text{K}^2$	15.99%
$(A-B+C)/(D-E)$	14.15 MK/W	2.27 MK/W	16.04%
$(dR_{\text{eR}}/dP_{\text{s}})'$	$1.40 \times 10^5 \Omega / \text{W}$	$0.0040 \times 10^5 \Omega / \text{W}$	0.29%
$dR_{\text{eR}0}/dT_0$	0.245 Ω / K	0.0002 Ω / K	0.08%
λ_{sR}	53.37 W/m·K	0.16 W/m·K	0.30%
R_{sR}	1.63 MK/W	0.007 MK/W	0.42%
$R_{\text{t,tot}}$	12.51 MK/W	2.27 MK/W	18.14%
A_{ID}	$1.25 \times 10^{-14} \text{ m}^2$	$0.19 \times 10^{-14} \text{ m}^2$	14.86%
λ_{ID}'	39.44 W/m·K	8.63 W/m·K	21.87%
Using the right sensor to extract R_{L}, R_{R}, λ_{ID} and R_{cL}			
Term	Value	Uncertainty	Relative Uncertainty
1 st $R_{\text{L}}(x=1.054 \text{ } \mu\text{m})$	2.89 MK/W	0.37 MK/W	12.83%
1 st $R_{\text{L}}(x=2.089 \text{ } \mu\text{m})$	5.79 MK/W	0.60 MK/W	10.40%
1 st $R_{\text{L}}(x=3.101 \text{ } \mu\text{m})$	5.79 MK/W	0.60 MK/W	10.40%
1 st $R_{\text{L}}(x=4.098 \text{ } \mu\text{m})$	11.76 MK/W	1.08 MK/W	9.19%
1 st $R_{\text{L}}(x=5.100 \text{ } \mu\text{m})$	11.98 MK/W	1.10 MK/W	9.17%
2 nd $R_{\text{L}}(x=1.054 \text{ } \mu\text{m})$	4.12 MK/W	0.47 MK/W	11.38%
2 nd $R_{\text{L}}(x=2.089 \text{ } \mu\text{m})$	7.29 MK/W	0.72 MK/W	9.90%
2 nd $R_{\text{L}}(x=3.101 \text{ } \mu\text{m})$	7.53 MK/W	0.74 MK/W	9.84%
2 nd $R_{\text{L}}(x=5.100 \text{ } \mu\text{m})$	11.15 MK/W	1.03 MK/W	9.25%
(dR_{L}/dx)	$2.00 \times 10^{12} \text{ K} / \text{W} \cdot \text{m}$	$0.30 \times 10^{12} \text{ K} / \text{W} \cdot \text{m}$	15.15%
A_{ID}	$1.25 \times 10^{-14} \text{ m}^2$	$0.19 \times 10^{-14} \text{ m}^2$	14.86%
λ_{ID}	40.15 W/m·K	8.52 W/m·K	21.22%
R_{cL}	1.35 MK/W	0.73 MK/W	53.98%
1 st $R_{\text{R}}(x=1.054 \text{ } \mu\text{m})$	9.67 MK/W	1.32 MK/W	13.60%
1 st $R_{\text{R}}(x=2.089 \text{ } \mu\text{m})$	6.78 MK/W	1.40 MK/W	20.63%
1 st $R_{\text{R}}(x=3.101 \text{ } \mu\text{m})$	6.78 MK/W	1.40 MK/W	20.62%
1 st $R_{\text{R}}(x=4.098 \text{ } \mu\text{m})$	0.80 MK/W	1.66 MK/W	207.38%
1 st $R_{\text{R}}(x=5.100 \text{ } \mu\text{m})$	0.59 MK/W	1.67 MK/W	283.88%

$2^{\text{nd}} R_R(x=1.054 \text{ } \mu\text{m})$	8.44 MK/W	1.35 MK/W	15.94%
$2^{\text{nd}} R_R(x=2.089 \text{ } \mu\text{m})$	5.28 MK/W	1.45 MK/W	27.56%
$2^{\text{nd}} R_R(x=3.101 \text{ } \mu\text{m})$	5.03 MK/W	1.46 MK/W	29.08%
$2^{\text{nd}} R_R(x=5.100 \text{ } \mu\text{m})$	1.42 MK/W	1.63 MK/W	114.80%
(dR_R/dx)	$-2.01 \times 10^{12} \text{ K/W} \cdot \text{m}$	$0.30 \times 10^{12} \text{ K/W} \cdot \text{m}$	14.78%
A_{1D}	$1.25 \times 10^{-14} \text{ m}^2$	$0.19 \times 10^{-14} \text{ m}^2$	14.86%
λ_{1D}	39.95 W/m·K	8.37 W/m·K	20.96%

2.6 Summary

In summary, we combine the EB in the SEM as a noncontact localized heat source with the suspended line-shaped metallic heat flux sensors and achieve the thermal resistance mapping along a cup-stacked CNT despite its relatively low EB energy absorption. In this technique, the two ends of the sample are anchored to the two suspended line-shaped sensors which have a relatively simple structure and smaller area. After the total thermal resistance is measured, a focused EB is irradiated at and moved along the CNT, the corresponding heat flux is determined by monitoring the average temperature rise of the sensor and then the spatially resolved thermal resistance is extracted. Subsequently, the true thermal conductivity of the CNT without the TCR error was extracted to be around $40 \text{ W/m} \cdot \text{K}$, the TCR was evaluated as around one-tenth of the total thermal resistance, which indicates the good EBID bonding condition and suggests the TCR can be neglected in this study. Moreover, this study demonstrates that higher resistance measurement accuracy is needed to detect the slight temperature fluctuation for the nanotube samples due to the relatively low EB energy absorption. This SEM-based *in situ* thermal measurement method can accelerate high-resolution nanomaterials characterization and the elucidation of nanoscale heat transfer.

3. Thermal contact resistance of a dynamically adjustable junction between MWCNTs

3.1 Introduction

Even though there are some striking endeavors have been conducted, studying the TCR at a single contact junction still faces some problems and can be summarized into three aspects: 1) The TCR measurement method at the nanoscale is severely lacking; 2) The tested contact condition is extremely limited; 3) The TCR measurement is not focused on the same two samples. The following introduces some studies shown in Fig. 3.1 as arguments. Li *et al.* [49] developed a non-contact laser-flash Raman mapping technique to simultaneously measure the TCR at the carbon fiber-fiber junction and their thermal conductivities, nevertheless, it is strenuous to implement to the nanoscale due to the low measurement resolution of Raman thermometry. By using the variable-length T-type method [48], the TCR at a junction between a Pt hot wire and a variety of microwire/microfiber samples is investigated [42, 116-118]. Besides, Velson *et al.* [119] devised a transient electrical heating method to measure the TCR between a Pt hot wire and another microwire. However, the junction is limited to that with a Pt wire since Pt wire serves as a heater/thermometer in their researches and their methods are also difficult to implement on the nanoscale due to the manipulation difficulties, which hinders their wider applicability. Apart from the above efforts, the TCR between individual MWCNTs [120, 121], silver nanowires [122-124], boron nitride nanotubes [125], V_2O_5 nanowires [126], and organic nanoribbons [127] are measured using the thermal bridge device-based method. However, since the two individual samples are bonded on the two suspended membranes respectively, it is difficult to measure the thermal resistance of each sample *in situ*. They have to additionally measure the thermal resistance of another sample with a similar suspension heat conduction length for the estimation, which may cause non-

and the Pt nanofilm is separately controlled by the manipulator and SEM platform, the contact condition between two MWCNTs can be dynamically and flexibly adjusted, which makes this method applicable to more diverse and complex contact conditions. Then the thermal resistance of each MWCNT is measured *in situ* using the T-type method. The TCR is extracted by subtracting the thermal resistance of the two MWCNTs from the total thermal resistance. The TCR results at different contact conditions can be further analyzed with the corresponding *in situ* captured SEM images. We intentionally adjust the contact condition and find that TCR significantly increases when the contact passes through contamination. In this way, we can elucidate the contact condition effects on the TCR at a single CNT-CNT junction for the same sample.

3.2 Measurement principle

In this method, as shown in Fig. 3.2(a), two CNT samples are anchored to a tungsten probe and a suspended Pt nanofilm sensor respectively by EBID. The Pt nanofilm serves simultaneously as a heater and a resistance thermometer, the probe acts as a heat sink at constant temperature T_0 . Since the motion of the probe and Pt sensor are separately controlled by the manipulator and SEM platform, the contact position and the angle between two CNTs are dynamically and flexibly adjustable.

Firstly, as shown in Fig. 3.2(a), the total thermal resistance ($R_{t,tot}$) is extracted based on the T-type method [9] by comparing the average temperature rise of the Pt sensor before and after two CNTs contact,

$$R_{t,tot} = R_{cp} + R_{CNT1} + R_c + R_{CNT2} + R_{cs} = \frac{3 \left(\frac{dR_{e0}}{dT_0} \right) l_{s1}^2 l_{s2}^2 - l_{s1} l_{s2} \left[\left(\frac{dR_{e0}}{dT_0} \right) l_s^2 - 12 A_s \lambda_s l_s \left(\frac{dR_e}{dP_s} \right) \right]}{A_s \lambda_s l_s \left[\left(\frac{dR_{e0}}{dT_0} \right) l_s^2 - 12 A_s \lambda_s l_s \left(\frac{dR_e}{dP_s} \right) \right]} \quad (3.1)$$

R_{cp} and R_{cs} are the thermal contact resistance of the junctions at the probe and sensor respectively.

$R_{CNT1} = l_1/(\lambda_1 A_1)$ and $R_{CNT2} = l_2/(\lambda_2 A_2)$ are the thermal resistance of two CNT samples with a thermal conduction path from the probe to the junction (l_1) and the junction to the sensor (l_2) respectively. λ_1 and λ_2 , A_1 and A_2 are the thermal conductivity and cross-sectional area of two CNTs respectively.

dR_{e0}/dT_0 is the slope of the electrical resistance-temperature relationship of the Pt sensor; dR/dP_s is the slope of the relationship between the measured electrical resistance of the Pt nanofilm (R_e) and Joule power (P_s) after two CNTs contact; A_s , λ_s and l_s are the cross-sectional area, the thermal conductivity, and the length of the sensor respectively; l_{s1} and l_{s2} are the lengths of two segments of the sensor divided by the attached CNT.

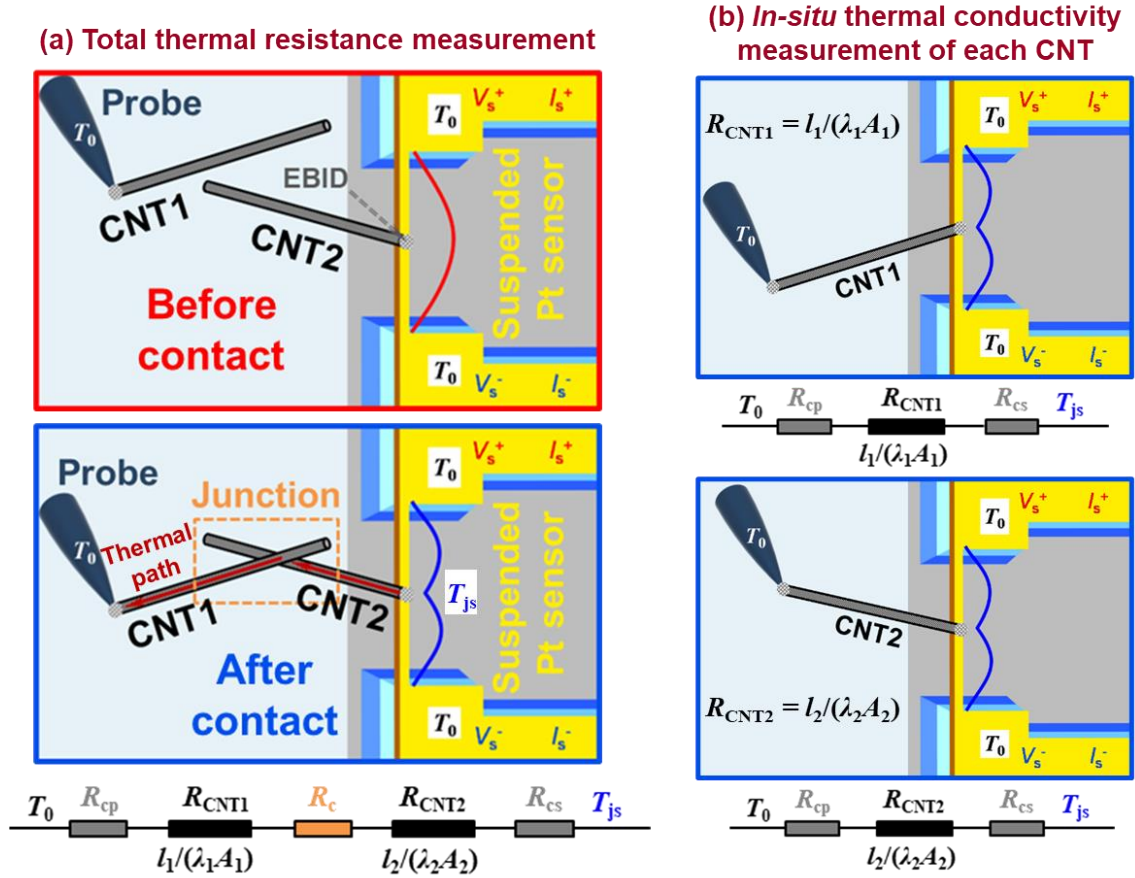


Figure 3.2 Schematic of the *in situ* evaluation technique for TCR at a dynamically adjustable junction with the corresponding thermal circuit. (a) Total thermal resistance measurement. (b) *In situ* thermal conductivity measurement of each CNT.

After the total thermal resistance measurement, as shown in Fig. 3.2(b), the thermal conductivity of the two CNT samples is measured by the T-type method *in situ* [52]. If we ignore the TCR between the probe and CNT1, CNT2 and the sensor, the TCR at the junction between two CNTs (R_c) can be

extracted as follows,

$$R_c = R_{t,tot} - R_{CNT1} - R_{CNT2} \quad (3.2)$$

3.3 Experimental study of TCR between two MWCNTs

The TCR between two MWCNTs with different contact conditions is experimentally studied for demonstration purposes as follows. Firstly, sample characterization and experimental preparation are conducted. Then the total thermal resistance after two MWCNTs contact and the *in situ* thermal conductivity measurement of each MWCNT are performed sequentially. Finally, the TCR between two MWCNTs for different contact conditions is obtained and analyzed with the corresponding SEM image.

3.3.1 Sample characterization and experimental preparation

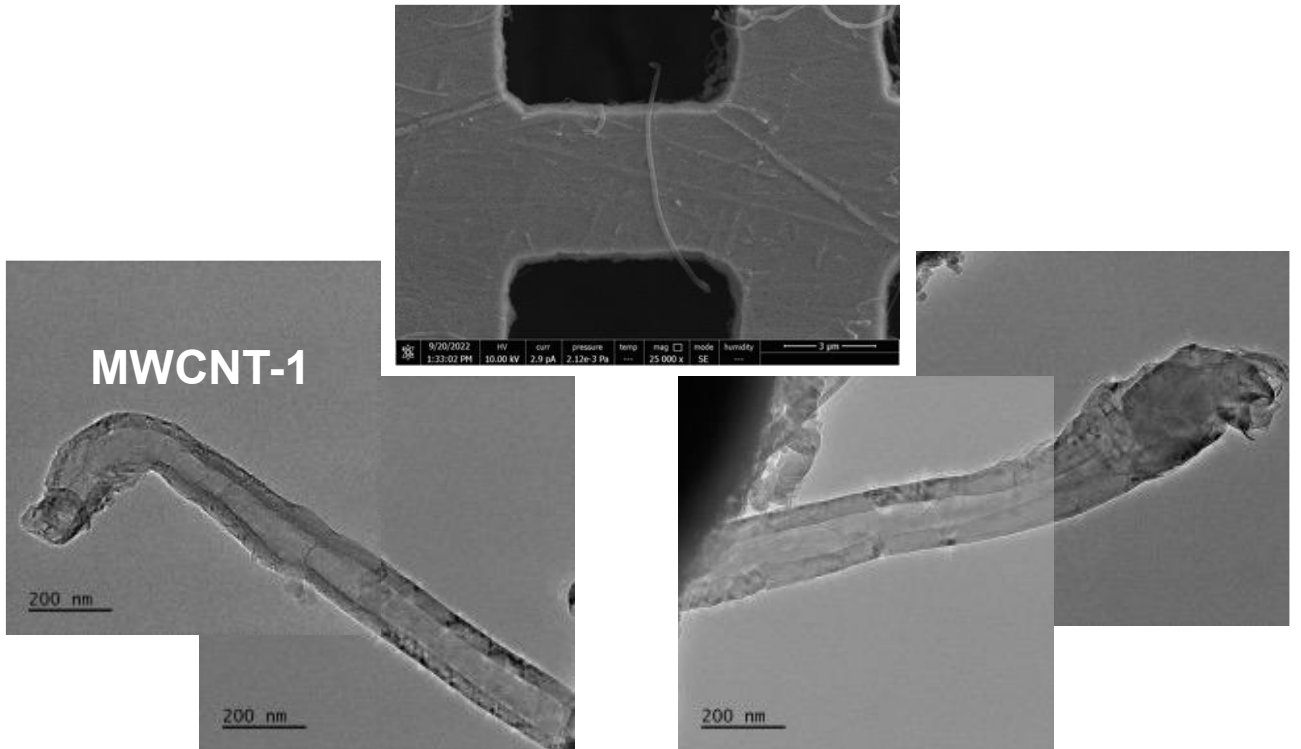


Figure 3.3 SEM and TEM images of MWCNT-1.

Figure 3.3 and Fig. 3.4 show the characterization images of MWCNT-1 and MWCNT-2,

respectively. From the TEM images, their outer diameter (D_o) and inner diameter (D_i) are measured. The outer and inner diameters can vary along the length and we measured the diameters at 50 different locations. D_o and D_i were measured to be 158.2 ± 9.3 nm and 73.3 ± 3.8 nm for MWCNT-1, and 240.0 ± 6.7 nm and 115.5 ± 11.3 nm for MWCNT-1.

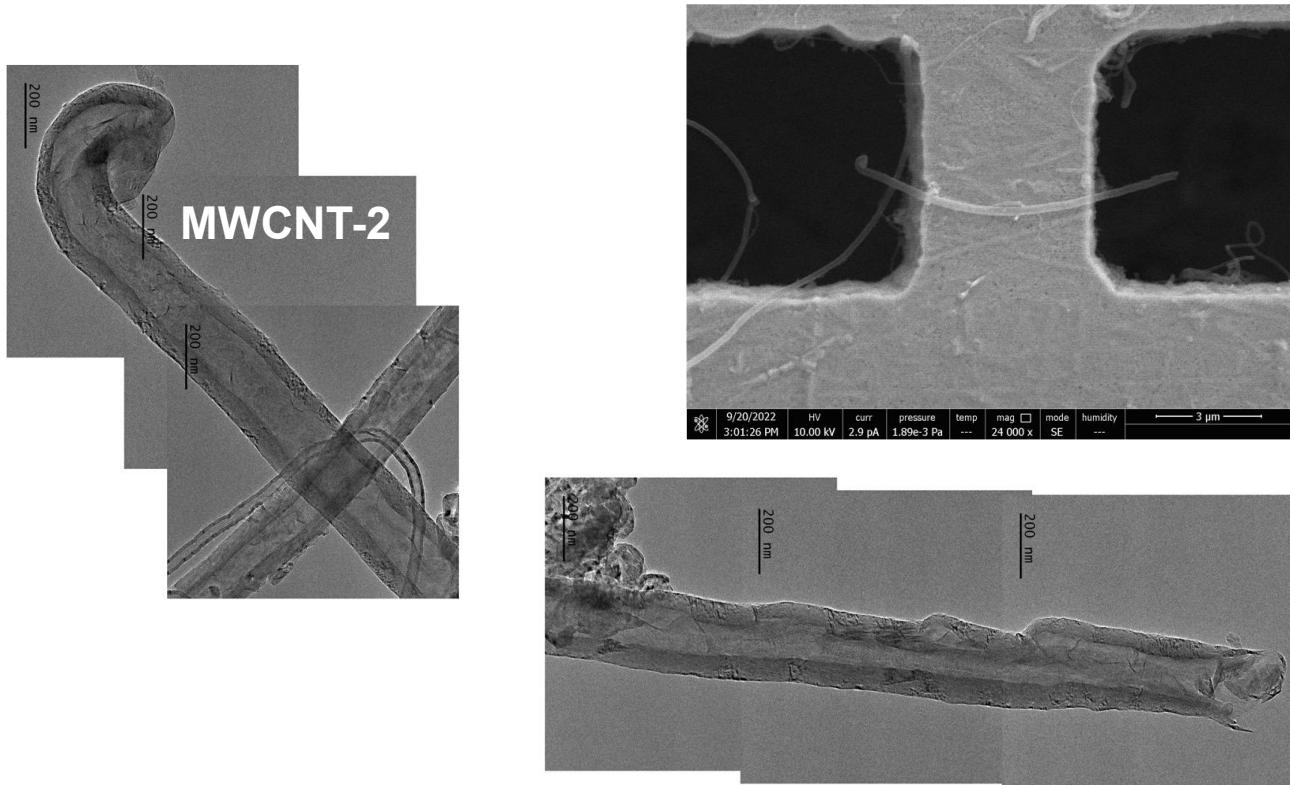


Figure 3.4 SEM and TEM images of MWCNT-2.

Two Pt sensors were also fabricated using the procedures introduced in Chapter 2 and characterized by SEM. As shown in Fig. 3.5, both are well suspended, then their electrical resistance-temperature relationship and thermal conductivity were calibrated.

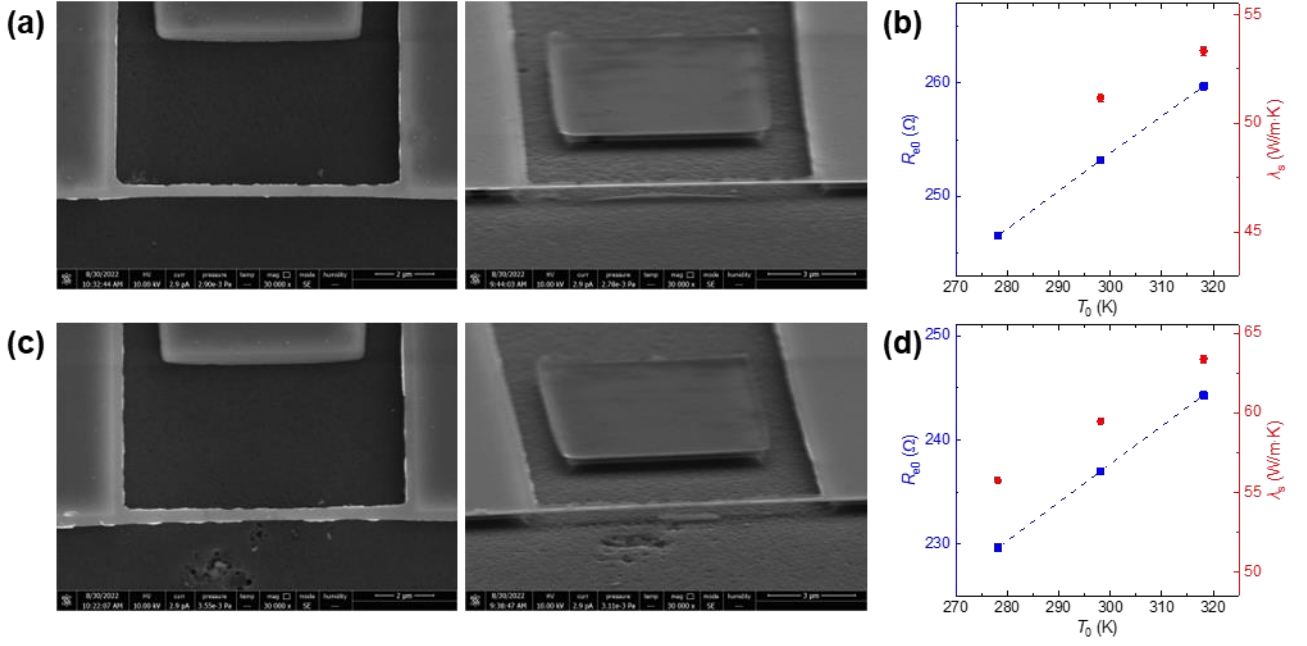


Figure 3.5 SEM images of the fabricated suspended Pt sensors and their calibration results.

Subsequently, using EBID, MWCNT-1 and MWNCT-2 were attached to a probe fabricated by electrochemical etching and one of the calibrated sensors respectively. The EBID parameters can refer to Table 2.1. Figure 3.6 shows the SEM images of MWCNT-2 transferred to a calibrated Pt sensor. There is attached contamination on MWCNT-2, in the subsequent TCR experiments, we deliberately adjust the contact conditions to make the contact pass through this contamination.

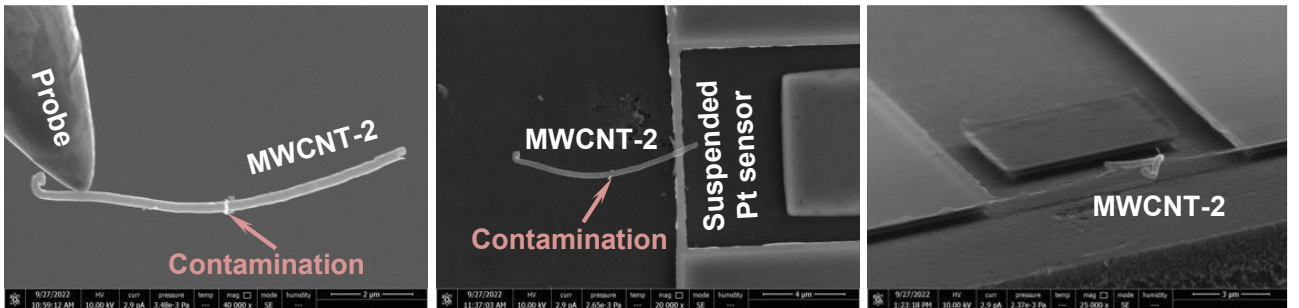


Figure 3.6 SEM images of MWCNT-2 transferred to the suspended Pt sensor, in which the attached contamination is highlighted.

3.3.2 Total thermal resistance measurement of the dynamically adjustable junction

Afterward, the feasibility test was performed. As shown in Fig. 3.7, inside the SEM chamber, we operated the manipulator (Kleindiek MM3A-EM) to make the CNT anchored to the probe gradually approach the CNT attached to the sensor which was mounted on the SEM platform. After two CNTs contact, a strong van der Waals force was observed to keep the contact very stable for a long time, which is critical to the successful implementation of this method. In addition, we monitored the electrical resistance of the sensor before and after two CNTs contacted and separated. As shown in Fig. 3.8, from the moment of contact, the resistance drops instantaneously, which is due to the connection of the heat conduction path from the sensor to the probe after the contact, resulting in a change in the temperature distribution along the length of the sensor from a parabolic profile to a double-parabolic profile. After the two CNTs are separated, the sensor resistance is restored as before. The above test corroborates the feasibility of highly sensitive thermal measurements.

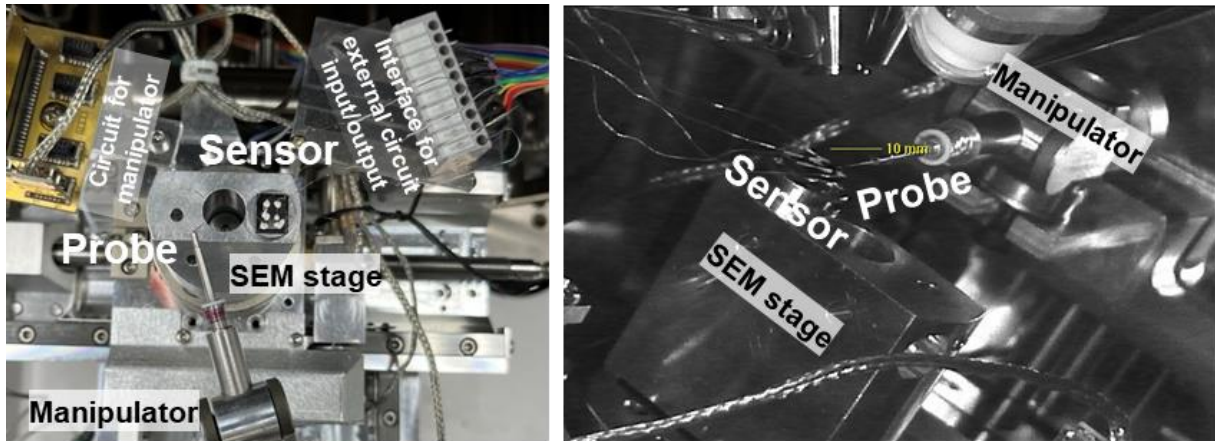


Figure 3.7 Photos of the TCR measurement of a dynamically adjustable junction between two MWCNTs.

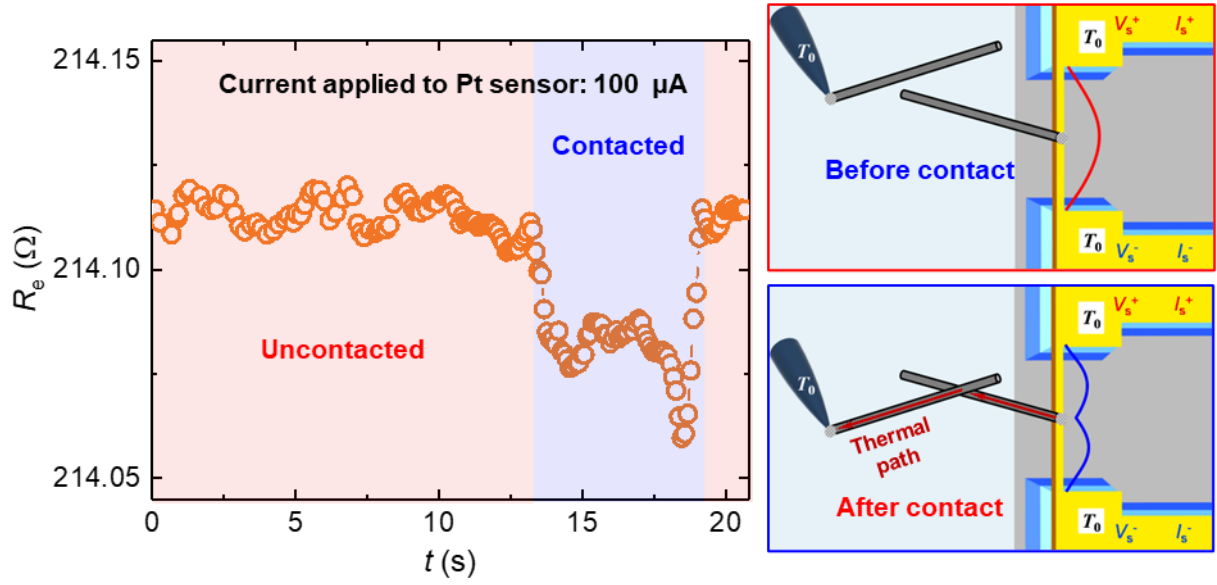


Figure 3.8 Electrical resistance of the sensor before and after the contact and separation of two CNTs.

Subsequently, benefiting from the strengths to control the motion of the manipulator and SEM platform separately, we adjusted the junction position and the angle between the two MWCNTs. Figure 3.9 shows the SEM images of tested junction conditions. A total of 11 contact conditions were investigated and they can be classified into 3 kinds of contacts: aligned contact (green), cross contact (orange), and contact through contamination (purple), which well corroborates the adjustability of the junction in our method. Aligned contact refers that the two MWCNTs having an overlapped contact length in the SEM image. Cross contact means that the two MWCNTs are in cross contact in the SEM image. The dependence of the change in the average temperature rise of the sensor before and after contact between the two MWCNTs on the Joule power is also given for each contact condition in Fig. 3.9, from which the corresponding total thermal resistance was extracted. To avoid the effect of temperature fluctuations in the SEM chamber, the thermal conductivity of the sensor was calibrated before each contact and is shown in Fig. 3.10. It is found that the thermal conductivity of the sensor is stable, and the chamber temperature was stable during the whole test. The extracted total thermal resistance results are summarized in Fig. 3.11.

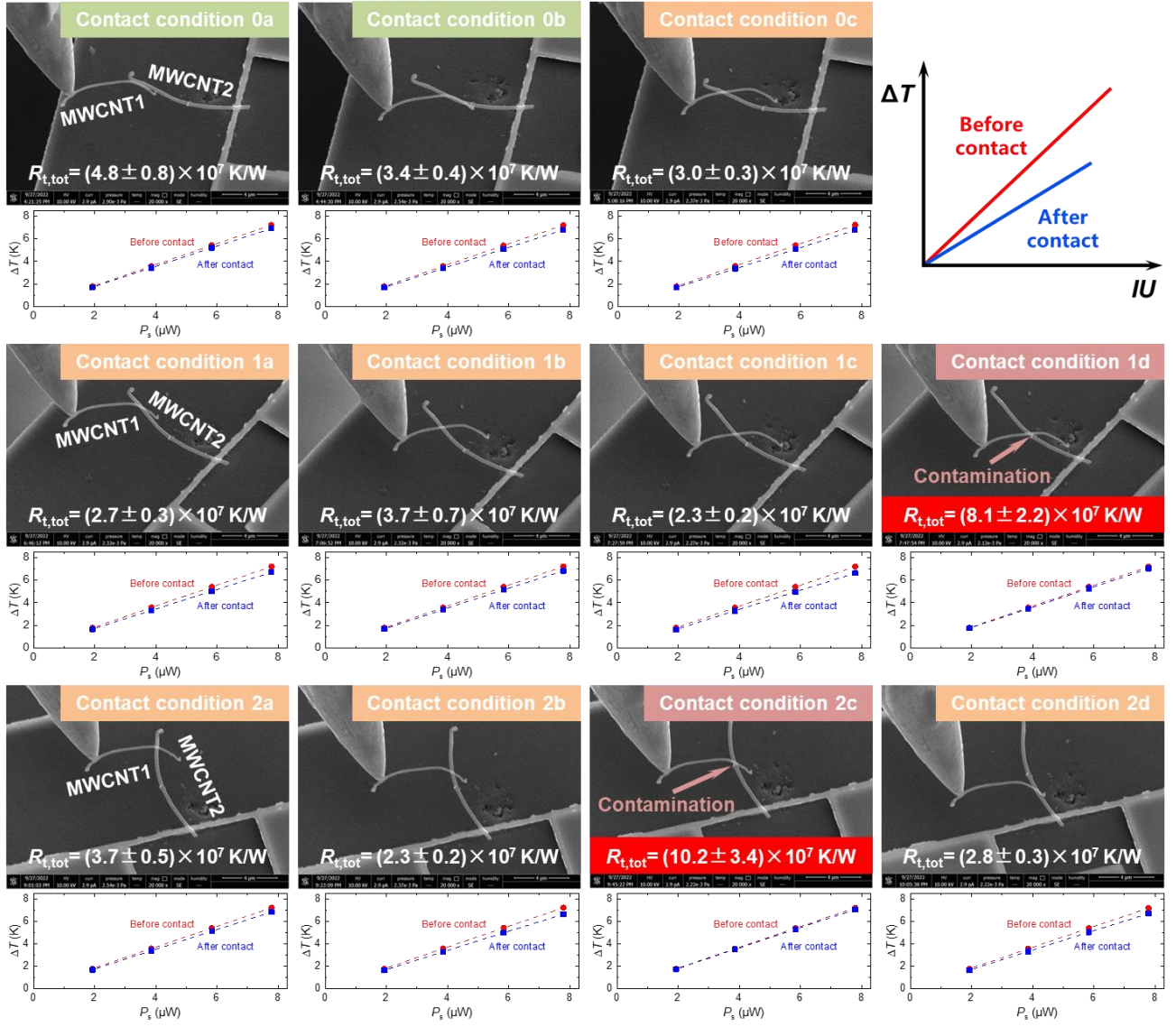


Figure 3.9 SEM images at different contact conditions and the corresponding dependence of the change in the average temperature rise of the sensor before and after contact between two MWCNTs on the Joule power. The obtained total thermal resistance is also given in each SEM image. 3 kinds of contacts: aligned contact (green), cross contact (orange), and contact through contamination (purple).

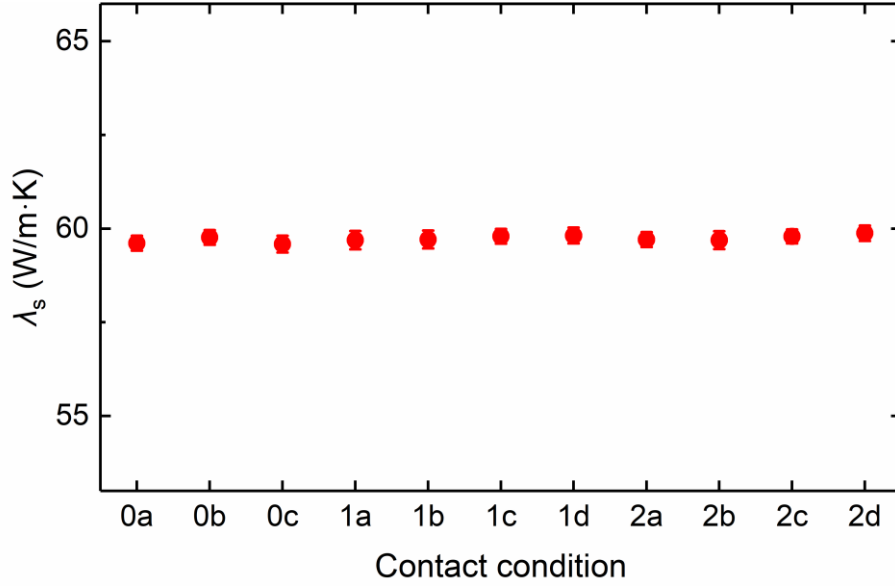


Figure 3.10 The calibrated thermal conductivity of the Pt sensor before each contact between the two MWCNTs.

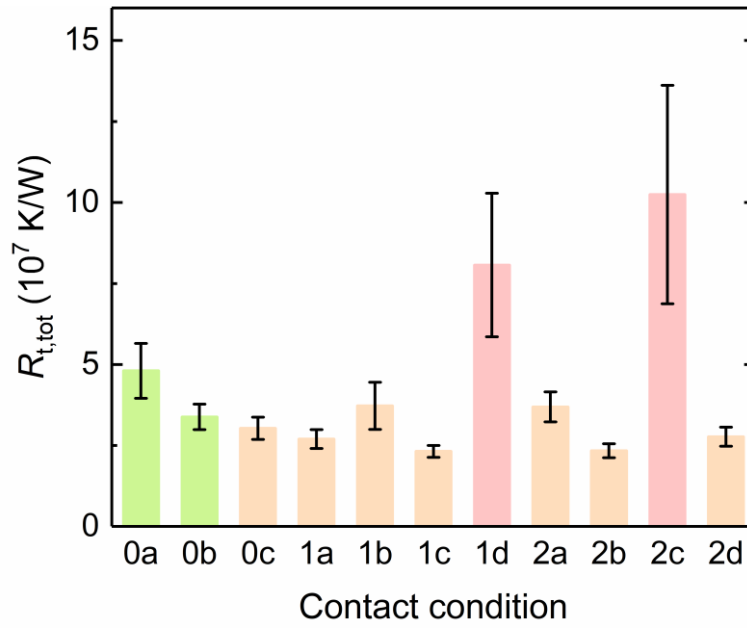


Figure 3.11 Summary of the total thermal resistance under different contact conditions between the two MWCNTs. 3 kinds of contacts: aligned contact (green), cross contact (orange), and contact through contamination (purple).

3.3.3 *In situ* thermal conductivity measurement of each MWCNT

One benefit of our method over the thermal bridge method is that the thermal conductivity of the CNT sample can be measured *in situ* by the conventional T-type method. Figure 3.12 demonstrates the

in situ thermal conductivity measurement of MWCNT-1 and MWCNT-2. The thermal conductivity is (594.8 ± 93.7) W/m·K for MWCNT-1 and (14.5 ± 1.2) W/m·K for MWCNT-2, and thus the thermal resistance of the two MWCNTs can be calculated separately. From the TEM images of each MWCNT and Fig. 3.12, the right end of MWCNT-2 shows more structural disorders, and it is contained in the heat conduction interval, however, the amorphous end of MWCNT-1 is not included in the heat conduction interval. Therefore, the thermal conductivity of MWCNT-2 is lower than that of MWCNT-1.

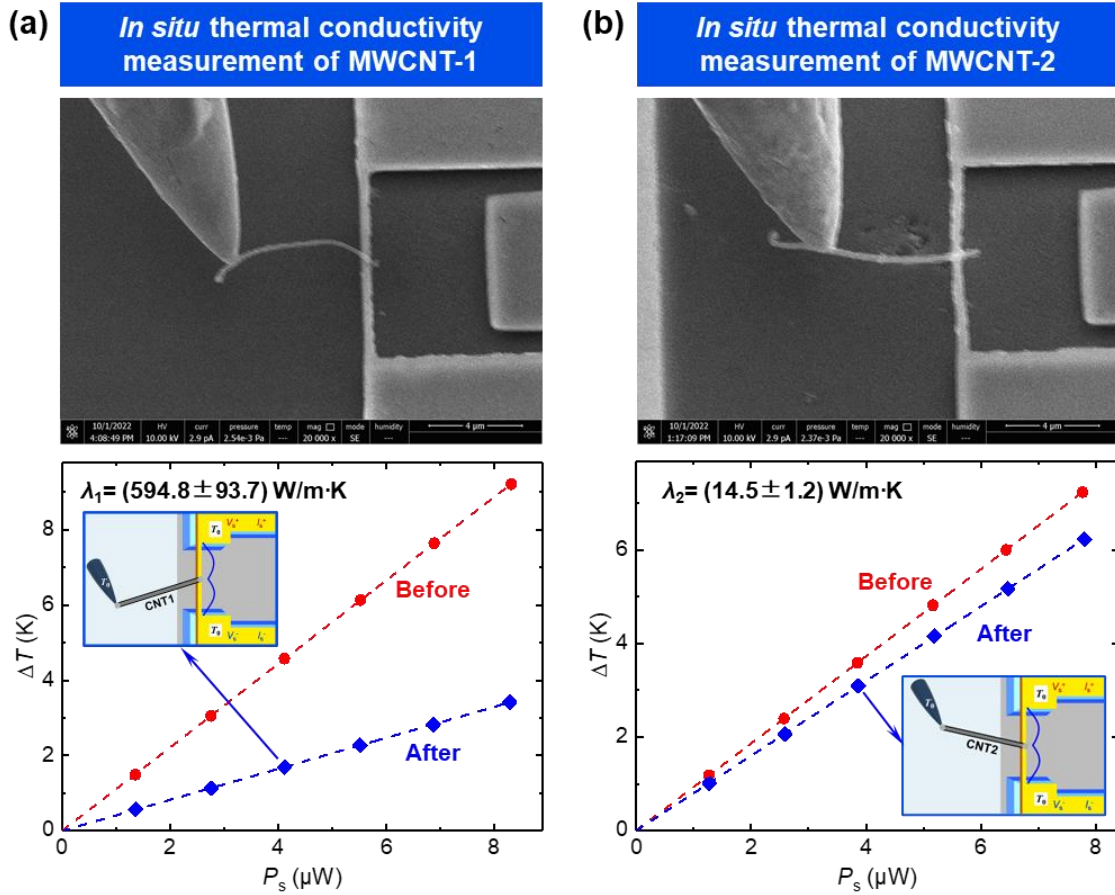


Figure 3.12 *In situ* thermal conductivity measurement of (a) MWCNT-1 and (b) MWCNT-2.

3.3.4 Thermal contact resistance between two MWCNTs

Based on f Eq. (3.2), the TCR between the two MWCNTs was extracted by subtracting the thermal resistances of the two MWCNTs from the total thermal resistance and is presented in Fig. 3.13. Figure

3.14(a) also delineates the contribution of the contact, MWCNT-1 and MWCNT-2 to the total thermal resistance for each contact condition. Note that for the aligned contact, the thermal conduction length of each MWCNT includes half of the overlapped contact length and is used for the calculation of the thermal resistance [120]. The orange pillar in Fig. 3.14(a) represents the thermal contact resistance. It is found that the TCR between cross contact and aligned contact in this study is equivalent. More interestingly, the TCR significantly increases when the contact passes through the attached contamination. Figure 3.14(b) also shows the thermal contact resistance divided by the overlapping area of the two MWCNTs in the SEM image. Note that the results of contact conditions a and b are not given, since they are aligned contact and it is not suitable to define and measure the overlapping area. The overlapping area in the SEM image is higher than the exact contact area between the two MWCNTs.

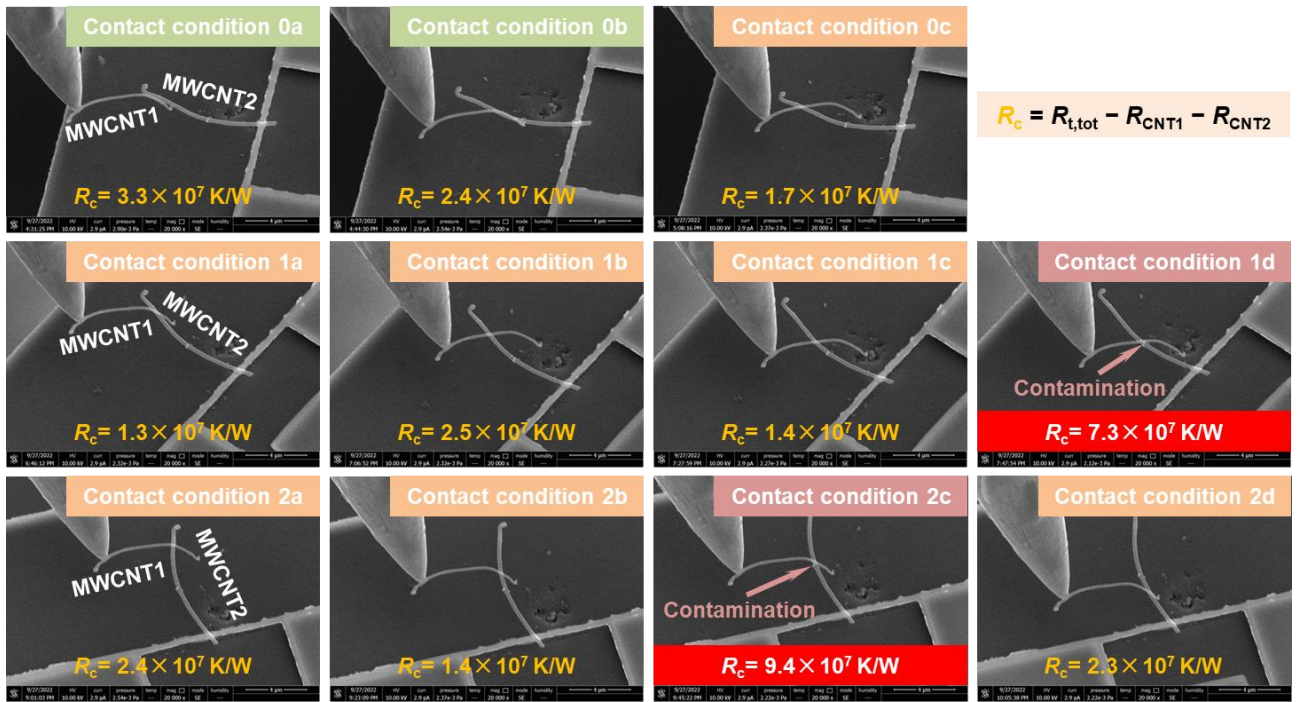


Figure 3.13 The extracted TCR results between the two MWCNTs for the different contact conditions. 3 kinds of contacts: aligned contact (green), cross contact (orange), and contact through contamination (purple).

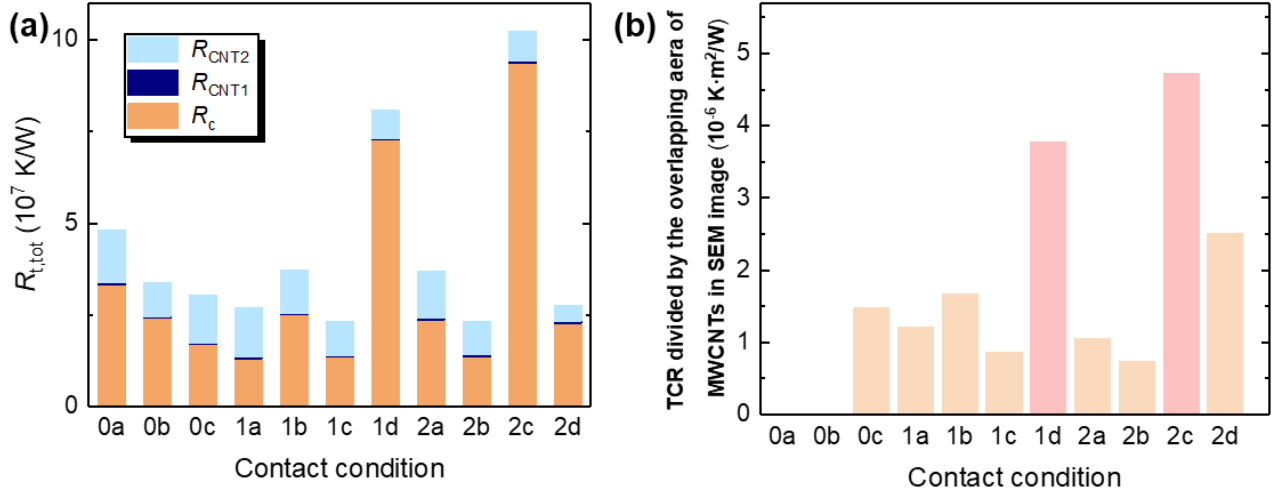


Figure 3.14 (a) The contribution of the contact, MWCNT-1 and MWCNT-2 to the total thermal resistance for each contact condition. (b) The thermal contact resistance divided by the overlapping area of MWCNTs in SEM image. The results of contact conditions a and b are not given since they are aligned contact and it is not suitable to define the overlapping area.

Due to the complexity of the contact conditions, the definition of the TCR in the experiments is still ambiguous. Our method is feasible to complex and diverse contact conditions, and the contact condition effect on the TCR can be studied with high-resolution contact morphology captured by SEM. Based on our TCR experimental results, as shown in Fig. 3.15, we have drawn schematic diagrams of top and side views of different kinds of contact conditions. In the experiments, what we can directly measure is the thermal resistance of the part in the red dotted box and we show them as the TCR in the above figures. For the ideal aligned contact shown in Fig. 3.15(a), the two samples contact well along the whole overlapped length where the heat is conducted along each sample while also crossing the interface. The interfacial thermal conductance along the overlapped length can be further solved. Since the samples are three-dimensional, the contact along the overlapped length is always not perfect and the aligned contact is imperfect. As shown in Fig. 3.15(b), the top view looks like good aligned contact, but the side view shows that the two samples are only in contact at the two ends of the overlapped length. The heat conducts along one of the samples while across the two contacts to another sample and conducts along it. From its thermal circuit, the TCR at the two contact areas (R_{c1} and R_{c2}) can be

evaluated by considering the partial thermal resistance of the two samples (R_{1D-1} and R_{1D-2}). For the cross contact, as shown in Fig 3.15(c), the TCR at the contact junction in the red dotted box contains partial thermal resistance of the two samples where the anisotropy of thermal conductivity needs to be considered, the interfacial thermal resistance between the two CNTs. When there is contamination as shown in Fig. 3.15(d), it is also necessary to ponder the thermal resistance of the contamination and the interfacial thermal resistance between the samples and the contamination. Further analysis based on the results of this chapter is in progress.

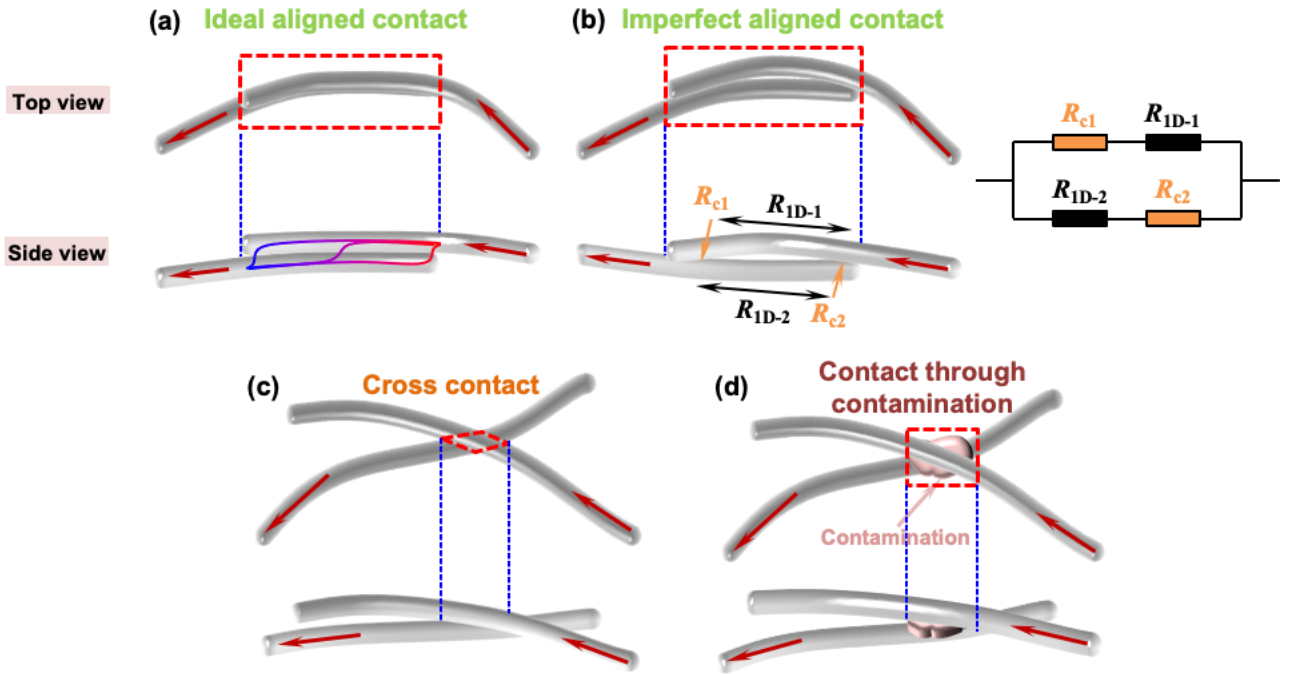


Figure 3.15 Schematic diagrams of top and side views of different kinds of contact conditions. The thermal resistance of the part in the red dotted box is shown as the TCR in the above figures.

3.3.5 Uncertainty analysis

The uncertainty analysis was performed similarly as in Chapter 2 and exhibited as error bars in each data graph. When we analyzed the uncertainty of this experiment, we recognized the importance of thermal resistance matching [48]. For the T-type method, the relative uncertainty of the measured

apparent thermal resistance ($R_{t,\text{tot}}$) is minimized when it is equal to the equivalent thermal resistance of the sensor (R_s) which is the thermal resistance of two segments of the sensor in parallel. As shown in Fig. 3.16, when the dimensionless thermal resistance ratio ($\gamma = R_{t,\text{tot}}/R_s$) is close to 0.25, the relative uncertainty of $R_{t,\text{tot}}$ is close to the minimum. It is also found that the relative uncertainty of dR_{e0}/dT_0 also has a significant impact based on the error propagation.

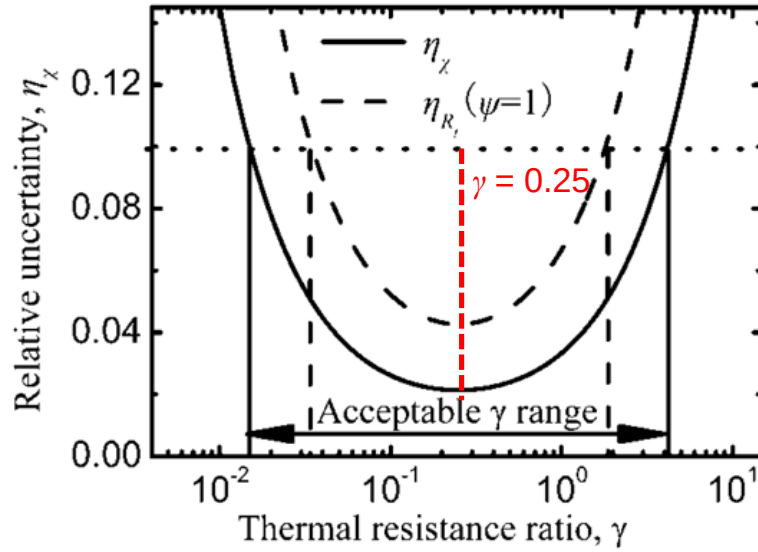


Figure 3.16 Relative uncertainty of the apparent thermal resistance as a function of the dimensionless thermal resistance ratio [48].

3.4 Summary

In summary, a method that enables *in situ* estimation of TCR at a single dynamically adjustable junction was developed in SEM. The strong Van der Waals force after sample contact makes the contact very stable. The thermal contact resistance results can be analyzed with the corresponding *in situ* obtained SEM images. The TCR between two MWCNTs with different contact conditions was measured for demonstration purposes. The TCR between cross contact and aligned contact in this study is equivalent, while the TCR significantly increases when the contact passes through the contamination. This method can be applied to wider contact conditions between nanotubes and nanowires and benefit the understanding of thermal transfer during contact.

4. Thermal conductivity measurement with concurrent internal structure observation

4.1 Introduction

The thermal conductivity of individual nanomaterials can vary from sample to sample due to the difference in the geometries and internal structures, and thus concurrent structure observation and thermal conductivity measurement at the nanoscale is highly desired but challenging. In this chapter, we develop an experimental method that facilitates *in situ* thermal conductivity measurement and internal structure observation of individual 1D materials using scanning transmission electron microscopy in a SEM (STEM-in-SEM) that incorporates the STEM detector into the standard SEM [128]. In this method, the two ends of the 1D nanomaterial are bonded on a tungsten probe and a suspended platinum nanofilm, respectively. The platinum nanofilm serves simultaneously as a heater and a resistance thermometer, ensuring highly sensitive thermal measurements. The platinum nanofilm is fabricated on the edge of the silicon wafer so that the electron beam can transmit through the 1D material and be detected by the STEM detector, which caters to the real-time observation of the inner nanostructure. Despite lower spatial resolution than TEM, STEM-in-SEM is much easier to operate than TEM and has a much lower accelerating voltage for the electron beam that can avoid possible damage to the nanomaterial. Using this method, we *in situ* measured the thermal conductivity of two cup-stacked CNTs and concurrently observed the internal hollow and non-uniform structures. The cup-stacked CNTs have a relatively complicated structure [12] and the thermal conductivity can depend more significantly on the structure than normal MWCNTs. We found that the sample with more structural disorders had a lower thermal conductivity. Our measurement method can pave the way to the sample-by-sample elucidation of the structure-property relationship for 1D materials.

4.2 Scanning transmission mode of scanning electron microscope

Figure 4.1 describes the schematic of the fundamental principles of SEM, TEM, and STEM-in-SEM [88]. STEM-in-SEM is a hybrid version of SEM and TEM and is implemented into standard SEM using its acceleration voltage, usually not exceeding 30 kV. The focused electron beam is scanned across the thin specimen by means of scanning coils, and electrons that transmit through the sample are detected and collected by an additionally equipped transmission detector underneath the specimen for imaging. STEM-in-SEM allows us to observe the internal structure of a thin sample. The image contrast is generated depending on the change in the energetic and angular distribution of the beam electrons. Since the purchase and operation of a TEM are costly and analyzing samples takes a long time, STEM-in-SEM is an inexpensive and fast alternative technique when the highest resolution is not required [129].

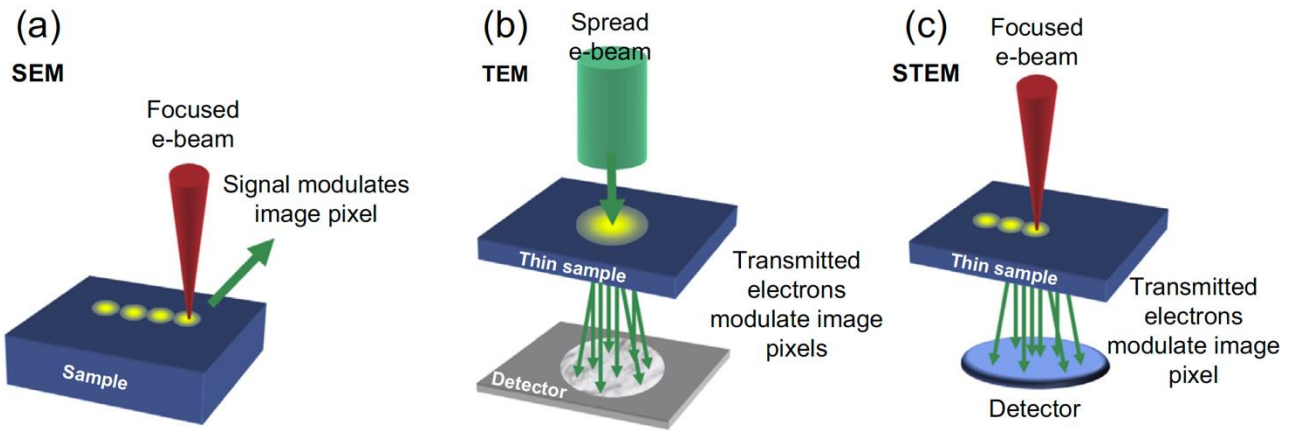


Figure 4.1 Imaging methodology schematic of (a) SEM (serial collection of data points), (b) TEM (parallel image acquisition), and STEM-in-SEM (serial collection of transmitted electrons) [88].

4.3 Experimental principle

Figure 4.2 delineates the schematic diagram of the *in situ* thermal conductivity measurement with concurrent internal structure observation. The two ends of a 1D sample are bonded on a tungsten manipulator probe and a suspended platinum nanofilm sensor by EBID, respectively. The *in situ* thermal

conductivity measurement is evolved from the T-type method [9, 21, 71] by comparing the temperature rise of the nanofilm sensor caused by the Joule heating before and after the 1D sample transfer, where the probe equates with the heat sink and the nanofilm sensor serves simultaneously as a heater and a resistance thermometer. Since the calibration of sensor properties and our *in situ* and real-time thermal characterizations are conducted under the high vacuum conditions inside the SEM chamber and the temperature rise is controlled small enough, the effects of both radiation and convection are negligible. The total thermal resistance ($R_{t,tot}$), which includes the thermal resistance of the 1D sample ($l_{1D}/\lambda_{1D}A_{1D}$) and the thermal contact resistance (R_c) between the sensor and the sample, can be extracted as follows [9, 108],

$$R_{tot} = \frac{l_{1D}}{\lambda_{1D}A_{1D}} + R_c = \frac{3 \left(\frac{dR_{e0}}{dT_0} \right) l_{s1}^2 l_{s2}^2 - l_{s1} l_{s2} \left[\left(\frac{dR_{e0}}{dT_0} \right) l_s^2 - 12 A_s \lambda_s l_s \left(\frac{dR_e}{dP_s} \right) \right]}{A_s \lambda_s l_s \left[\left(\frac{dR_{e0}}{dT_0} \right) l_s^2 - 12 A_s \lambda_s l_s \left(\frac{dR_e}{dP_s} \right) \right]} \quad (4.1)$$

where λ_{1D} and A_{1D} are the thermal conductivity and the cross-sectional area of the 1D sample, respectively; l_{1D} is the length of the 1D sample between the two connecting points at the heat sink and the Pt sensor; dR_{e0}/dT_0 is the slope of the electrical resistance-temperature relationship of the Pt sensor; dR_e/dP_s is the slope of the relationship between the measured electrical resistance of the Pt sensor (R_e) and Joule power (P_s) after the 1D sample transfer; A_s , λ_s and l_s are the cross-sectional area, the thermal conductivity, and the length of the sensor, respectively; l_{s1} and l_{s2} are the lengths of the sensor between the junction and the ends of the sensor, as depicted in Fig. 4.2.

We assembled the measurement circuit modules, the STEM detector, and other accessories in the SEM chamber, and utilized the STEM-in-SEM for the concurrent internal structure observation during the thermal conductivity measurement. As illustrated in Fig. 4.2, the suspended nanofilm is deliberately fabricated on the edge of the silicon wafer [52, 130-132] so that the electron beam can transmit through the 1D sample and the internal structure can be imaged by the STEM detector.

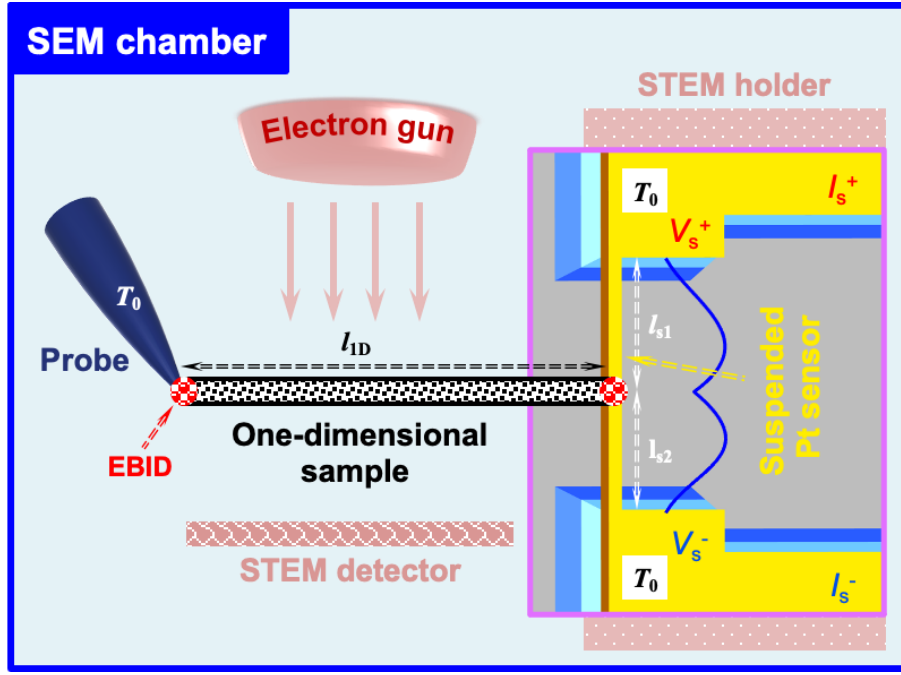


Figure 4.2 Schematic illustration of the *in situ* thermal conductivity measurement with concurrent internal structure observation using STEM-in-SEM.

4.4 Experimental procedures

Using the above-developed experimental technique, we *in situ* measured the thermal conductivity of two high-temperature treated cup-stacked CNTs (CNT-a and CNT-b) and concurrently observed their internal structures.

Firstly, the performance of STEM-in-SEM for the internal structure observation of the cup-stacked CNT was tested. As shown in Fig. 4.3, the hollow structure of the CNT is clearly visible. Besides, we are also familiar with the operation procedures and technical parameters of STEM-in-SEM. The most important point to note is that before inserting the STEM detector, to avoid its damage by collision with devices in the SEM chamber, the working height of the STEM holder needs to be checked. As shown in Fig. 4.4, the suspended sensors used for the experiment of CNT-a and CNT-b were also fabricated on the edge of the silicon wafer as the procedures introduced in Chapter 2. Their calibration results of the electrical resistance and thermal conductivity are shown in Fig. 4.5.

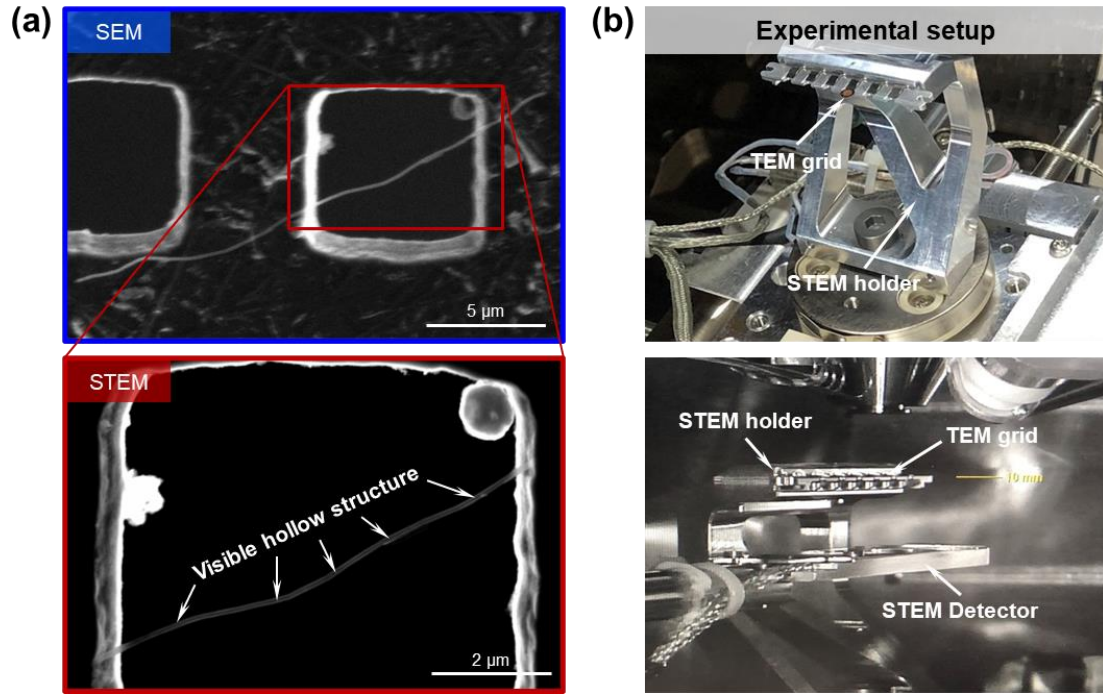


Figure 4.3 Performance test of STEM-in-SEM for the observation of the internal structure of a cup-stacked CNT. (a) The SEM and STEM images of CNT-a on the TEM grid. (b) Photo of STEM holder.

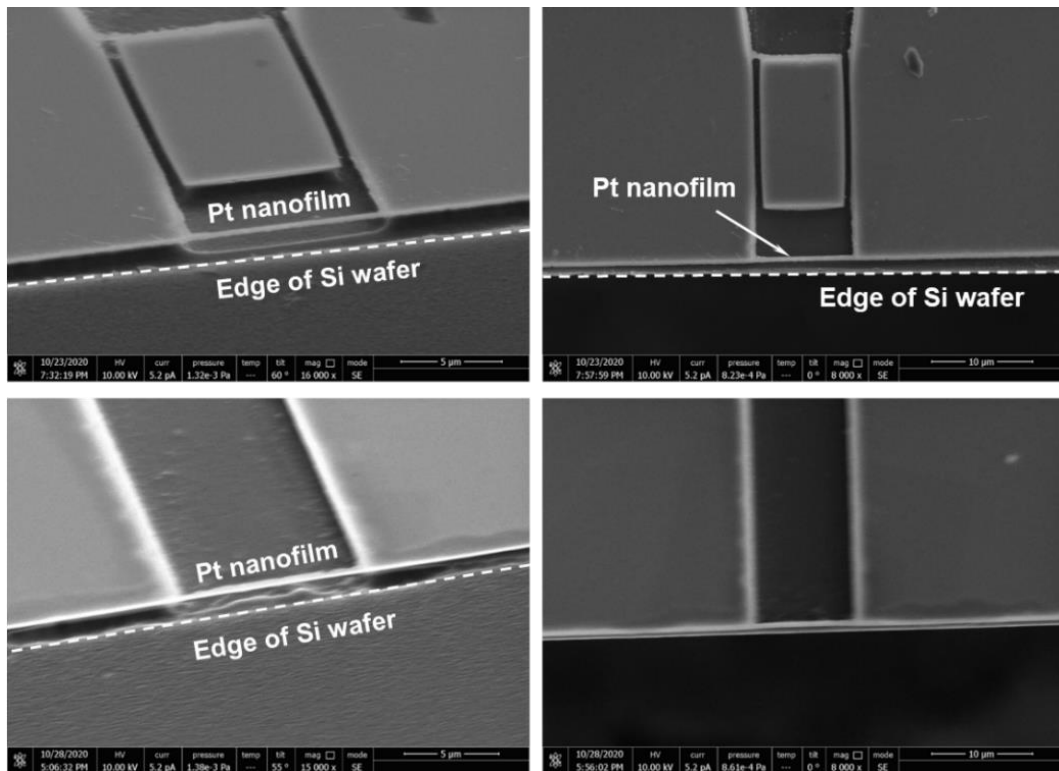


Figure 4.4 SEM images of the fabricated suspended platinum nanofilms on the edge of the silicon wafer.

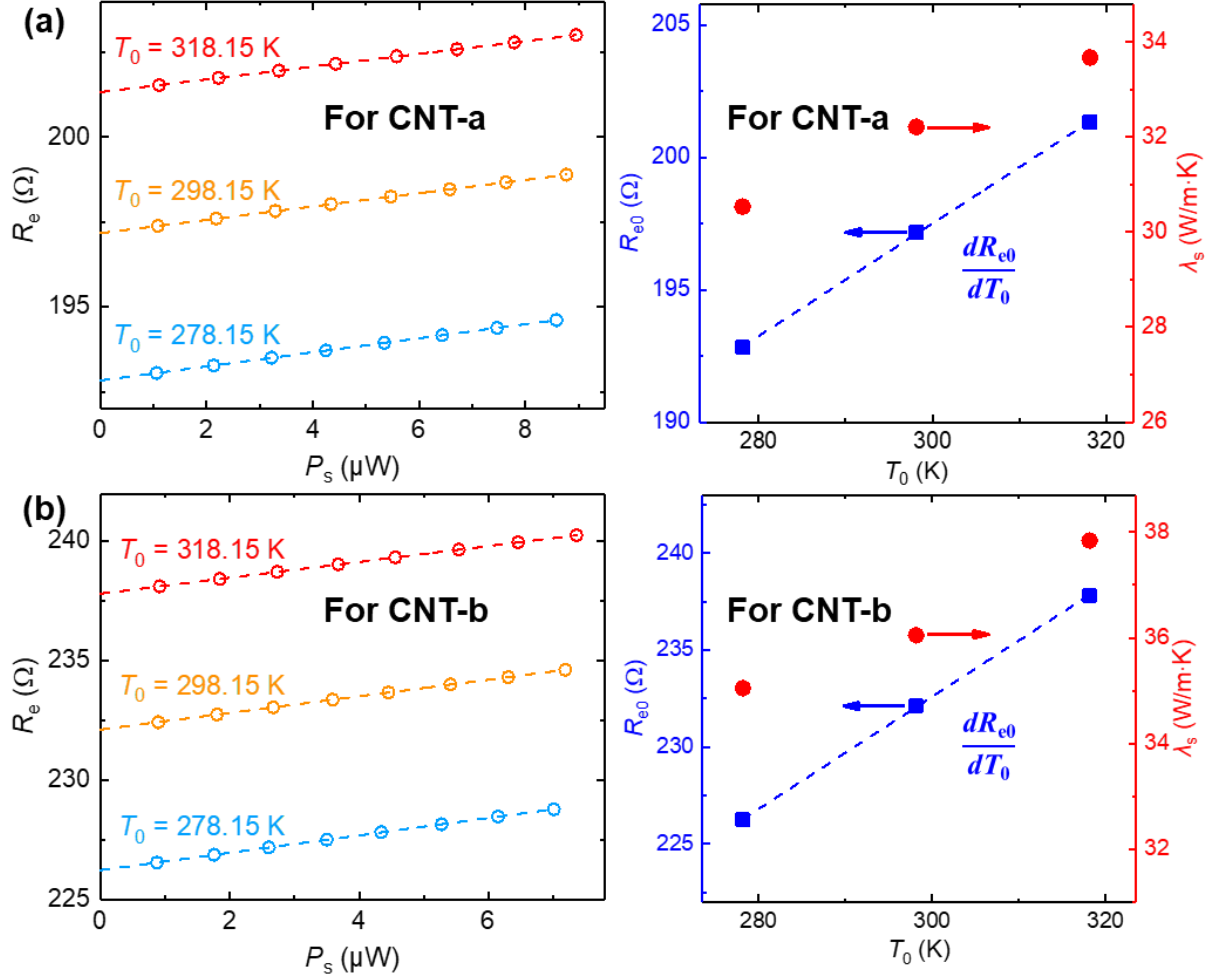


Figure 4.5 The calibration results of the electrical resistance and thermal conductivity of the Pt sensors before transfer (a) CNT-a and (b) CNT-b respectively.

The details about how the samples were picked up and transferred to the measurement devices can refer to Chapters 2 and 3. Figure 4.6 shows the photos of the experimental setup for the *in situ* and real-time thermal characterization. After the calibration measurement of the nanofilm sensor on a Peltier stage [Fig. 4.6(b)]. As shown in Fig. 4.6(c and d)), the silicon wafer with calibrated nanofilm sensor was fixed on a STEM holder that then was mounted into the SEM sample platform. The manipulator probe with the CNT attached was fixed on the SEM chamber wall. On the SEM sample platform, there are two circuit interfaces for the manipulator and external measurement, respectively. In the external measurement circuits, there is a DC current source (Advantest R6243) and two high-precision digital multimeters (Keithley 2002, 8.5 digits), of which a digital multimeter and a standard resistor (Yokogawa

2792) are used for detecting the electric current.

Subsequently, in the SEM mode, the manipulator was employed to overlap another end of the CNT on the nanofilm sensor, and EBID (the magnification of SEM observation is around 15000) was performed to bond the CNT and the nanofilm. Note one important point the working height of CNT transfer [Fig. 4.6(c)] and *in situ* thermal conductivity measurement with concurrent internal structure observation [Fig. 4.6(d)] is different. As a result, before switching to the STEM mode with the electron accelerating voltage of 30 kV, it is necessary to raise the height of the platform to safely insert the STEM detector. Another point to note is that the movement of the silicon wafer and probe are controlled by the SEM platform and the manipulator respectively, so after the EBID and during the real-time observation and *in situ* thermal measurements, we can only use the <Beam Shift> function in the SEM to move the image to the center.

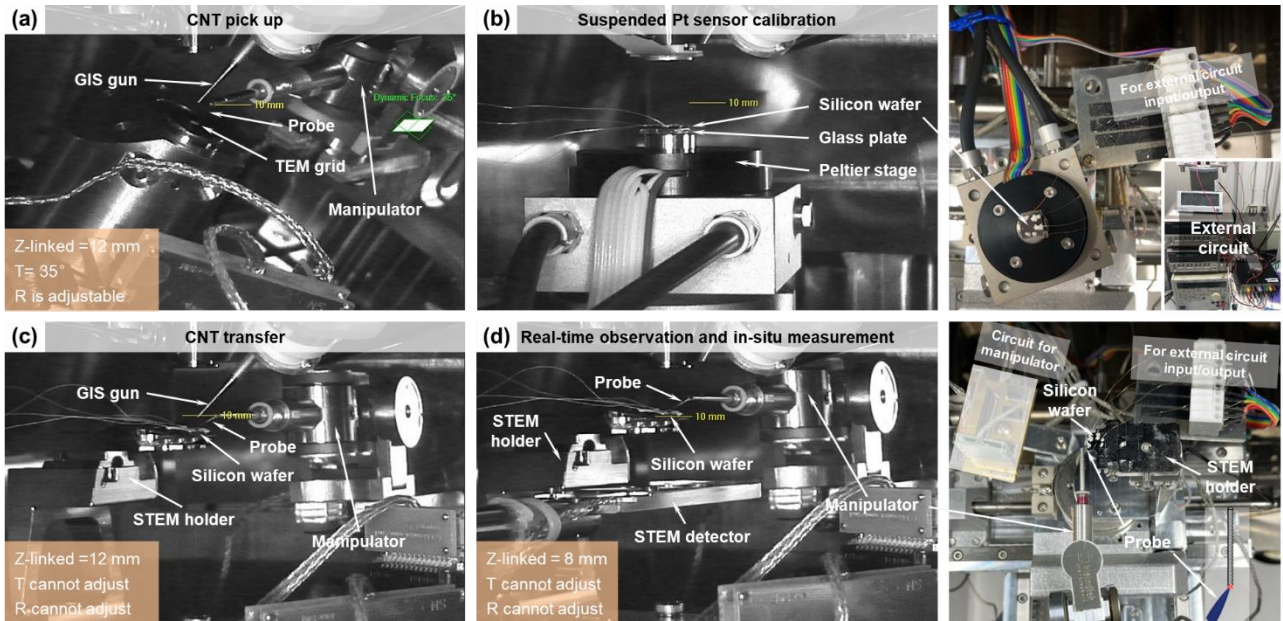


Figure 4.6 Photos of the experimental setup for *in situ* and real-time thermal characterization. (a) CNT pick up. (b) Suspended Pt nanofilm sensor calibration on a Peltier stage. (c) CNT transfer. (d) *In situ* thermal conductivity measurement with concurrent internal structure observation.

Figure 4.7 shows the acquired SEM and STEM images of CNT-a and CNT-b in the *in situ* thermal

conductivity measurement, where the probe, CNT, and the edge of the silicon wafer can be clearly distinguished. To prevent the effect of EB heating on the sensor and the sample, the EB was turned off when we conducted the thermal conductivity measurement. Figure 4.7(c) also presents the typical TEM micrograph of this kind of CNT, in which the cupped wall can be identified. The TEM image was acquired with an electron accelerating voltage of 200 kV. However, the electron accelerating voltages here for SEM and STEM observations were 10 kV and 30 kV, respectively. We have compared the STEM images with different modes and found the high-angle annular dark field (HAADF) mode gives the best imaging performance, where the internal hollow structure of the cup-stacked CNT can be distinguished. We measured the outer diameter (D_o) and inner diameter (D_i) of the CNTs from the STEM images. The outer and inner diameters can vary along the length and we measured the diameters at about 50 different locations. D_o and D_i were measured to be 103.0 ± 4.3 nm and 32.9 ± 4.5 nm for CNT-a, and 118.9 ± 8.6 nm and 52.9 ± 8.4 nm for CNT-b. The image brightness of CNT-a is almost uniform in the SEM image in Fig. 4.7(a), but significantly changes along the length in the STEM image in Fig. 4.7(b). The dark segment of CNT-a in Fig. 4.7(b) indicates that the CNT was significantly bent after being transferred to the measurement device, so we had to measure the length of CNT-a from the STEM image before the CNT transfer [Fig. 4.3(a)]. In contrast, CNT-b has a uniform image brightness in the STEM image of Fig. 4.7(e), indicating that CNT-b nearly lies in the same plane. We measured the CNT lengths between the probe and the nanofilm to be $14.5 \mu\text{m}$ for CNT-a and $10.0 \mu\text{m}$ for CNT-b. In addition, we can see the white dot-like structural defects or impurities in CNT-a. Thus, on the whole, we observed more structural disorders or non-uniformity in CNT-a than in CNT-b, which can cause a lower thermal conductivity in CNT-a. Note that in the previous SEM-based *in situ* thermal measurements [130, 133], it is impossible to *in situ* measure the inner diameter of the measured segment, not to mention the evaluation of the non-uniformity in the internal structure. The visualization of the internal structure of 1D material during the *in situ* thermal conductivity measurement is a major achievement in this study.

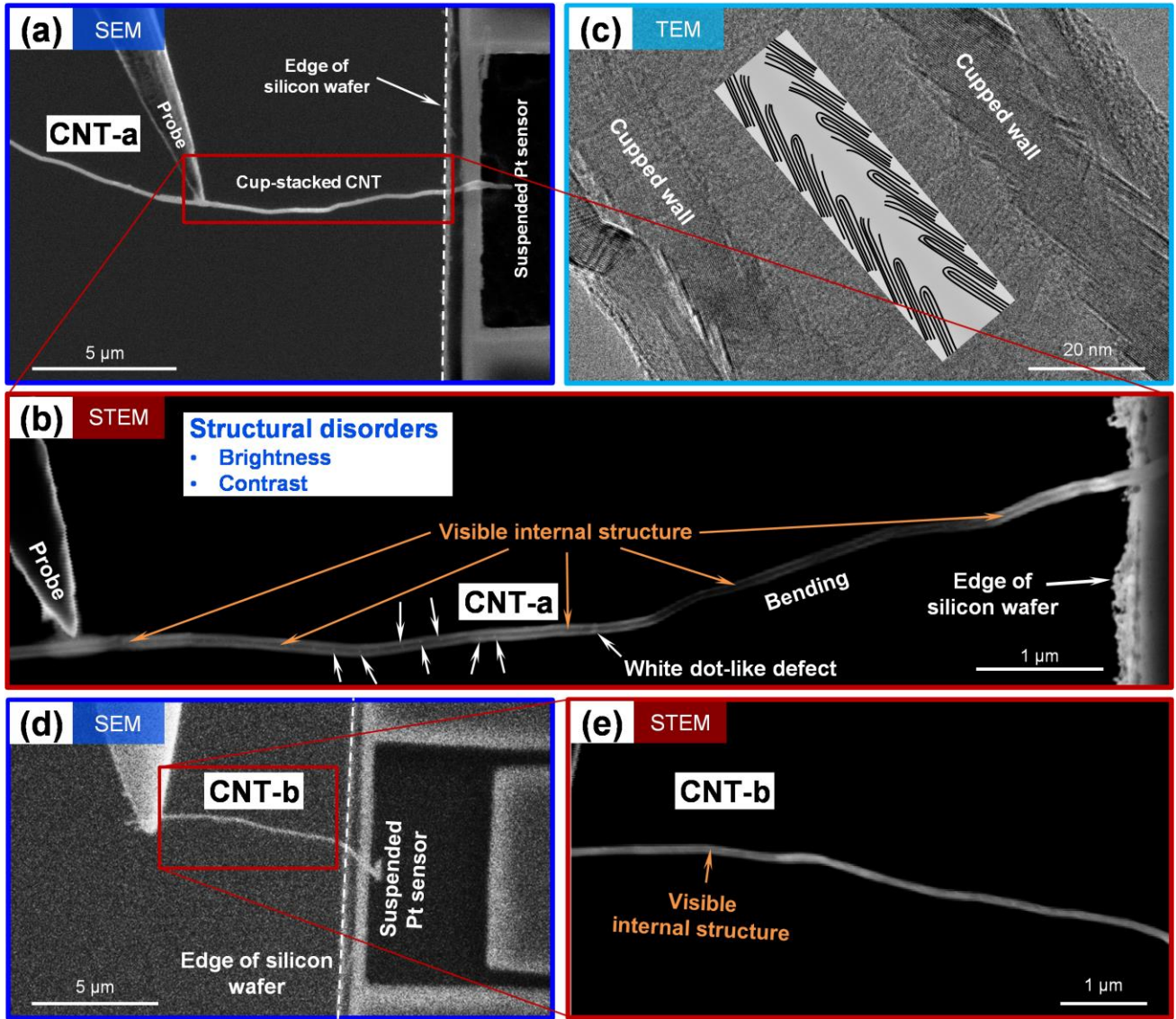


Figure 4.7 (a) SEM and (b) STEM images of CNT-a during the *in situ* thermal conductivity measurement. (c) The typical TEM micrograph of the cup-stacked CNT, which is on the same TEM grid with CNT-a. Inset: schematic illustration of the cup-stacked CNT. (d) SEM and (e) STEM images of CNT-b during the *in situ* thermal conductivity measurement.

4.5 Results and discussion

Figure 4.8 shows the *in situ* thermal measurement results. From the calibration results as shown in Fig. 4.5, the slope of the relationship between the electrical resistance and temperature of the two nanofilm sensors dR_{e0}/dT_0 for CNT-a and CNT-b is $0.213 \pm 0.003 \text{ } \Omega/\text{K}$ and $0.289 \pm 0.003 \text{ } \Omega/\text{K}$ respectively. Before the CNT transfer, as shown in Fig. 4.8 (a and b), the dependence of change in the electrical

resistance of the sensor ($\Delta R_e = R_e - R_{e0}$) on the Joule power was measured again. From the SEM images of the sensors and PVD parameters, the suspended nanofilm sensors used for CNT-a and CNT-b are 9.6 μm and 9.7 μm in length, 674.7 nm and 464.3 nm in width, and 40 nm in thickness. According to Eq. (2.12), the thermal conductivity of the two sensors was calculated to be $32.0 \pm 0.03 \text{ W/m}\cdot\text{K}$ and $34.2 \pm 0.03 \text{ W/m}\cdot\text{K}$, respectively. After the CNT transfer, to eliminate the heating effect of the electron beam, we turned off the electron beam when we conducted the thermal conductivity measurement. The change in the sensor resistance decreased after being bonded with the CNT samples since part of the heat flux went through the CNT to the heat sink (*i.e.* the tungsten probe) and the average temperature rise of the nanofilm decreased. Figure 4.8(c) illustrates the difference in the average temperature rise of the nanofilm sensors after and before CNT transfer. Then, the total thermal resistance for CNT-a and CNT-b was extracted to be $(8.9 \pm 5.0) \times 10^7 \text{ K/W}$ and $(3.3 \pm 0.4) \times 10^7 \text{ K/W}$ based on Eq. (4.1), respectively. Although we cannot separate the thermal contact resistance (R_c) in our measurement, R_c is negligible as reported in the literature with similar contact conditions [9, 51, 71, 77] since we bonded the CNT firmly with the sensor and the heat sink using EBID. Thus, we took R_c in Eq. (4.1) as 0 and calculated the thermal conductivities which here correspond to the lower bound of the actual thermal conductivities. Here we used the shell cross-sectional area of the CNT for the thermal conductivity calculation, which is the same as the previous measurements on cup-stacked CNTs [13, 77]. As shown in Fig. 4.8(d), the thermal conductivity of CNT-a and CNT-b is $21.7 \pm 12.4 \text{ W/m}\cdot\text{K}$ and $33.8 \pm 8.0 \text{ W/m}\cdot\text{K}$, respectively, which approximately fall in the range of the reported thermal conductivity of this kind of cup-stacked CNT in previous measurements [13, 77]. The uncertainty analysis was performed similarly as in Chapter 2 and exhibited as error bars in each data graph. It should be pointed out that the previous measurements in [13] did not provide the uncertainty, while the uncertainty reported in [77] could be underestimated. The thermal conductivity of cup-stacked CNTs is dominated by the interfacial thermal resistance between graphene or graphite cups, which can be affected by structural bending and disorders. The thermal conductivity difference between CNT-a and CNT-b can be explained by the structural difference

observed in the STEM images as discussed earlier, as well as the sample variation in the crystallization defect levels that cannot be observed with STEM-in-SEM.

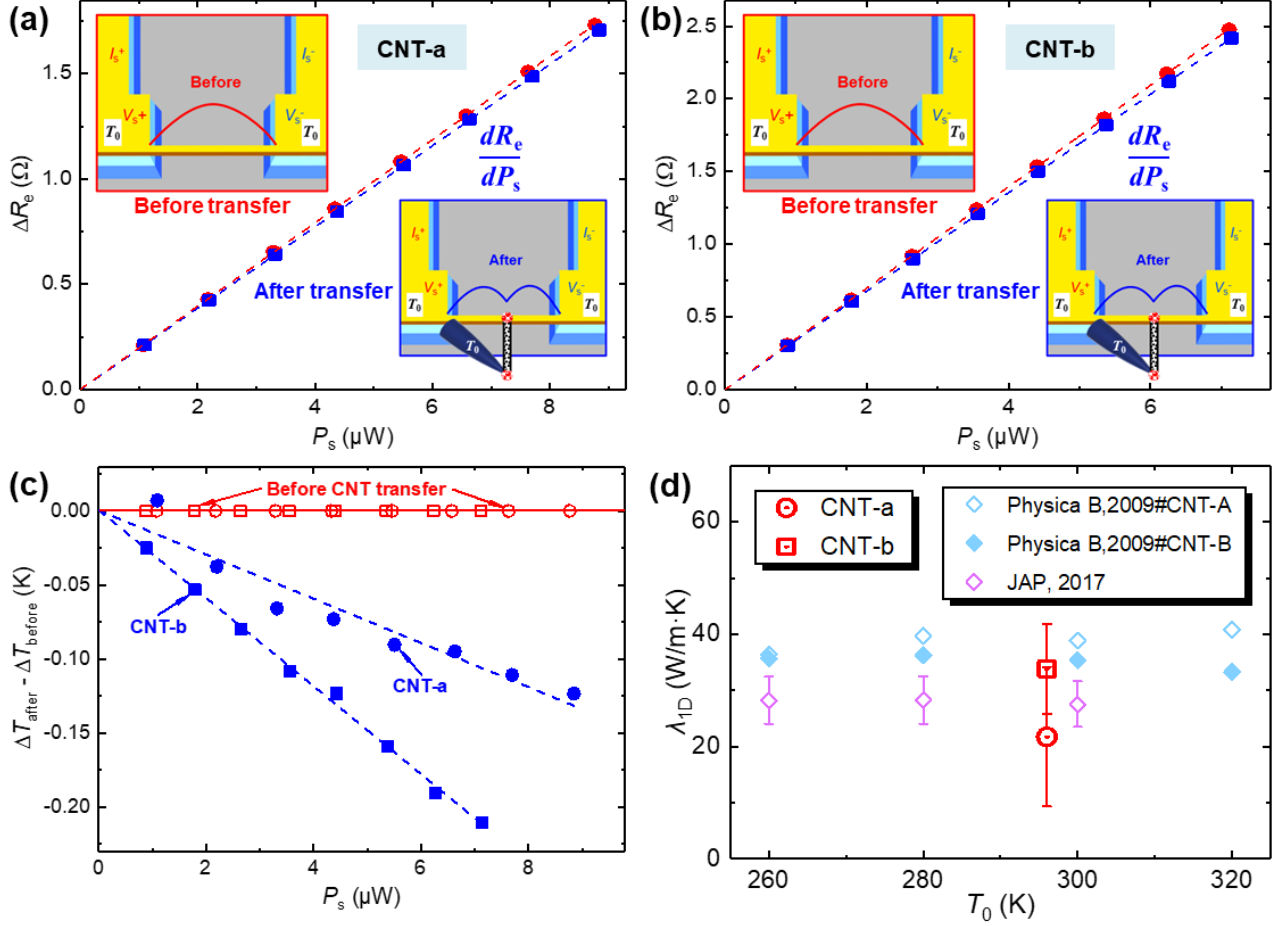


Figure 4.8 The dependence of the change in the sensor resistance on the Joule power before and after transferring (a) CNT-a and (b) CNT-b. (c) The difference in the average temperature rise of the sensor after and before the CNT transfer. (d) The thermal conductivity of CNT-a and CNT-b plotted with the literature results [13, 77].

One concern about our method is whether the electron beam can damage the sample since the electron beam can introduce defects in graphene [134]. Actually, for MWCNTs or nanowires, the electron-beam-induced damage is negligible under TEM observation where the acceleration voltage is normally 200 kV or 300 kV [12, 104, 107]. In this work, the acceleration voltage of STEM-in-SEM observation is 30 kV, which is much lower than TEM and ensures the sample safety. Besides, the data was stable during the measurement, which also confirmed the negligible electron-beam effect. We also

evaluated the heating effect of the electron beam irradiation by monitoring the temperature change in the Pt sensor. From Fig. 4.9, we found that the electron beam does heat the sample and the temperature change caused by the EB irradiation is less than 0.6 K. To avoid the EB heating effect, we turned off the EB when we conducted the thermal conductivity measurement of the CNTs, so the EB irradiation does not affect the thermal conductivity results.

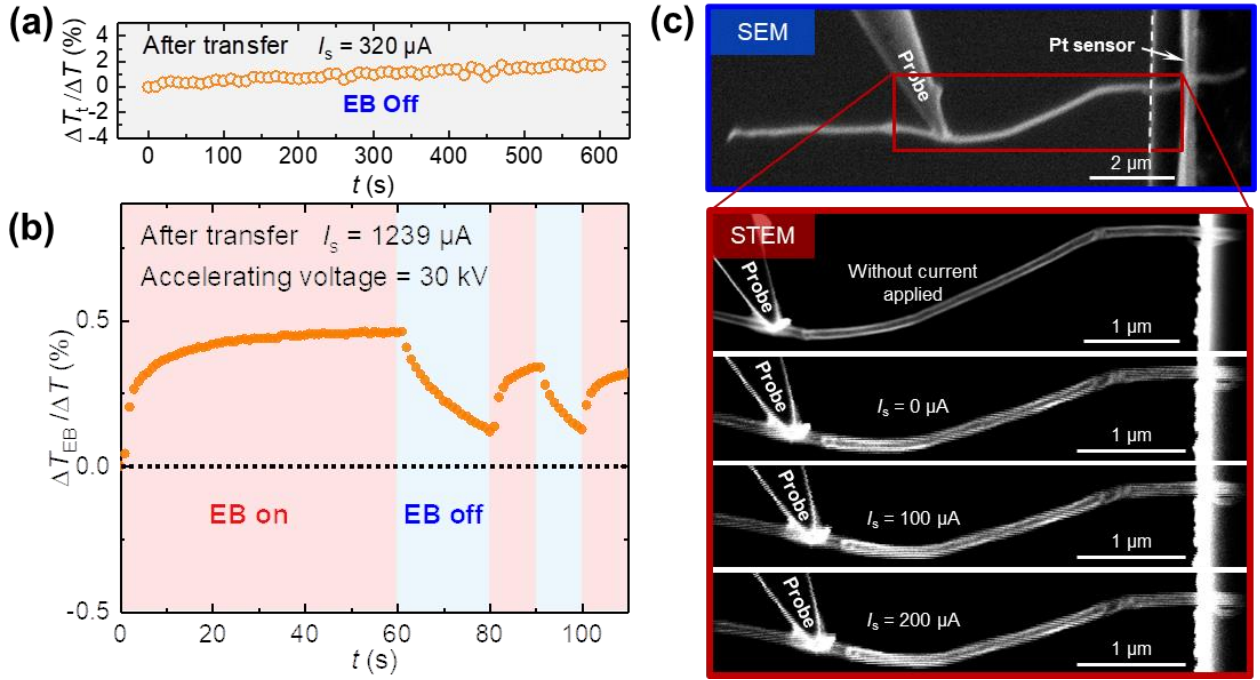


Figure 4.9 Tests on the effects of the electron beam irradiation and the current applied to the nanofilm sensor on thermal characterization. (a) The resistance and (b) the change in the average temperature rise of the nanofilm during the heating effect test of the electron beam irradiation. (c) The effect of the current applied to the nanofilm sensor on the real-time STEM images.

4.6 Summary

In summary, we have developed an experimental method that enables concurrent thermal conductivity measurement and internal structure observation of single 1D materials using STEM-in-SEM. The nanofilm sensor is fabricated on the edge of the silicon wafer to allow the electron beam to transmit through the 1D material and be detected by the STEM detector, which caters to the real-time

observation of the inner nanostructure. Utilizing this setup, we observed the internal non-uniform structures of the cup-stacked CNTs and measured the thermal conductivity *in situ*. The thermal conductivity results fall in the range of the previously reported values, while the thermal conductivity difference between our measured samples can be attributed to the structural difference. The sample with more structural disorders has a lower thermal conductivity. Our experimental method can find wide applications in the sample-by-sample elucidation of the structure-property correlation for 1D materials in real-time.

5. Modulation of thermal transport in cup-stacked CNT by liquid filling

5.1 Introduction

The modulation of the thermal transport property of graphene-based materials has spurred intense research, and the proposed tactics also advance our understanding of the fundamental mechanisms. In this chapter, inspired by the modulation of heat transfer at the interface by intercalation, we utilized the liquid filling to modulate the thermal transport in the cup-stacked CNT experimentally. We fabricated and measured the thermal conductivity of four water-infused CNTs (including one temperature-dependent measurement) and one LiCl-infused CNT (temperature-dependent measurement) based on the technique developed in Chapter 4 and the conventional T-type method. The experimental results demonstrate that liquid filling can significantly enhance the thermal conductivity of the cup-stacked CNT. Unlike the typical MWCNT, the dry cup-stacked CNT is composed of a chain of truncated graphene cups stacked together, which contains many interfaces, and its thermal conductivity is dominated by the interfacial thermal resistance between graphene cups. We attribute the thermal transport enhancement to the strengthened interfacial coupling between graphene cups due to the penetration of water molecules between the graphene cups, which is further supported by the reported molecular dynamics (MD) simulation studies and additional TEM observations. Our results are instructive for tuning thermal transport in graphene-based nanocomposites.

5.2 Unique behavior of water confined in nanoscale

Fascinatingly, water filling into the nanoscale cavity makes CNT an ideal platform for the nanofluidics research [135-142], and a series of breathtaking unique water behaviors under nanoscale confinement have been uncovered as shown in Fig. 5.1, such as new ice phases not seen in the bulk ice [143], astonishing high water flow rates due to slippage [144], unusual hydrogen-bonding [145], the

extreme phase transition temperature of the confined water [146], strong tube diameter dependence of the melting point of the confined ice [147] and so forth. The confined water structure inside CNT has been exultantly observed by TEM [104, 107, 148], optical microscopy [149], and environmental scanning electron microscopy (ESEM) [150] as shown in Fig. 5.2, however, these efforts mostly stopped at the qualitative *in situ* study of the temperature effect heating via electron irradiation on the confined water [148, 150-152]. Although the molecular dynamics simulation [153] predicted that the water-filled CNTs would exhibit a thermal conductivity reduction due to interactions with the water molecules, the impact of water filling on the thermal transport properties of individual CNT has not been measured experimentally yet, which is largely due to the low success rate of water filling and the challenge in manipulating the water-filled CNT to the thermal characterization platform.

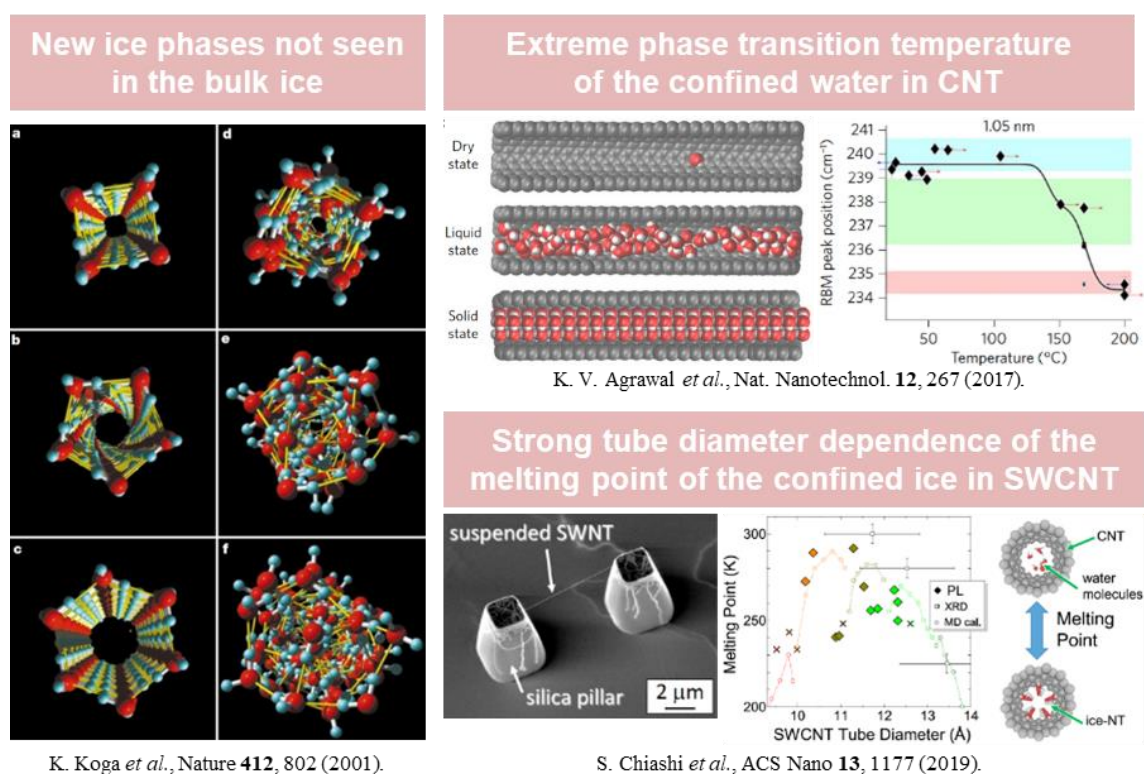


Figure 5.1 Study on the unique properties of nanoscale confined water in CNT [143, 146, 147].

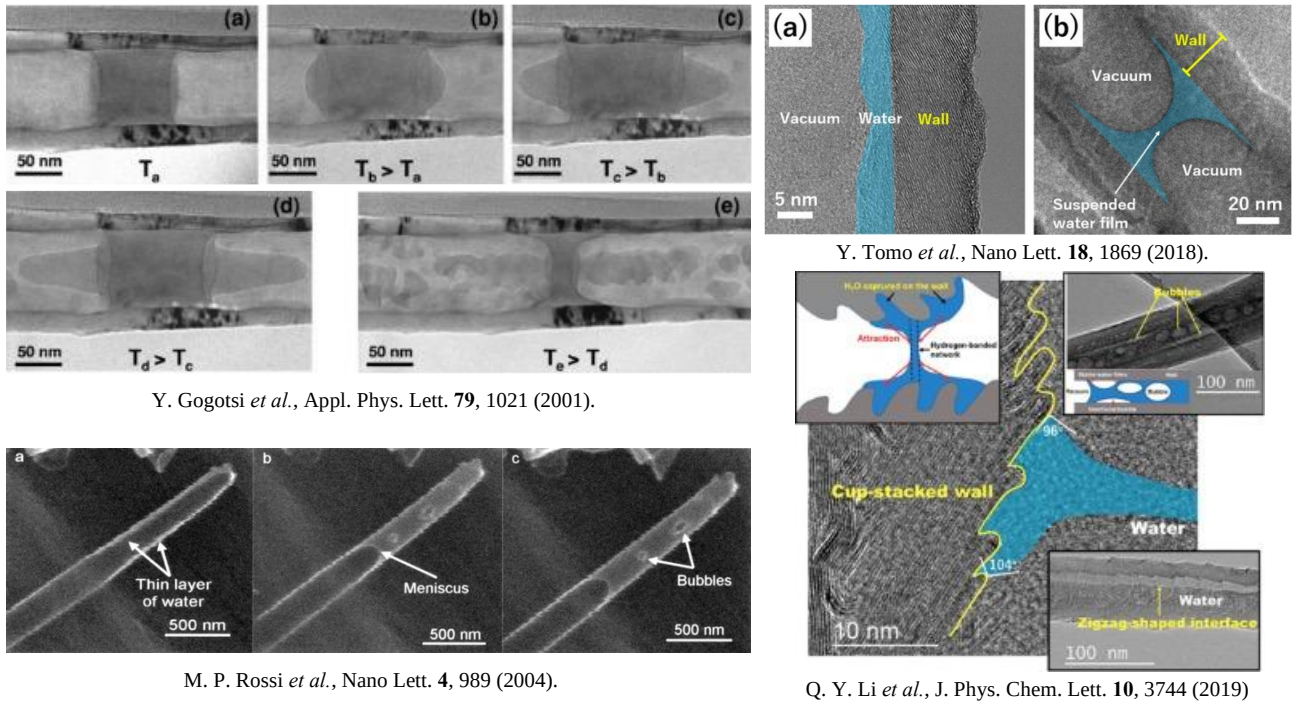


Figure 5.2 Experimental observation of nanoscale confined water in CNT [104, 107, 148, 150].

5.3 Experimental method

5.3.1 Experimental procedures

Figure 5.3 shows the experimental procedures. Briefly, the cup-stacked CNTs with high-temperature treatment in powder form [12, 104] were dispersed into acetone. Subsequently, several droplets of the suspension were dropped onto a TEM grid. After drying in the vacuum chamber for one day, we adjusted the chamber humidity by controlling the chamber pressure during the condensation process to infuse water into the CNTs with the ESEM [107]. Figure 5.4(a) shows the schematic diagram of the method to fill water into the CNTs [107]. The processes of the pressure adjustment is also given in Fig. 5.4(b), with the red rectangle indicating the range in the simplified phase diagram of water [154]. The LiCl-infused CNTs were fabricated by soaking the dry CNTs in a prepared LiCl solution (0.034 mol/L). By subsequent TEM characterization, the liquid-infused CNT was picked up with a tungsten probe and transferred to a calibrated sensor, which can be referred to Chapters 2 to 4. The position of the liquid-infused CNTs under different electron microscopes was determined by recording the relative

position of a hole we made in the TEM grid and the liquid-filled CNTs.

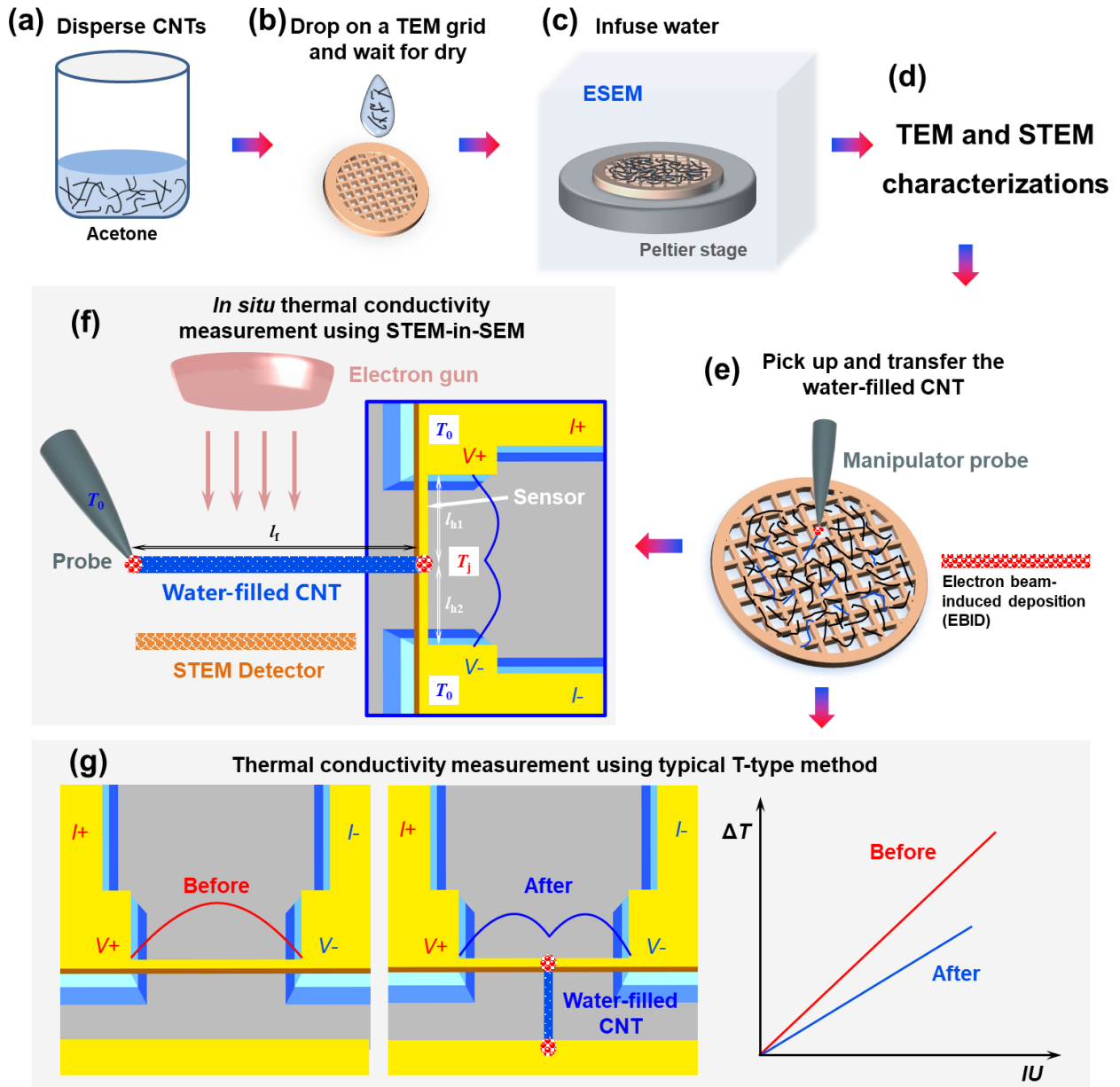


Figure 5.3 Experimental procedures of the thermal conductivity measurement of liquid-infused CNTs by the method developed in Chapter 4 and the conventional T-type method.

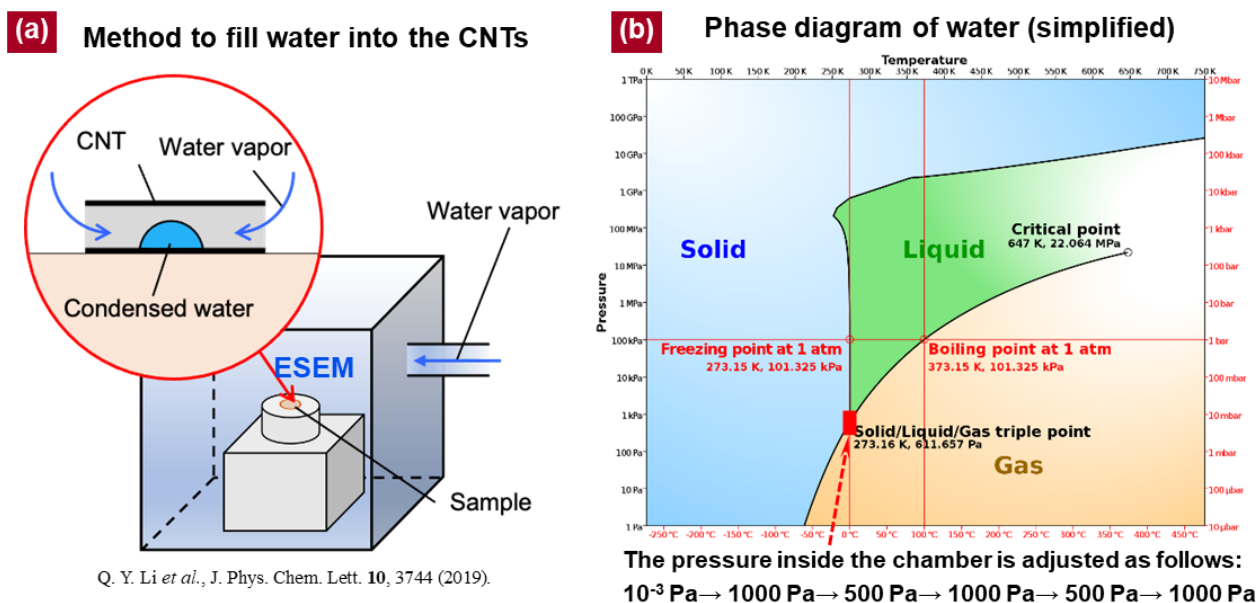


Figure 5.4 (a) Schematic of the method to fill water into the CNTs [107]. (b) Simplified phase diagram of water [154]. The red rectangle denotes the adjusted pressure range inside the SEM chamber using ESEM mode.

As shown in Fig. 5.3(f and g), the thermal conductivity of the liquid-infused CNTs is measured by two methods: the method developed in Chapter 4 and the conventional T-type method. Since the previous relevant experimental endeavors [40, 77] cannot capture the real-time structure information of the CNT/confined substance composite during the *in situ* quantitative thermal measurements, the method developed in Chapter 4 is used to concurrently identify the inner structure of the water-infused CNT during the *in situ* thermal conductivity measurement. To extract the temperature dependence of the thermal conductivity, the conventional T-type method [9] is used.

5.3.2 Characterization and thermal conductivity measurement of liquid-infused CNTs

Although the confined water structure inside CNT has been exultantly observed by TEM [104, 107, 148], optical microscopy [149], and ESEM [150], there is no report using STEM to observe the water structure inside CNT. Firstly, the feasibility and performance of the STEM to observe the confined water structure in the CNT were tested separately. Figure 5.5 shows the STEM and corresponding TEM images of three water-infused CNTs, from which the water, interface, bubble, and meniscus structures

were successfully identified although its resolution is not as high as that of TEM.

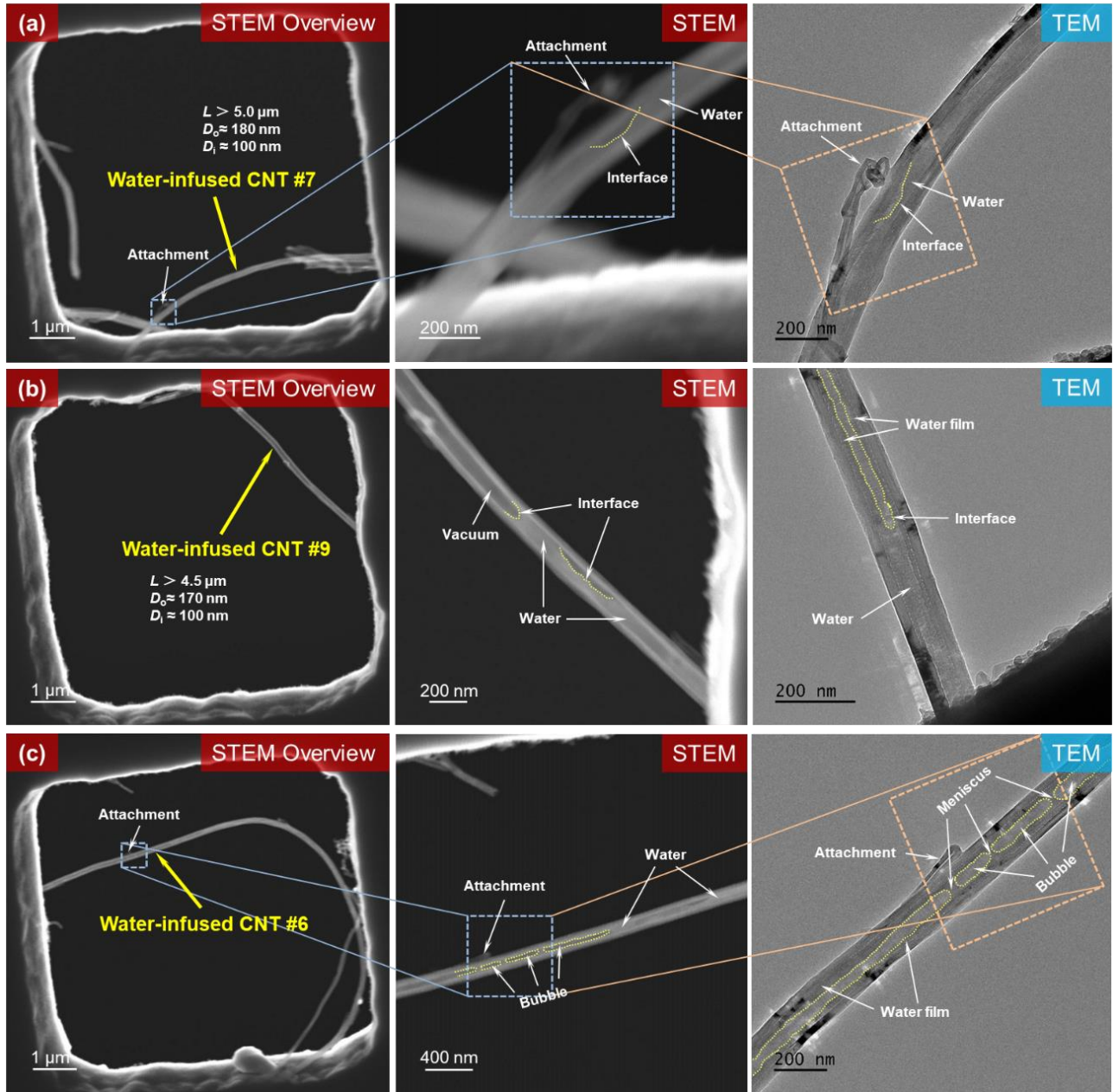


Figure 5.5 Feasibility and performance test of the STEM to observe the confined water structure in the CNT. STEM images and their corresponding TEM images.

In advance of the thermal conductivity measurement, TEM characterization was performed to find the suitable liquid-infused CNT and acquire high-magnification images for reference (the geometric parameters were also measured). Then the thermal conductivity measurement of liquid-infused CNTs

was conducted. The measurement details can be referred to Chapters 2 to 4. Figures 5.6 to 5.8 present the SEM and STEM images of the *in situ* and real-time thermal conductivity measurements of liquid-infused CNT#1, liquid-infused CNT#2, and liquid-infused CNT#3, respectively. Figure 5.9 and Fig. 5.10 show the SEM images of the temperature dependence measurement of the thermal conductivity of water-infused CNT#4 and LiCl-infused CNT by the conventional T-type method, respectively. Their TEM characterization images and the thermal conductivity at SEM chamber temperature or 300 K are also given in the corresponding figures. The liquid infusion part is highlighted in each figure as well.

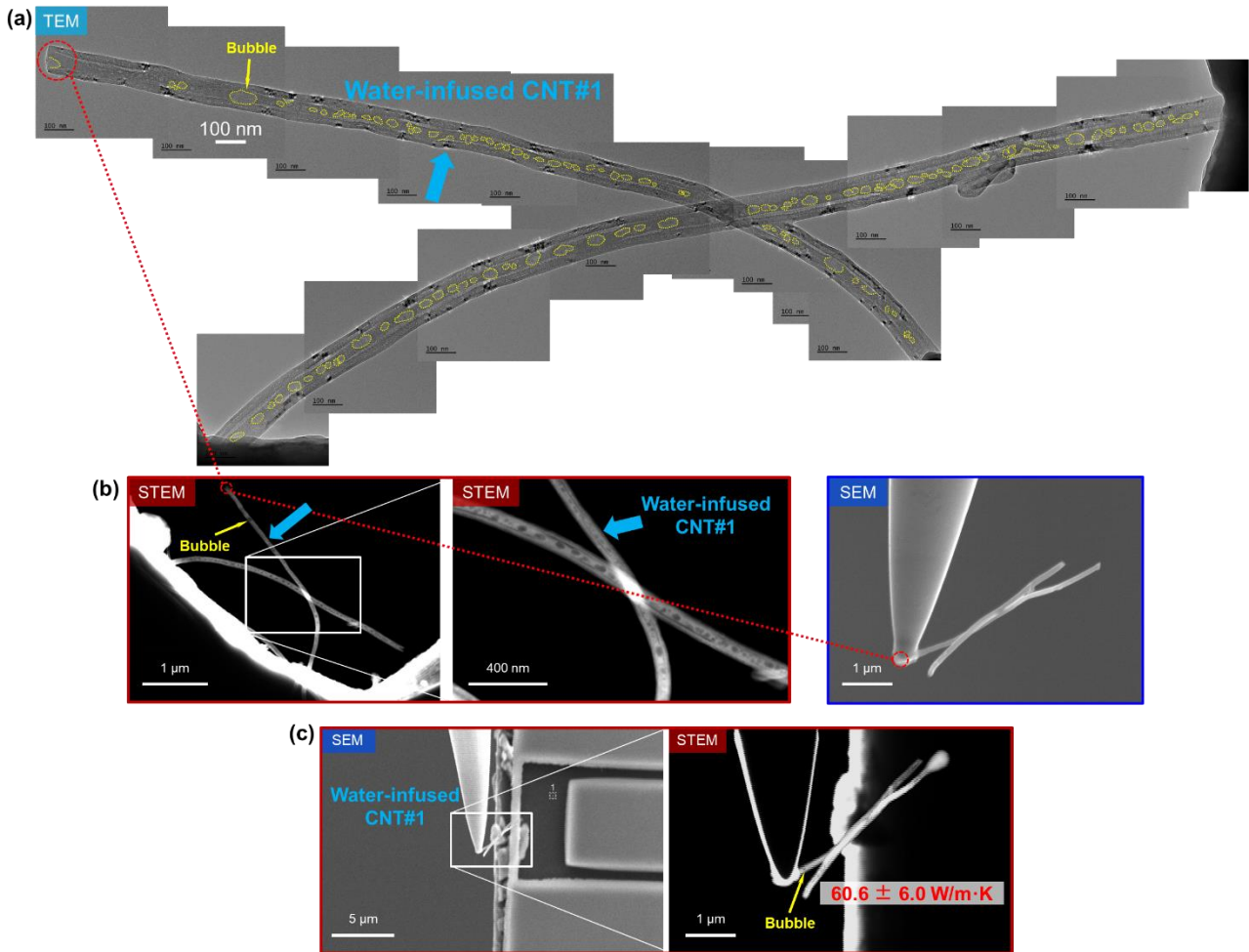


Figure 5.6 TEM characterization images of water-infused CNT#1, and SEM and STEM images of its *in situ* and real-time thermal conductivity measurement.

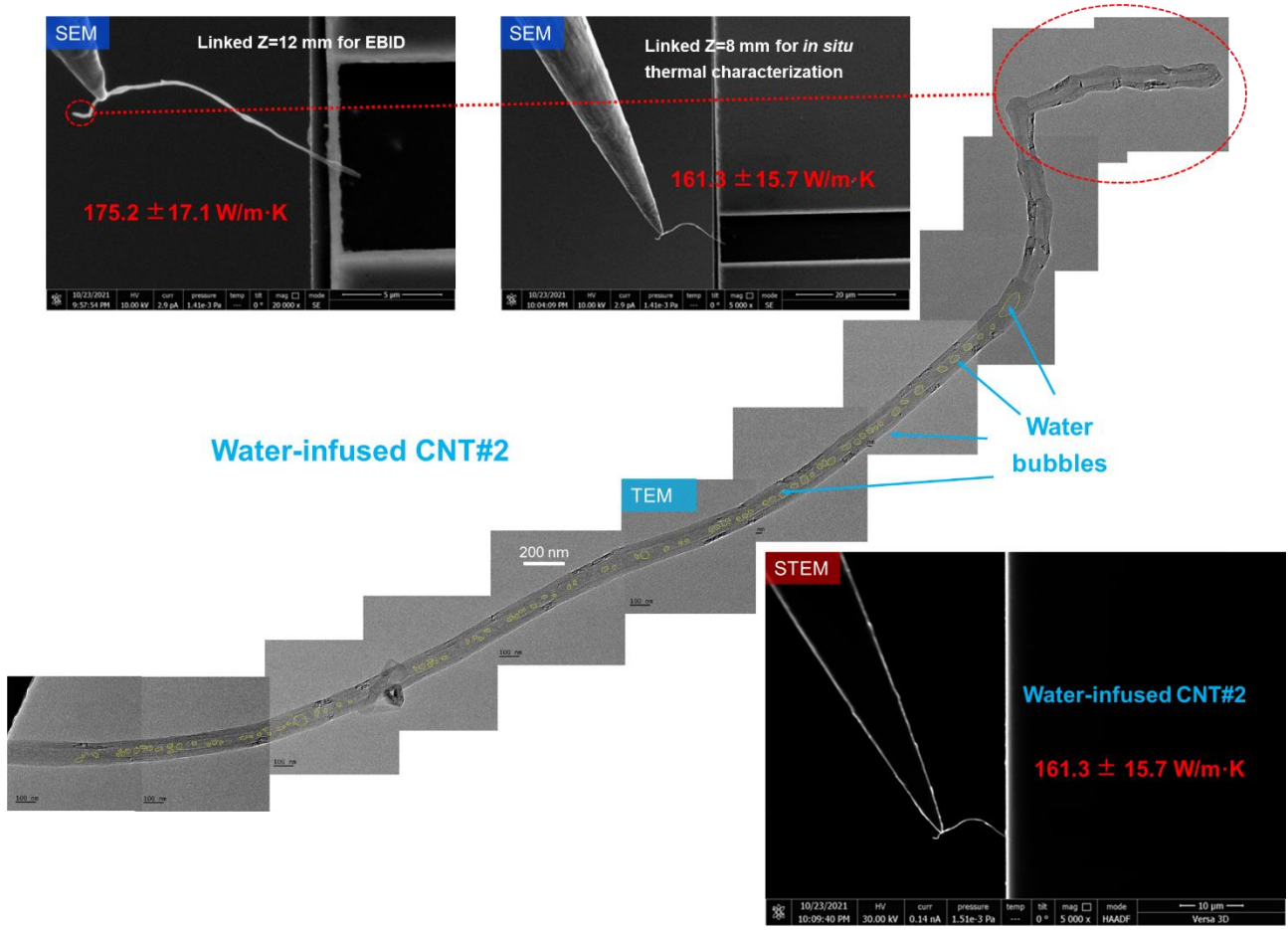


Figure 5.7 TEM characterization images of water-infused CNT#2, and SEM and STEM images of its *in situ* and real-time thermal conductivity measurement.

From the TEM images, it is found that even under the high vacuum condition of the TEM, there is an amount of water and bubbles confined. The bubble is begotten from the dissolved air in water under the high-vacuum environment and highlighted with the yellow arrow in each TEM image.

As shown in Fig. 5.6(b), the STEM images of water-infused CNT#1 before picking up, the confined water and the CNT walls have similar contrast while the confined bubbles have a deeper black. Even though the water film adhering to the CNT inner wall that can be observed with TEM [104, 107] is difficult to identify, the water-bubble structure confined in CNT is observed competently, which is largely due to the special structure when water, bubbles, and CNT walls coexist. Besides, the linear interface between the CNT wall and the confined water which is also called zigzag-shaped liquid-gas interface [107] is also clearly visible. In the STEM image of Fig 5.6(c), a bubble is successfully

identified and emphasized, which can be corroborated by the TEM image. By comparing the difference in contrast, some smaller bubbles and the interfaces between the CNT wall and the inside can also be distinguished. Its weakened resolution may originate from the silicon wafer that electrons cannot transmit, which can be corroborated by the high brightness of the wafer edge as well.

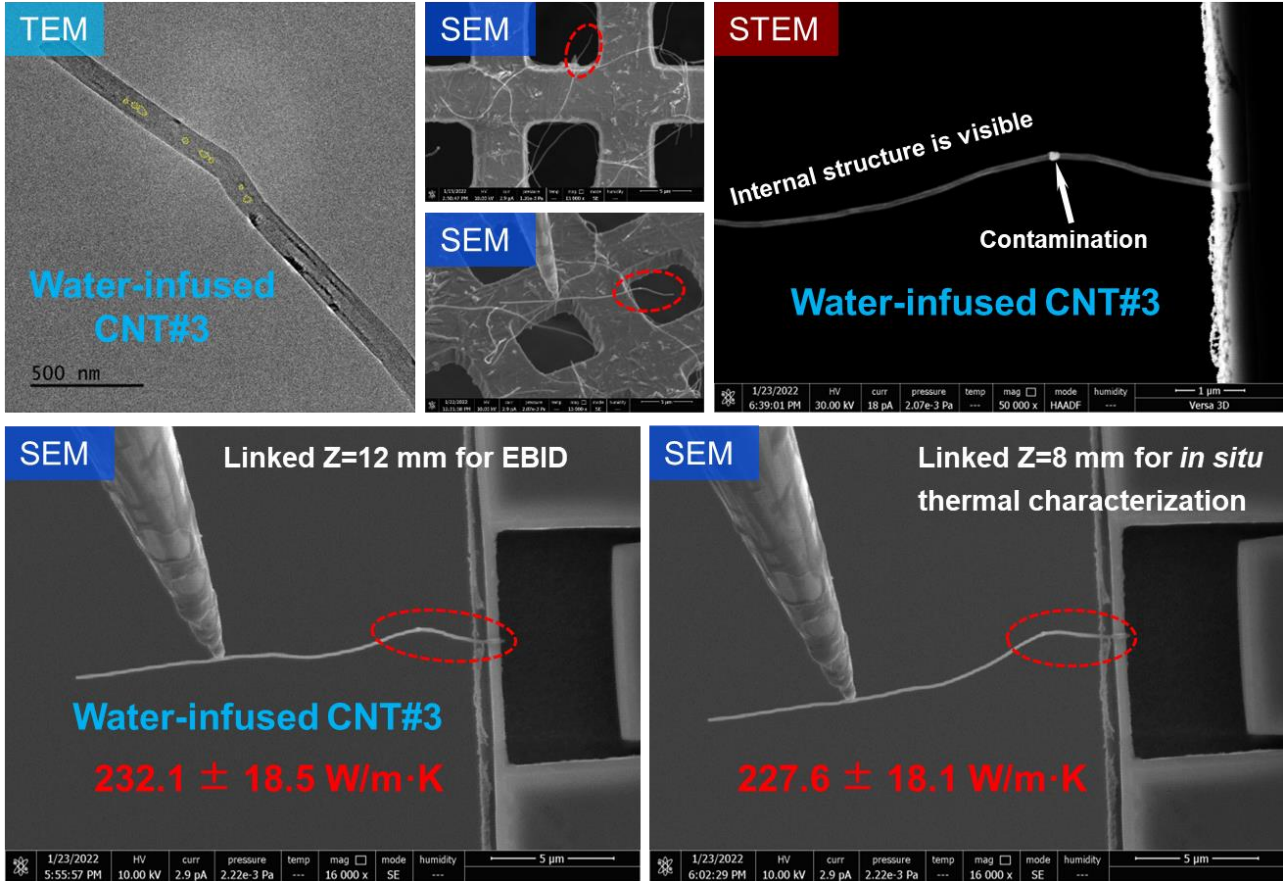


Figure 5.8 TEM characterization images of water-infused CNT#3, and SEM and STEM images of its *in situ* and real-time thermal conductivity measurement.

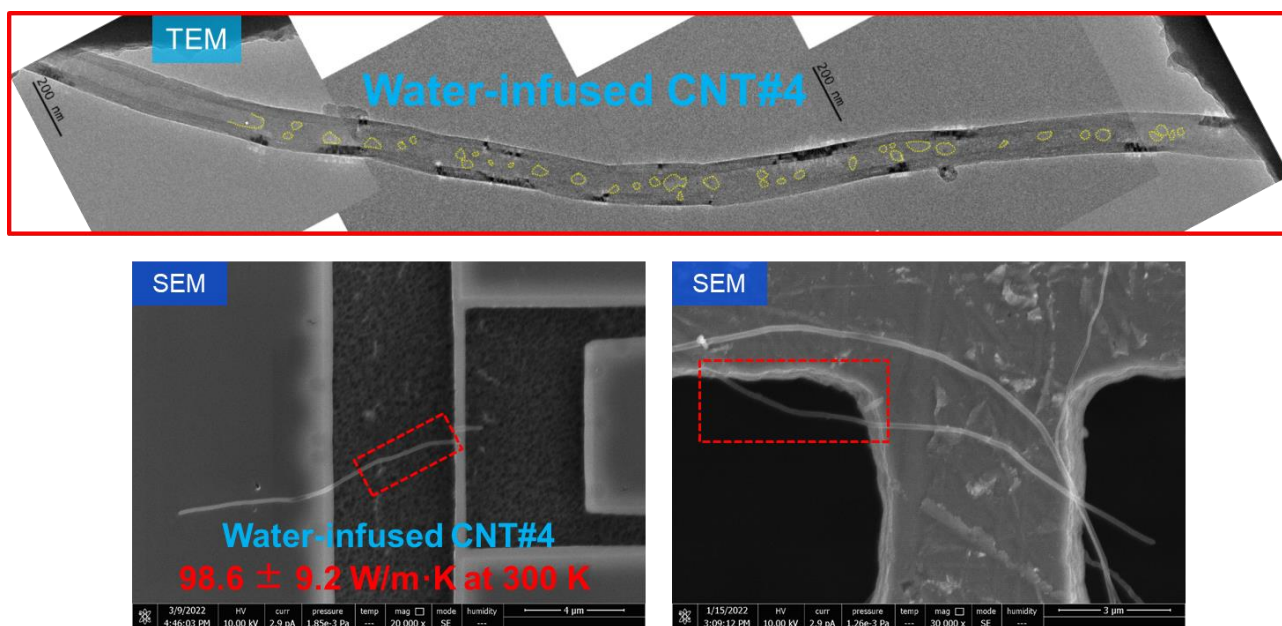


Figure 5.9 TEM characterization images of water-infused CNT#4, and SEM images of its temperature dependence measurement of thermal conductivity.

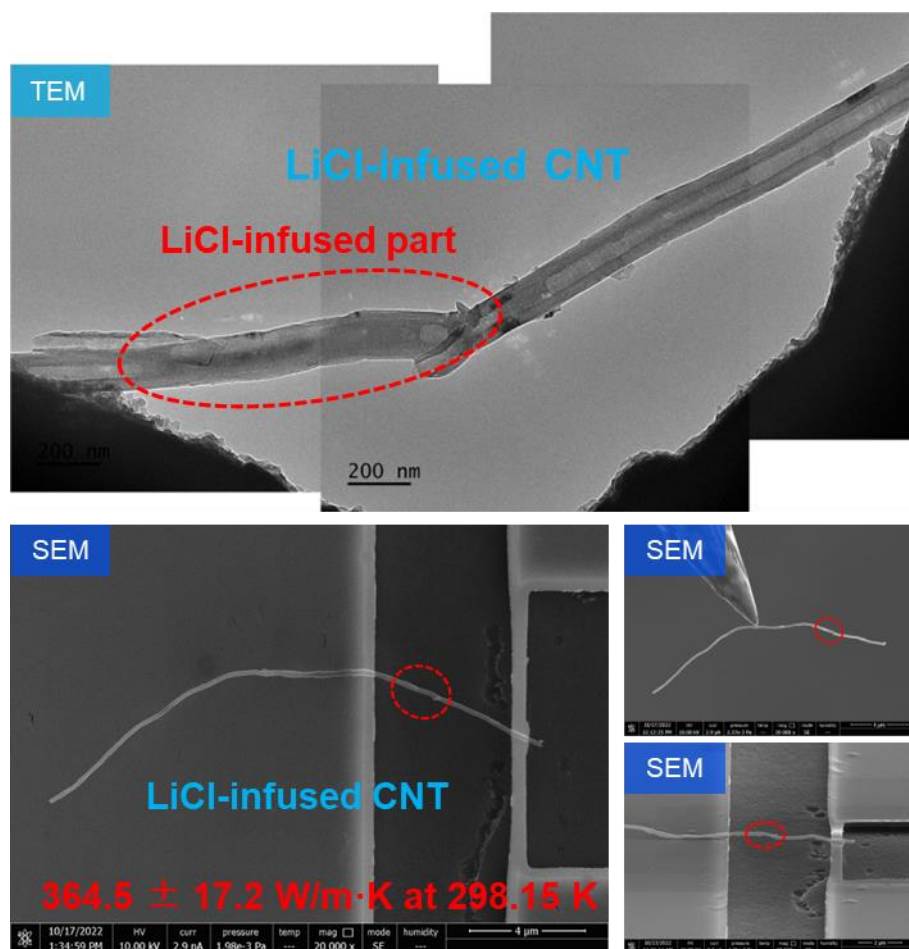


Figure 5.10 TEM characterization images of LiCl-infused CNT, and SEM images of its temperature dependence measurement of thermal conductivity.

5.4 Results and discussion

Figure 5.11 demonstrates the thermal conductivity of the liquid-infused CNTs. Grippingly, the water-infused CNTs exhibit a considerably higher thermal conductivity than the dry cup-stacked CNTs [13, 52, 77, 155]. Moreover, the LiCl-infused CNT shows a much higher thermal conductivity of around 360 W/m·K. Here, we stress that the heat radiation effect of another water-infused CNT attached to water-infused CNT#1 was neglected since the thermal measurement was performed under vacuum and the temperature rise of the nanofilm was small enough. The considerably enhanced thermal transport indicates the noteworthy impact of water filling to modulate the thermal transport properties of cup-stacked CNT. For comparison, Kodama *et al.* [40] demonstrated that the fullerene encapsulation reduced the thermal conductivity of the single-walled carbon nanotube (SWCNT) to around 40%, and Yamada *et al.* [77] presented that the ionic liquid infusion led to a 50% reduction in the thermal conductivity of the cup-stacked CNT.

Considering the additional thermal conduction path provided by the confined liquid, we first equated the heat conduction in liquid-infused CNT to a thermal resistance circuit composed in parallel of carbon wall and internal confined liquid. The water-infused CNT#1 is considered as a core-shell structure. The confined water is the core, and the carbon wall is the shell, and its equivalent thermal resistance was calculated. Nevertheless, due to the low thermal conductivity of water, the calculation implied that the confined water can only reduce the thermal resistance by about 0.4 % if water-infused CNT#1 has uniform outer and inner diameters. As a result, the contribution of the confined water to the axial heat conduction along the CNT is ignorable. Even though the molecular dynamics (MD) simulation [156] reported that the confinement of CNT would enhance the thermal conductivity of water in the axial direction, this contribution is still inappreciable.

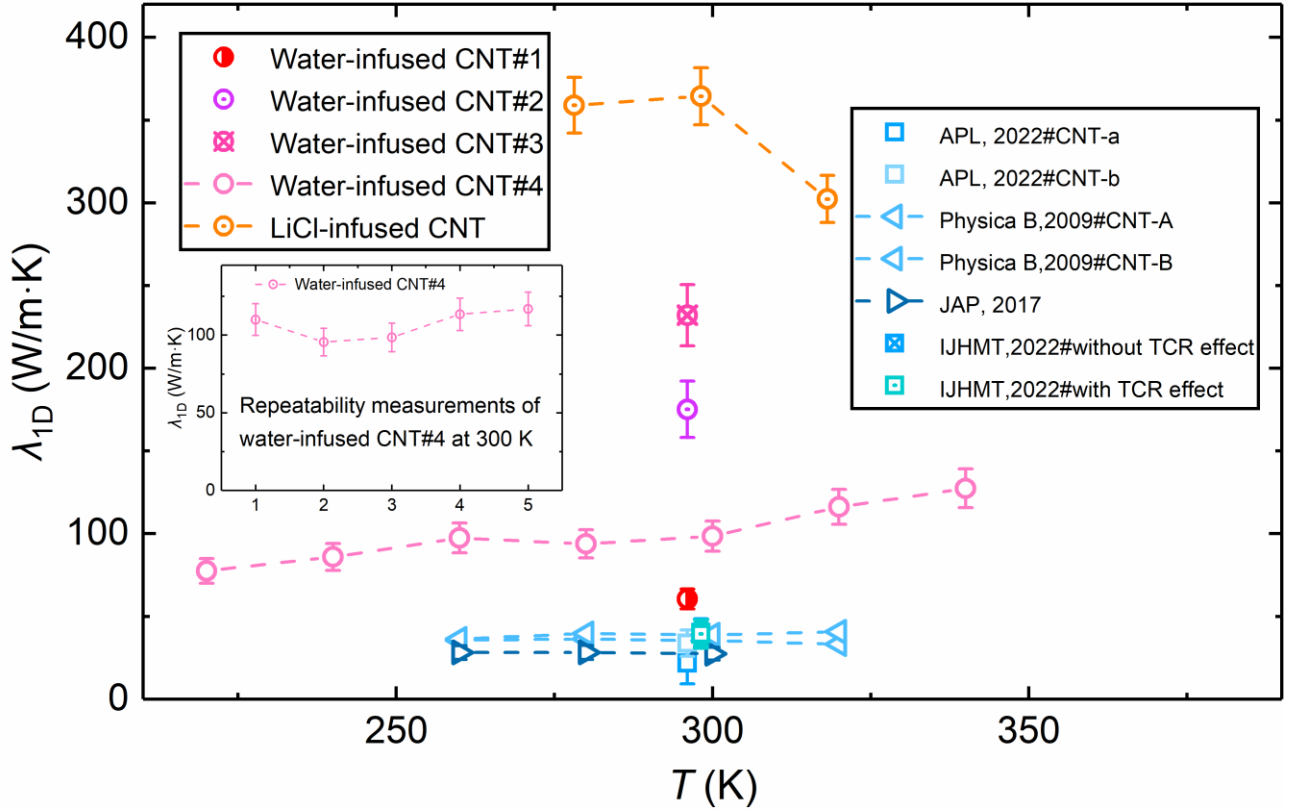


Figure 5.11 Summary of the measured thermal conductivity of the liquid-infused CNTs. Inset: The repeatability measurements of water-infused CNT#4. The reported results of dry cup-stacked CNT are given for comparison [13, 52, 77, 155].

There should be a strengthened interaction between the graphene cup and the confined water, which can enhance thermal transport. Since the effective thermal conductivity of the cup-stacked CNT is dominantly weakened by the interfacial thermal resistance between graphene cups, we then turn to ponder the role of water intercalation between the graphene cups. Despite the hydrophobicity of cup-stacked CNT, the nanometer-thin free water films have been experimentally observed to exist stably inside the cup-stacked CNTs [104, 107]. In addition, the thin water film and the interfacial bubbles were found to have a very long lifetime due to the pinning effect [157]. As shown in the TEM images of water-infused CNTs and Fig. 5.12(c and d), the water film always carpets one side of the inner wall of the CNT with a considerably long total distance, while another side presents a discernible water-gas interface. On the side overspread by water film, water overlies fully the open and loop edges of the graphene cups, which causes an indistinct interface between water and carbon wall. The above situations

can be corroborated by the previous study [104, 107].

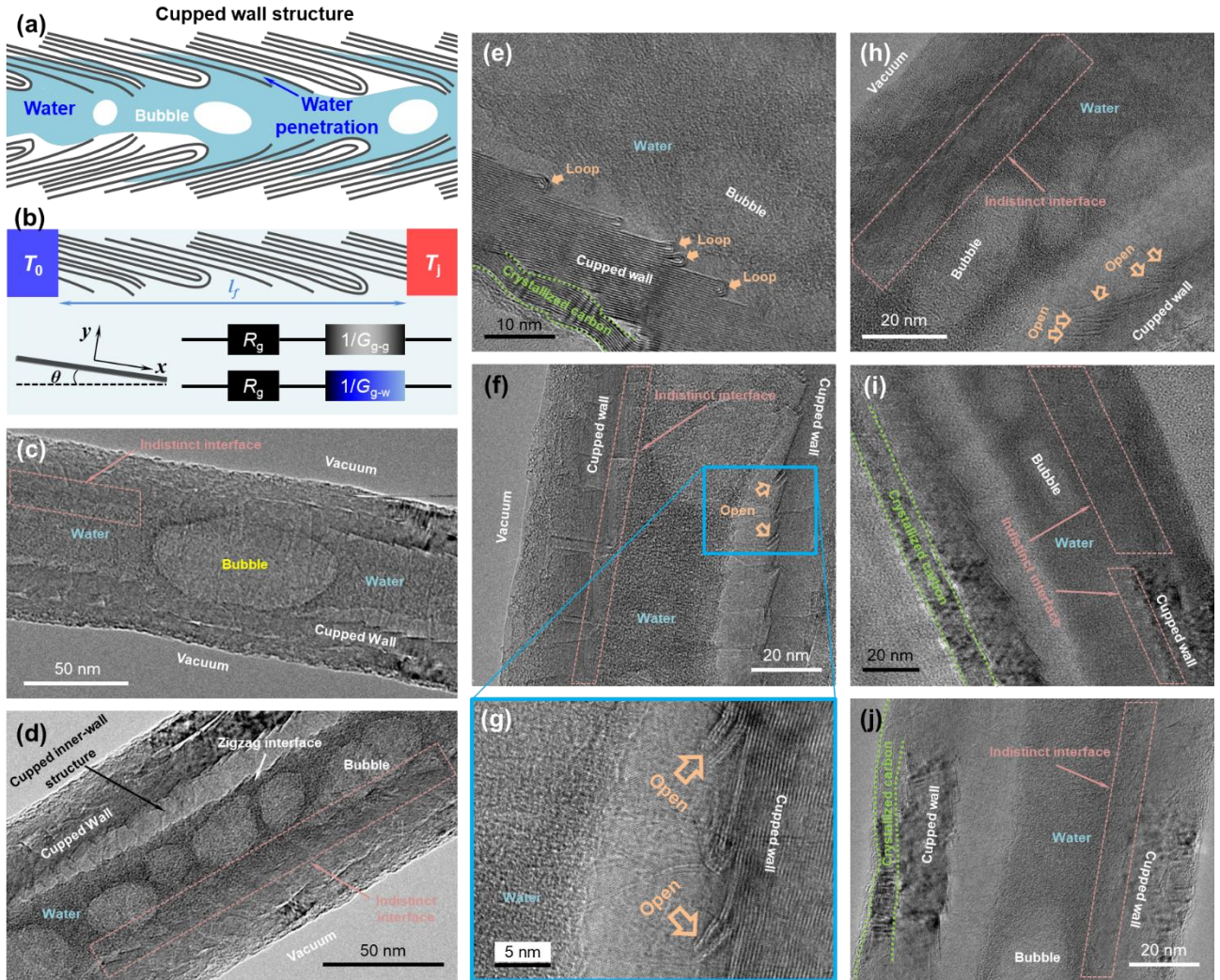


Figure 5.12 Mechanism of the enhanced thermal transport in the cup-stacked CNTs by water filling. (a) Schematic illustration of water covering the open and loop edges of the graphene cups and penetrating between the graphene cups. Part of the graphene cup-cup interfaces changes to graphene cup-water interfaces. (b) Thermal resistance circuit of the cup-stacked CNT without and with water filling. (c and d) TEM images of water-infused CNT#1. (e to g) TEM images of (e) loop edges and (f and g) open edges in water-infused CNTs. (h to j) TEM images of the indistinct interface on the side of the inner carbon wall that is overspread by water film in water-infused CNTs.

The reasons for this structure can be explained as follows. Since the images acquired by TEM are two-dimensional, the nonuniform distribution of the confined water may cause differences on the two sides. As shown in Fig. 5.13(a), the thickness of the water film at cross section A is relatively thick,

which may affect the imaging and cause an indistinct interface at the left side. At cross section B, the boundary of the confined water is visible. Besides, the interface between the confined water and the internal vacuum area is also clear. At cross section C, the lattice fringe of the carbon wall can be identified. Figure 5.13(b) is used for reference here. In addition, the bubbles tend to beget from the dissolved air in water under the high-vacuum environment. When the inner surfaces on both sides of the CNT have the equivalent interaction strength with the confined water, the confined water will eventually form an ultrathin water film lying on the inner surface of both sides of the CNT as shown in Fig. 5.14(a) or a suspended ultrathin water meniscus as shown in Fig. 5.14(b) [104]. However, due to the inhomogeneous structure and shape variation of the carbon wall and the nonuniform distribution of the confined water, the confined water may interact more strongly with one side of the inner surface of the CNT.

As a result, during the water-filling process, the water molecules can penetrate the space between the graphene cups [Fig. 5.12(a)] and break the weak cup-cup interlayer interactions. For reference, the initial interlayer cup–cup spacing and the diameter of a water molecule are comparable, about 0.34 nm and 0.27 nm respectively. It is also noted that the high vacuum condition outside the CNT can further promote water penetration. Part of the graphene cup-cup interfaces changes to graphene cup-water interfaces. As predicted by some MD simulations, the water penetration can facilitate thermal transport through enhanced interfacial thermal conductance (ITC) at the graphene cup-water interface, which further leads to a significant enhancement of the axial thermal conductivity of the cup-stacked CNT. Interestingly, for the conventional MWCNT, the contribution of water penetration to the axial thermal conductivity will be negligible.

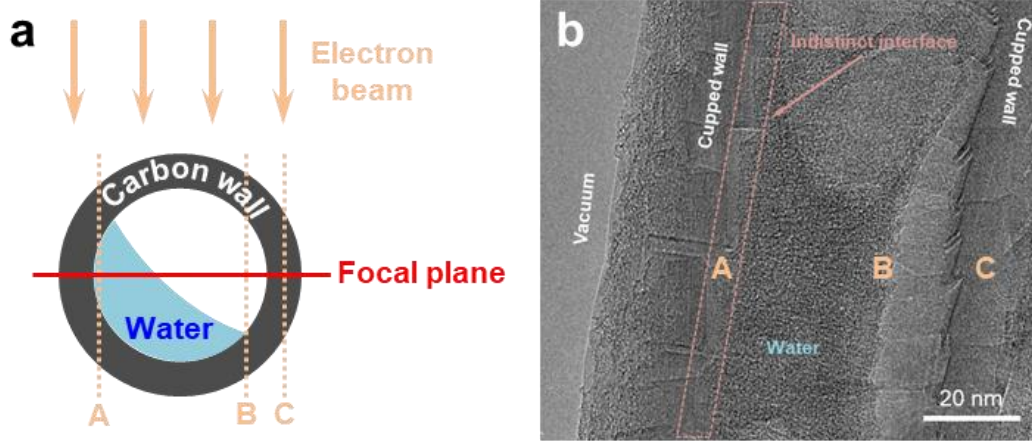


Figure 5.13 (a) Cross-sectional view of the non-uniform distribution of the confined water inside a CNT. (b) TEM image of a water-filled CNT for reference.

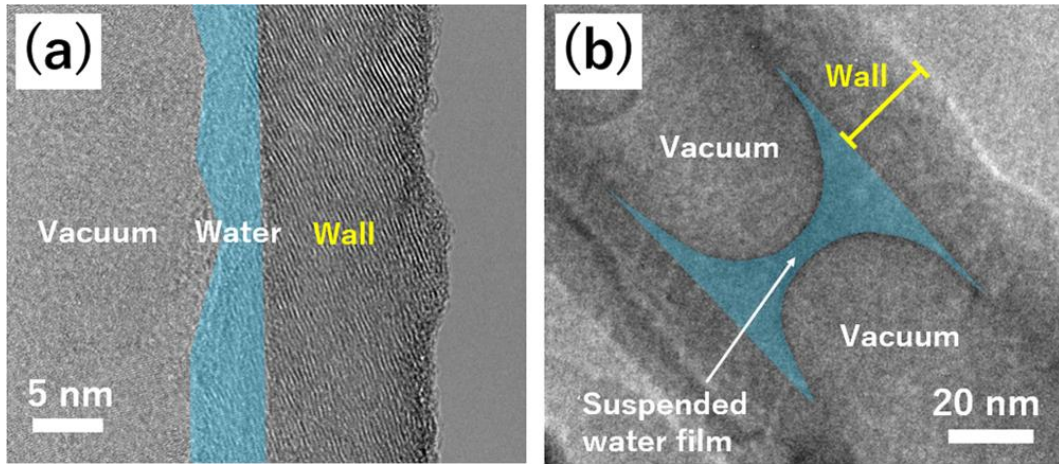


Figure 5.14 TEM micrographs of (a) an ultrathin water film lying on the surface of the CNT and (b) a suspended ultrathin water film. Thin water films are colored blue for better contrast [104].

To support our explanation, we carried out the additional TEM characterization of water-infused CNTs and dry CNTs to gain more structural details of the graphene cup. Moreover, the enhanced thermal conductivity was also quantitatively analyzed based on the reported MD work. From Fig. 5.15, it is corroborated that there is no confined water structure in the same batch of CNTs without water-filling treatment. As shown in Fig. 5.12(e to g) and Fig. 5.16(a), the graphene cup presents both open and loop edges, and water molecules can overspread and fill the open edges and have the possibility of further penetrating between the cups especially when the outside of CNT is the high vacuum. The prospective

strengthening of the water-carbon wall interaction can be corroborated by the indistinct interfaces [Fig. 5.12(f, h to j) and Fig. 5.16(b)]. Figure 5.16 (c) shows the protruding edges and open edges in a dry CNT. From Fig. 5.17, which is the overview of the water-filled CNT shown in Fig. 5.12(f and g), it is confirmed that the water always overlays one side of the inner wall with a substantial long total distance.

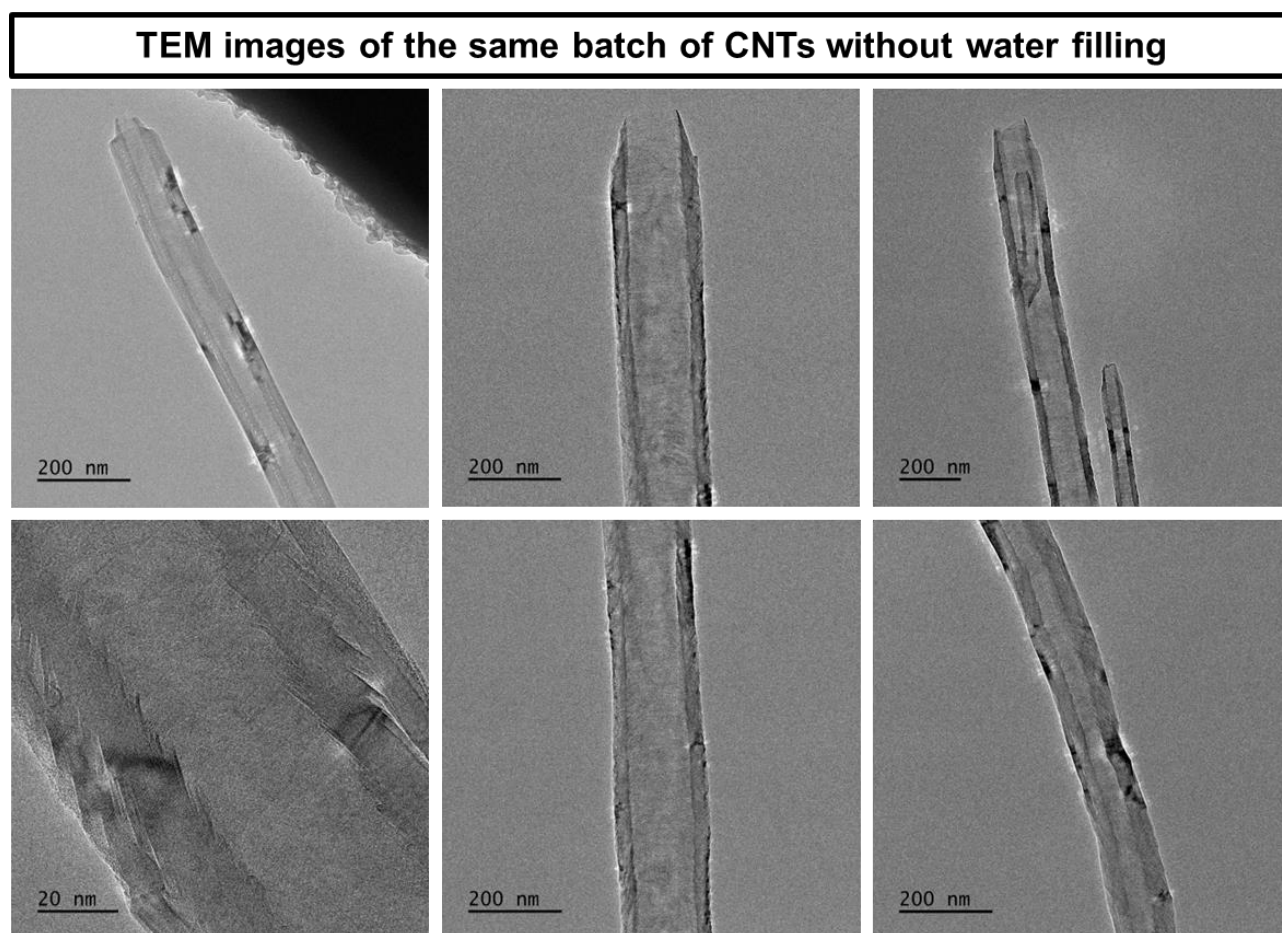


Figure 5.15 TEM images of the same batch of CNTs without water-filling treatment.

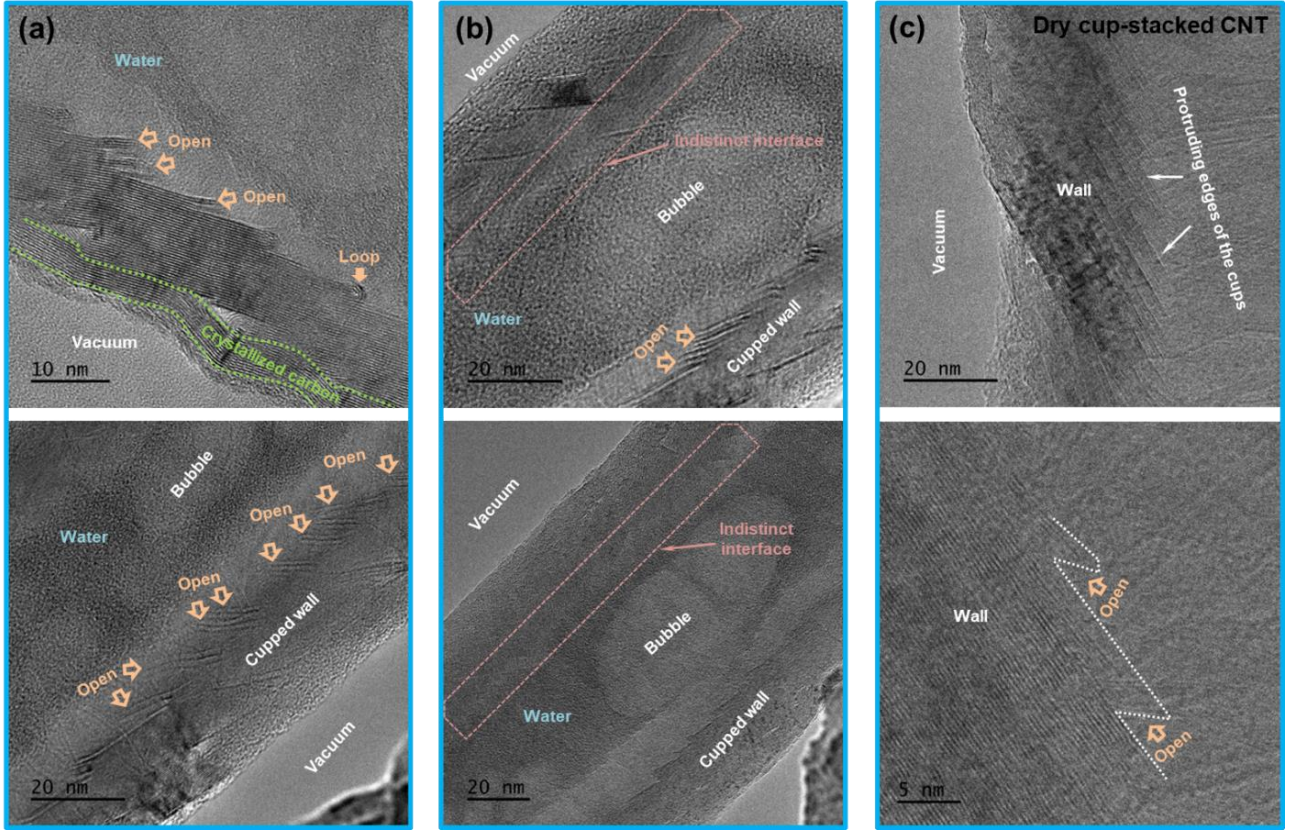


Figure 5.16 Additional TEM characterization of water-filled CNTs and dry CNTs. (a) The open and loop edges of the graphene cups in water-infused CNTs. (b) The indistinct interface on the water film-overspread inner wall in water-infused CNTs. (c) The protruding edges and open edges in a dry CNT.

For the quantitative analysis, using MD simulations, Maruyama *et al.* [158] estimated the ITC at SWCNT-SWCNT and SWCNT-confined water interfaces to be a value of $4.04 \text{ MW/m}^2\cdot\text{K}$ and $5.01 \text{ MW/m}^2\cdot\text{K}$ at 300 K respectively, manifesting there is an enhancement in ITC ascribable to the confined water. Han *et al.* [159] also demonstrated an equivalent ITC of $4.9 \text{ MW/m}^2\cdot\text{K}$ between two adjacent graphene layers (G_{g-g}). While for the SWCNT-surfactant-water interface, Huxtable *et al.* [160] derived a higher ITC from transient absorption measurements to be $12 \text{ MW/m}^2\cdot\text{K}$, which is consistent with $15 \text{ MW/m}^2\cdot\text{K}$ [161], $16.7 \text{ MW/m}^2\cdot\text{K}$ [162] and $18 \text{ MW/m}^2\cdot\text{K}$ [163] of single-layer graphene-water interface (G_{g-w}) investigated by the MD simulations. As shown in Fig. 5.12(b), since the angle between the cup surface and CNT longitudinal axis (θ) is evaluated as 9.59° [13], the thermal conductivity of the graphene cup along the CNT axis (λ_h) can be expressed as $\lambda_h = \lambda_x \cos^2 \theta + \lambda_y \sin^2 \theta$ where λ_x and λ_y are the

in-plane and cross-plane thermal conductivity of graphene respectively. Thus the thermal resistance of the graphene cup (R_g) is estimated as $1.72 \times 10^{-13} \text{ m}^2 \cdot \text{K/W}$ taking λ_x and λ_y as $2000 \text{ W/m} \cdot \text{K}$ and $1.5 \text{ W/m} \cdot \text{K}$ [164] respectively. It is found that it is five or six orders of magnitude smaller than the interfacial thermal resistance of the graphene cup-cup interface ($1/G_{g-g}=2.04 \times 10^{-7} \text{ m}^2 \cdot \text{K/W}$) and graphene cup-water interface ($1/G_{g-w}=5.55 \sim 6.66 \times 10^{-8} \text{ m}^2 \cdot \text{K/W}$), which demonstrates that the interfacial thermal resistance between graphene cups dominates the heat conduction in the cup-stacked CNT. The calculated ratio of $(R_g+1/G_{g-g})/(R_g+1/G_{g-w})$ is equivalent to the ratio of the thermal conductivity of water-infused CNT and dry cup-stacked CNT.

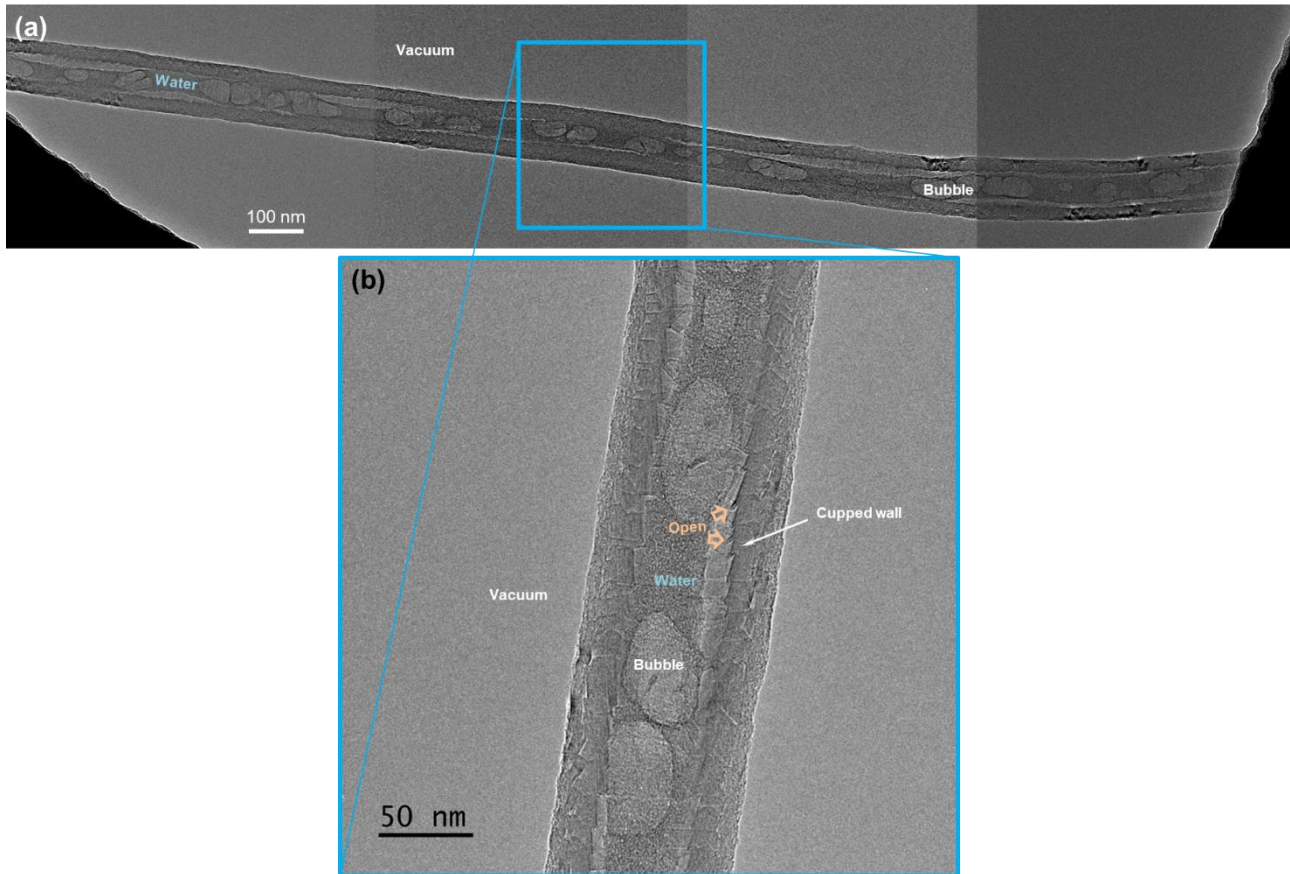


Figure 5.17 Overview TEM images of the water-filled CNT that is shown in Fig. 5.12(f and g). (a) TEM image showing that the water film always carpets one side of the inner wall of the water-filled CNT with a considerably long total distance, while another side presents a discernible water-gas interface. (b) Magnified image of the squared area in panel (a) to emphasize the open edges of the graphene cup.

Furthermore, it was reported that ITC at the graphene-water interface increases with the graphene layer owing to the more vibrational density of states overlapping at the interface, as a result, two-layer graphene could couple better with water and the ITC is heightened by around 150% compared with single-layer graphene [161]. It suggests that if the water is not sufficiently permeated between the graphene cups, just as shown in Fig. 5.12(a), the ITC at the graphene cup-water interface can be further improved. Besides, by utilizing the MD simulations, a variety of factors that can enhance the ITC have been also unveiled, such as the interlayer functionalization by oxygen atoms [161], the charge decoration [165], the graphene hydrophilization and cross-plane pressure [163] for the graphene-water interface, and the surfactant molecules [166] and the atoms adsorbed on a solid surface [167] for the solid-liquid interface. The *in situ* and real-time thermal characterization with a resolution of angstroms may help confirm this enhanced ITC. The details of the contribution of interaction between the carbon wall and confined water to thermal transport need further exploration.

It is also found that there are crystallized carbon layers on the outside of the graphene cup-stacked structure. Additional experiments will be conducted to eliminate its effect such as using the liquid-infused CNT sample without the outside crystallized carbon layers.

5.5 Summary

In this chapter, we successfully modulated the thermal transport in cup-stacked CNTs by liquid filling. We prepared CNTs infused with pure water and LiCl solutions and measured their thermal conductivities with our *in situ* STEM-in-SEM setup. The internal structures of three water-infused CNTs were also observed in real-time. We also measured the temperature dependence of thermal conductivity for a water-infused and a LiCl-solution-infused CNT. The liquid-infused cup-stacked CNTs exhibited higher thermal conductivity (60-360 W/m·K) than the dry samples (about 40 W/m·K). This thermal conductivity enhancement can be attributed to the strengthened interfacial coupling between graphene layers due to the penetration of water molecules or ions into the gaps between graphene cups. which is

supported by the molecular dynamics simulation results in the literature. We deem that this study is enlightening for tuning thermal transport in graphene-based nanocomposites.

6. Conclusions and future works

6.1 Conclusions

This dissertation presents our study of utilizing SEM for the measurements and modulation of thermal transport in 1D materials, summarized below.

Chapter 2 aims to extract the TCR at the sample-sensor junction in the nanoscale thermal conductivity measurement. In the developed method, the focused EB in SEM is used to heat the 1D sample locally, while the two metal lines simultaneously measure the heat fluxes induced by the EB heating. The *in situ* thermal resistance mapping along a single cup-stacked CNT was performed. Its thermal conductivity without the TCR error is extracted to be around 40 W/m·K and the TCR is evaluated as around one-tenth of the total thermal resistance. Moreover, this study demonstrates that higher resistance measurement accuracy is needed to detect the slight temperature fluctuation for the nanotube samples due to the relatively low EB energy absorption. This SEM-based *in situ* thermal measurement method can accelerate high-resolution nanomaterials characterization and the elucidation of nanoscale heat transfer.

Chapter 3 presents an experimental method to study the contact condition effects on the TCR at a single junction between the same two 1D material samples in SEM. The junction condition is dynamically and flexibly adjustable. Using this method, we measured the TCR between two MWCNTs with different contact conditions. The TCR results were studied in combination with the SEM-captured images of the contact morphology. It is also found that the TCR significantly increases when the contact passes through contamination, while the TCR results of the cross contact and aligned contact are equivalent in this study. This method is applicable to more diverse and complex contact conditions between 1D materials and benefits the understanding of thermal transfer during contact.

Chapter 4 focuses on the concurrent thermal conductivity measurement and internal structure

observation of individual 1D material using STEM-in-SEM. Using this method, we *in situ* measured the thermal conductivity of two cup-stacked CNTs and concurrently observed the internal non-uniform structures. We found that the sample with more structural disorders had a lower thermal conductivity. This method can find wide applications in the sample-by-sample elucidation of the structure-property correlation for 1D materials.

Chapter 5 reports the experimental study on the modulation of thermal transport in the cup-stacked CNT by liquid filling. We prepared CNTs infused with pure water and LiCl solutions and measured their thermal conductivities with our *in situ* STEM-in-SEM setup. The internal structures of three water-infused CNTs were also observed in real-time. We also measured the temperature dependence of thermal conductivity for a water-infused and a LiCl-solution-infused CNT. The liquid-infused cup-stacked CNTs exhibited higher thermal conductivity (60-360 W/m·K) than the dry samples (about 40 W/m·K). The enhancement is attributed to the strengthened interfacial coupling between graphene cups due to the penetration of water molecules or ions into the gaps between the graphene cups, which is further supported by the reported MD simulation studies. The results of this study are instructive for tuning thermal transport in graphene-based nanocomposites.

6.2 Future works

The future works are summarized as follows.

1. The results in Chapter 3 are going to be analyzed in detail to establish a deeper understanding of thermal transfer during contact and the contact condition effects on the TCR.
2. The method developed in Chapter 3 can be combined with the simultaneous measurement of the electrical transport through the contact between the 1D materials. Besides, this method can also be used to study the effect of the interlayer on the TCR.
3. The CNTs filled with other kinds of liquid have been fabricated and characterized, and their thermal conductivity measurements will be conducted.

4. The effect of the outside crystallized carbon layers on the thermal conductivity of the liquid-infused CNT needs to be eliminated by measuring the sample without the outside crystallized carbon layers.

List of Publications

Journal Articles

1. **D. Li**, Q. Y. Li, K. Takahashi, Thermal resistance mapping along a single cup-stacked carbon nanotube with focused electron beam heating, *International Journal of Heat and Mass Transfer*, 198, 123418 (2022). (Chapter 2 of PhD dissertation)
2. **D. Li**, Q. Y. Li, T. Ikuta, K. Takahashi, Concurrent thermal conductivity measurement and internal structure observation of individual one-dimensional materials using scanning transmission electron microscopy. *Applied Physics Letters*, 120, 043104 (2022). (Chapter 4 of PhD dissertation)
3. R. Abe, Y. Sekimoto, S. Saini, K. Miyazaki, Q. Y. Li, **D. Li**, K. Takahashi, T. Yagi, M. Nakamura, Round robin study on the thermal conductivity/diffusivity of a gold wire with a diameter of 30 μm tested via five measurement methods, *Journal of Thermal Science*, 31, 1037 (2022).
4. T. Miao, M. Xiang, **D. Li**, X. Wang, Electrical and thermal transport properties of high crystalline PdTe_2 nanoribbons under a strong magnetic field, *Nanoscale*, 14, 10101 (2022).
5. J. Zheng, T. Miao, R. Xu, X. Ping, Y. Wu, Z. Lu, Z. Zhang, D. Hu, L. Liu, Q. Zhang, **D. Li**, Z. Cheng, W. Ma, L. Xie, L. Jiao, Chemical synthesis and integration of highly conductive PdTe_2 with low-dimensional semiconductors for p-type transistors with low contact barriers. *Advanced Materials*, 33 (27), 2101150 (2021).
6. T. Miao, M. Xiang, **D. Li**, Electrical and thermal transport properties of PdTe_2 nanofilm. *Journal of Engineering Thermophysics*, 41, 3041 (2020). In Chinese.
7. T. Miao, **D. Li** (Student First Author), X. Wang, W. Ma, X. Zhang, Ultraweak influence of strong magnetic field on electrical and thermal transport properties of a polycrystalline gold nanoribbon. *Physical Review B*, 100, 235402 (2019).
8. T. Miao, D. Yu, L. Xing, **D. Li**, L. Jiao, W. Ma, X. Zhang, Current rectification in a structure: ReSe_2/Au contacts on both sides of ReSe_2 . *Nanoscale Research Letters*, 14, (2019).
9. T. Miao, **D. Li** (Student First Author), S. Shi, Z. Ji, W. Ma, X. Zhang, Q. Zhong, X. Wang, Essential role of enhanced surface electron-phonon interactions on the electrical transport of suspended polycrystalline gold nanofilms. *RSC Advances*, 8, 20679 (2018).

Conference Presentations

1. **D. Li**, Q.Y. Li, K. Takahashi, *In situ* adjusting thermal contact resistance between individual carbon

- nanotubes in a scanning electron microscope, 第 43 回日本熱物性シンポジウム, 和歌山県和歌山市, Online, October 25-27, 2022 (Oral). (Chapter 3 of PhD dissertation)
2. **D. Li**, Q.Y. Li, T. Ikuta, K. Takahashi, High-resolution thermal conductivity mapping for one-dimensional materials with concurrent internal structure observation, 第 59 回日本伝熱シンポジウム, 岐阜県岐阜市, May 18-20, 2022 (Poster). (Chapter 2 and Chapter 4 of PhD dissertation)
 3. **D. Li**, Q.Y. Li, T. Ikuta, K. Takahashi, *In-situ* and real-time thermal characterization of individual water-filled nanotubes inside a scanning transmission electron microscope, 21st Symposium on Thermophysical Properties, Boulder, Colorado, USA, Online, June 20–25, 2021 (Oral). (Chapter 5 of PhD dissertation)
 4. **D. Li**, Q.Y. Li, T. Ikuta, K. Takahashi, Modulation of thermal transport in individual carbon nanotubes by water filling, 2nd Asian Conference on Thermal Sciences, Fukuoka, Japan, Online, October 3–7, 2021 (Oral). (Chapter 5 of PhD dissertation)
 5. **D. Li**, Q.Y. Li, T. Ikuta, K. Takahashi, *In-situ* thermal characterization and real-time internal structure observation of individual water-filled carbon nanotubes, 第 58 回日本伝熱シンポジウム, Online, May 25-27, 2021 (Oral). (Chapter 5 of PhD dissertation)
 6. T. Miao, **D. Li**, Ultrasmall influence of strong magnetic field on the electrical and thermal transport properties of polycrystalline gold nanoribbon, 7th International Symposium on Micro and Nano Technology, Qingdao, China, April 26-28, 2019 (Poster).

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