Proceedings of the 17th International Heat Transfer Conference, IHTC-17
14 – 18 August 2023, Cape Town, South Africa

IHTC-17 | ID: XXXX

# NANOSCALE THERMAL MEASUREMENTS -- NEW CHALLENGES AND NEW OPPORTUNITIES

**Xing Zhang**

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Engineering Mechanics, Tsinghua University, Beijing, 100084, China

## ABSTRACT

Since the end of the 18th century, when Benjamin Thompson Rumford and Humphry Davy proved the kinetic theory of heat through experiments, measurements have become important approaches in thermal science research, especially for new phenomena, new concepts, and new technical challenges. More than 200 years has passed with many significant scientific and technological developments and with core engineering problems undergoing a remarkable transformation of scale, nanoscale measurements have become a new challenge in heat transfer research. This Fourier lecture will briefly review the development of nanoscale thermal measurement techniques and use the speaker's research experience to describe in detail several representative nanoscale thermal measurement methods. Among the contact measurement methods, the T-type method provided accurate measurements of the thermal conductivity of an individual multi-walled carbon nanotube, eliminating the influences of thermal contact resistance and thermal radiation for the first time. After more than 20 years of development, the integrated T-type method now provides simultaneous measurements of nine different physical parameters. The H-type method has successfully been applied to the study of thermal rectification of asymmetric monolayer graphene and $MoSe_2$-$WSe_2$ lateral heterostructures, breaking records for thermal rectification of nanomaterials and making history. For non-contact measurement methods, the dual-wavelength flash Raman (DFR) method provides high temporal and spatial resolution while eliminating the effect of the laser absorption coefficient which greatly improves the measurement accuracy. This method can be used to measure the properties of bulk materials, suspended and supported 1D and 2D nanomaterials and 2D anisotropic nanomaterials. The speaker further improved and successfully applied the DFR method to power devices, all-solid-state lithium batteries, and life science materials with more promising prospects. This lecture shows that nanoscale thermal measurements are not only a challenging heat transfer field but also an opportunity for heat transfer researchers to extend their research across many other disciplines. Groundbreaking work in these fields is expected to rapidly expand and lead to many new and exciting developments.

**KEY WORDS:** Thermal measurement, Nanoscale, T-type method, H-type method, Dual-wavelength flash Raman method

## 1. INTRODUCTION

The development history of thermal research can be traced back to ancient Greece where philosophers attempted to define the concept of heat which became the embryonic form of Caloric Theory. A more

*Corresponding Author: x-zhang@tsinghua.edu.cn

scientific understanding of heat developed from the beginning of the 17th century when Francis Bacon concluded from phenomena such as heat generated by friction that heat is an expanding, bounded motion acting on small particles. Hooke, who observed sparks with a microscope, believed that heat 'is not something else, but a very active and violent movement of the parts of an object'. This led to observations and experiments becoming the starting point of scientific thermal theory. Since the end of the 18th century, when Benjamin Thompson Rumford and Humphry Davy proved Kinetic Theory through quantitative measurements, measurements have also become important approaches in thermal science research, especially for new phenomena, new concepts, and new technical challenges. Experimental measurements can be reliable evidence for existing theories and can also lead to new conjectures. In fact, Baron Jean Baptiste Joseph Fourier studied many experimental results and in 1822 published his Thermal Theory Analysis which included the famous Fourier's law, which still guides heat transfer research today.

More than 200 years has passed with many significant scientific and technological developments and with many core engineering problems undergoing a remarkable transformation of scale. Nanotechnology, as an emerging area, has started a new revolution with the fabrication, measurement, and manipulation of materials on nanometer scales. This has led to great challenges for thermal science research, especially for the classic Fourier's law. Due to their size and surface effects, the thermal conductivities of nanomaterials differ significantly from the bulk values. Although the heat flux is still proportional to the temperature gradient, the thermal conductivity is no longer a constant, but a variable related to the length, width, and even the substrate which requires nanoscale measurements. However, due to the ultra-small scale of these nanomaterials, classical experimental measurement methods are no longer applicable, which has led to the challenge to develop nanoscale thermal measurement techniques.

To meet this challenge, researchers have done much work in the field of nanoscale thermal measurements. To compare the nanoscale measurement results with bulk material properties and to reveal the nanoscale mechanism, researchers still use the thermal conductivity concept, but with the thermal conductivity being a function of the size and other key parameters. Fourier's law now has new vitality for nanoscale materials. This Fourier lecture briefly reviews the development of nanoscale thermal measurement techniques and uses the speaker's research experience to describe several representative nanoscale thermal measurement methods in detail. Meanwhile, the microelectronics, battery and life science fields all urgently require the support of nanoscale measurement techniques to enhance their detection and analysis capabilities, which has led to great opportunities for heat transfer researchers. Therefore, this study also presents extended applications of nanoscale measurement techniques for temperature and stress detection in chips, interface characterization of all-solid-state lithium batteries, and life sciences studies. This lecture seeks to inspire and motivate researchers to deepen their exploration of heat transfer mechanisms and to further broaden their research areas to achieve influential and exciting research results.

## 2. CONTACT THERMAL MEASUREMENT METHOD

In 1991, Dr. Iijima discovered the existence of carbon nanotubes under an electron microscope and described their unique nanostructures[1]. In the following decade, researchers successfully characterized the extraordinary electrical, electrochemical and mechanical properties of carbon nanotubes. However, due to the great difficulty and complexity of thermal measurements of carbon nanotubes, the existing classic contact measurement methods, such as the hot wire method[2] and the 3ω method[3], were not really adequate for these measurements, so there was an urgent need to develop new measurement methods. For this reason, around the turn of the century, new nanoscale thermal measurement techniques were successively developed, such as the microfabricated suspended device method, T-type method and H-type method, laying the foundation for modern contact thermal measurement methods.

## 2.1 Microfabricated suspended device method

In 2001, Majumdar's group developed the microfabricated suspended device method for measuring the thermal conductivity of multi-walled carbon nanotubes (MWCNTs)[4]. Figure 1(a) and 1(b) show scanning electron microscope (SEM) images of the suspended microdevices and the measurement results for different diameter MWCNTs. Two islands are suspended by slender cantilevers with one being a heating island and the other a probing island. During the measurements, the sample bridges between the two islands to form a heat transfer channel. When a bias voltage is applied to the heating island, the generated Joule heat is transferred through the sample to the probing island, resulting in resistance and temperature changes. The sample thermal resistance is obtained from the heating power and the temperatures of the two islands at equilibrium which is then used to calculate the sample thermal conductivity. The results showed that the thermal conductivity of 14 nm diameter MWCNTs exceeded 3000 W/m·K.

The heat transfer model for the microfabricated suspended device method is simple with convenient data processing. In addition, this method is not limited by the sample electrical conductivity; thus, this method has a wide range of applications. The microfabricated suspended device method has been applied to thermal conductivity measurements of a variety of nanowires[5] and nanofilms[6, 7] and can be further used to study thermal rectification in nanomaterials[8, 9]. However, the large surface area of the islands makes the thermal radiation effect non-negligible and the measurement uncertainty due to background radiation and ambient radiation can reach 100%[10]. In addition, the complex suspended microdevice structures require very sophisticated nanofabrication techniques. A better solution would involve a simplified device structure with smaller islands.

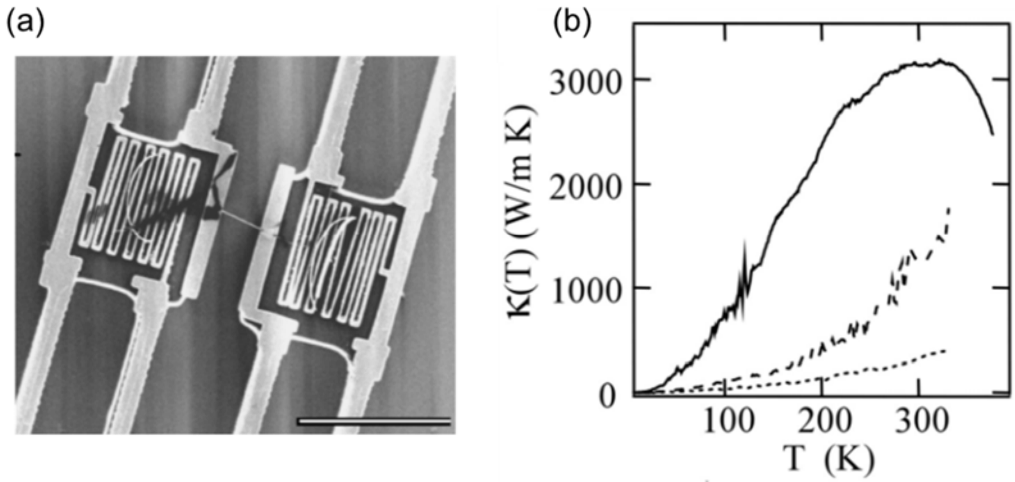


**Fig. 1.** Microfabricated suspended measurement device and results. (a) SEM images of the suspended islands with the MWCNTs. (b) Thermal conductivity of the MWCNTs with solid line, broken line and dotted line representing MWCNTs with diameters of 14 nm, 80 nm and 200 nm, respectively.

## 2.2 T-type method

The T-type method for micro/nanowires was developed by the speaker in 1998[11]. In late 1999, this method was successfully used to measure the thermal conductivity of carbon fibers which showed a quantitative relationship between the thermal and the electrical conductivity of carbon fibers, which is still a significant result for current research[12]. In 2005, the speaker measured the thermal conductivity of an individual multi-walled carbon nanotube using the T-type method. The sample is successfully bonding with a nano hot wire through nanomanipulation, eliminating the thermal contact resistance influence in carbon nanotube measurement for the first time and obtaining an accurate result. The effect of the definition of the cross-sectional area of carbon nanotubes on the thermal conductivity measurement results was also analyzed[13]. In the T-type method, the sample thermal conductivity is obtained from the temperature rise of a hot nanowire before and after bridging the measured sample. The T-type method is simpler and easier to fabricate than the microfabricated suspended device method. In addition, since the thermal conductivity is obtained from the difference between the two measurements, the radiative heat loss from the hot nanowire is eliminated and does not affect the final measurement.

In the past 20 years, the speaker's research group has further improved the T-type method and developed the variable-length T-type method[14], 3ω T-type method[15] and AC heating-DC probing T-type method[16-18] (Fig. 2). Thus, the T-type method has been widely used to measure the thermal and electrical properties of micro/nanowires and to discover many interesting physical phenomena, such as the metal-insulator transition in $Bi_2S_3$ nanowires[18] and the greatly enhanced power factor in bromine-doped graphene fibers[19]. These methods have been integrated into an automated measurement system for the integrated T-type method. The system is capable of simultaneous measurements of the electrical conductivity, temperature coefficient of resistance, thermal conductivity, thermal diffusivity, specific heat, heat absorption coefficient, Seebeck coefficient and *ZT* value for a total of eight different physical properties parameters, along with simultaneous measurement of the thermal contact resistance between the hot wire and the sample.

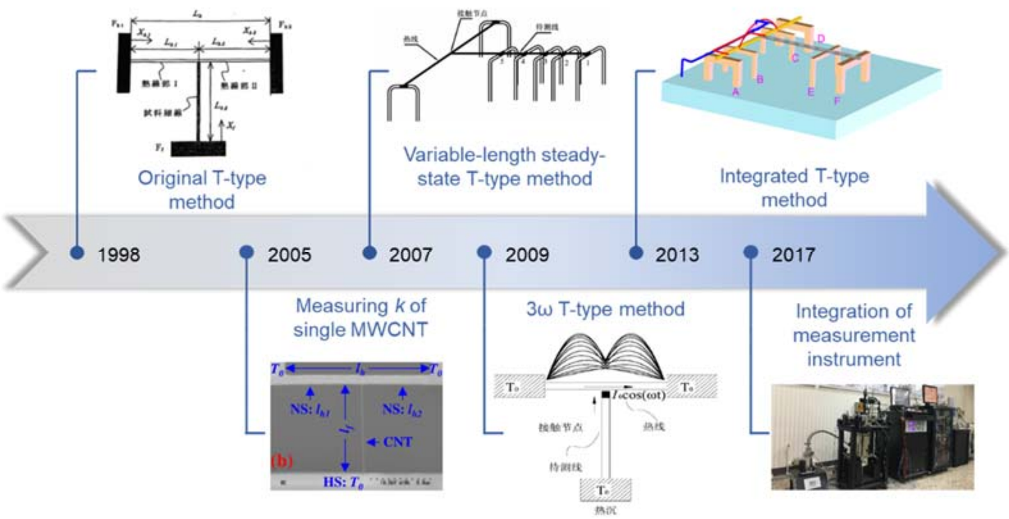


**Fig. 2.** Development of the T-type method

## 2.3 H-type method

Since the T-method has only one hot wire, this method is not suitable for changing the heat flow direction to study the thermal rectification of nanomaterials. To solve this problem, the H-type method[20] was developed in the same year as the T-type method, 1998. The H-type method replaces the heat sink in the T-type method with another hot wire. independent heating of the two hot wires allows changing the heat flow direction through the sample. However, nanofabrication limitations limited development of this method. Today, advanced nanofabrication methods and more powerful numerical computations have made the H-type method more useful. The H-type sensor is fabricated directly on the $Si/SiO_2$ substrate without any additional transfer process which allows for precise positioning of the sample. In addition, finite element heat transfer analyses allow modelling of arbitrarily complex H-type device structures. As a result, in recent years, the speaker's research group has used the H-type method to achieve significant breakthroughs in studies of thermal rectification of nanomaterials [21, 22].

In 2017, the speaker's group used the H-type method to experimentally study the thermal rectification effect in suspended monolayer graphene[21]. They found a thermal rectification factor of 10% in a pristine monolayer graphene with nanoparticles deposited on one side or with a tapered width due to the asymmetric phonon scattering varying with the heat flux direction (Fig. 3(a)). Furthermore, a large thermal rectification factor of 26% was achieved in a defect-engineered monolayer graphene with nanopores on one side caused by the inseparable dependence of the thermal conductivity on the temperature and space. The thermal rectification ratio of 26% was the highest measured value for phonon-dominated thermal rectification at that time. Recently, the speaker's group further focused on thermal rectification in monolayer lateral $MoSe_2$-$WSe_2$ heterostructures[22]. They fabricated a monolayer $MoSe_2$-$WSe_2$ heterostructure H-type device that possessed simultaneous thermal rectification and electrical rectification characteristics. A high ON/OFF ratio of up to $10^4$ and thermal rectification factors as high as 96% were simultaneously measured when the interface between the heterostructures was perpendicular to the heat or current flow direction (Fig. 3(b)). The combination of the mismatch of the phonon spectra overlap in the two directions and the interface morphology induced phonon localization together resulted in a high thermal rectification ratio of 96% in monolayer $MoSe_2$-$WSe_2$ heterostructures. The high thermal rectification ratio of 96% again broke the previous record in semiconductor nanomaterials. Owing to the simultaneous thermal and electrical rectification effect, the monolayer lateral heterostructure rectifier greatly enhanced the heat dissipation. The hot spot temperature rise in this material can decrease by 20% without other external cooling methods. This work presents a new pathway for designing novel nanoelectronic devices with enhanced thermal dissipation and was published in Science in 2022.

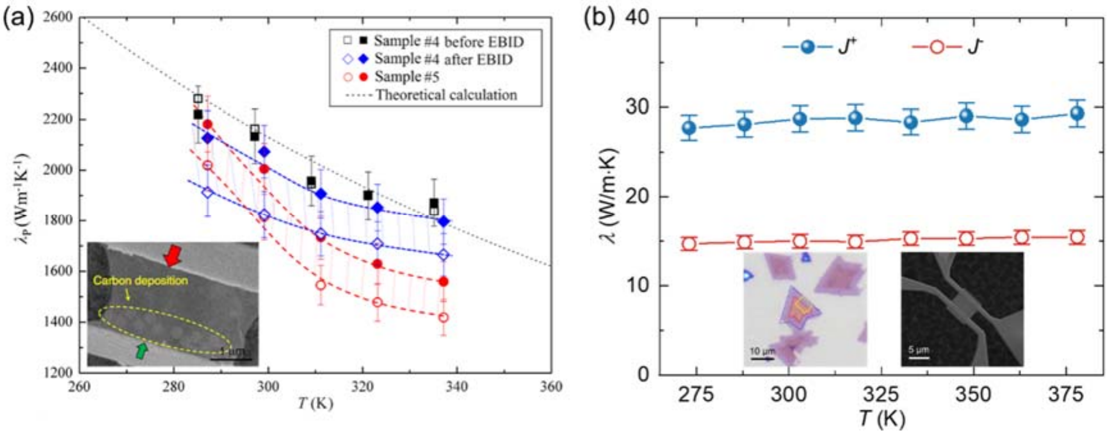


**Fig. 3.** Application of the H-type method for studying the thermal rectification effect. (a) Suspended monolayer graphene with nanoparticles deposited on one side. (b) Monolayer $MoSe_2$-$WSe_2$ lateral heterostructure.

## 3. NON-CONTACT THERMAL MEASUREMENT METHOD

Contact thermal measurement methods are mainly based on electrical resistance based temperature measurements, which give accurate temperature measurements. However, these contact thermal measurement methods require complex electrode preparation or sample transfers, which makes the measurement process very tedious and inevitably damages the sample. Therefore, non-contact thermal measurement methods have become more popular in recent years due to their in-situ, non-destructive natures with no need for additional sample processing. The most representative methods are the transient thermoreflectance method and the Raman spectroscopy method.

### 3.1 Transient thermoreflectance method

Thermoreflectance techniques were first developed in the 1970s with continuous wave light sources used for heating and sensing[23]. As pico- and femtosecond pulsed lasers were developed, Paddock and Eesley first used picosecond transient thermoreflectance to measure the thermal diffusivity of metal films in the 1980s using the prototype of what became the time-domain thermal reflectance (TDTR) method, also as known as the 'pump-probe' technique[24, 25]. The TDTR method measures the thermoreflectance response as a function of the delay time between the arrival of the pump and probe pulses on the sample surface, where the pump beam deposits a periodic heat flux on the sample surface and the probe beam detects the corresponding temperature change through the reflectance change (Fig. 4). Many scientists have made outstanding contributions to developing TDTR. Several advanced TDTR variations have been developed, such as the frequency-domain thermoreflectance (FDTR) method[26], the time-resolved magneto-optic Kerr effect (TR-MOKE) method[27] and the Asynchronous optical sampling (ASOPS) method[28], which are less expensive with increased measurement sensitivity and data acquisition efficiency. Furthermore, in addition to the frequent practice of measuring the through-plane thermal conductivity and the interface thermal conductance, advanced TDTR configurations have also been developed by varying the modulation frequency, laser spot size and shape, and laser beam position. The combination of different configurations allows TDTR to measure a wide range of thermal property parameters (e.g., specific heat and anisotropic thermal conductivity) and to be used with various sample conditions (e.g., liquids and rough coatings). The sub-picosecond time resolution provided by ultrafast pulsed lasers has enabled the use of TDTR to study of heat carrier dynamics, such as phonon mean free paths and electron-phonon coupling[29-31].

TDTR requires a smooth surface to detect the reflectivity variations used to determine the temperature changes with previous systems coating the sample surface with metal as a sensor. In practical measurements, the metal sensor thickness was always greater than 10 nm, which significantly limited the measurement sensitivity of the thermoreflectance method for ultrathin nanofilms with only several atomic layers. However, our group has used advanced nanofabrication methods to make a new monolayer graphene/copper structure. Copper is no longer a coating film, but is the substrate of the monolayer graphene, so the reflectivity variation influenced by graphene can be analyzed. This design was used to measure the ultrafast carrier dynamics between the monolayer graphene and the copper[32] and can be further used with the transient thermoreflectance method to study ultrathin nanofilms.

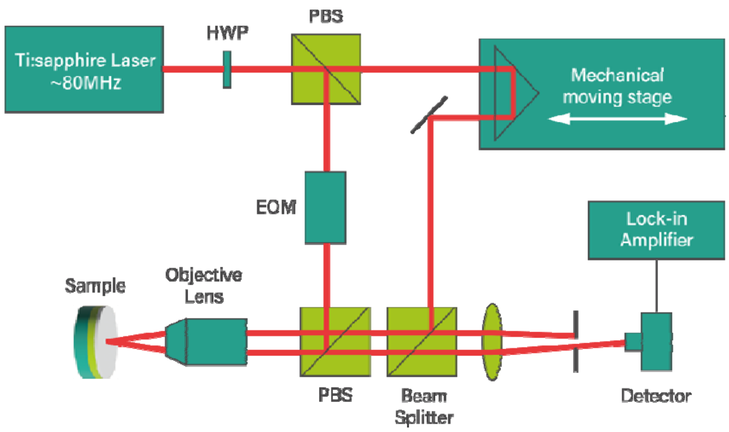


**Fig. 4.** Measurement principle and optical path diagram for the TDTR method.

### 3.2 Raman spectroscopy method

In 2005, the successful micromechanical cleavage of monolayer graphene shattered the misconception that monolayer graphene does not exist in a free state and sparked a research frenzy among scholars in various fields[33]. However, due to the measurement requirement of a high surface reflectance or a sensor coating, the TDTR method was found to be not applicable to ultra-thin graphene, especially for suspended graphene, so there was an urgent need to develop a new measurement method. This challenge led to the development of the Raman spectroscopy method. In 2008, Balandin et al.[34] first employed Raman spectroscopy to measure the thermal conductivity of suspended monolayer graphene (Fig. 5). Since then, the steady-state Raman method has been widely applied to nanoscale thermal measurements. This method uses the Raman peak shift or the Raman intensity ratio as the temperature indicator. A laser is used to heat the sample to steady-state with the thermal conductivity then directly obtained from the relationship between laser power and sample temperature rise. This simple, convenient steady-state Raman method has been used to characterize various kinds of two-dimensional (2D) materials to study the temperature, substrate, thickness and in-plane anisotropic effects[35-37]. However, the thermal conductivity measurement uncertainty by the steady-state Raman method is still unsatisfactory due to the difficulty in accurately determining the nanomaterial laser absorptivity.

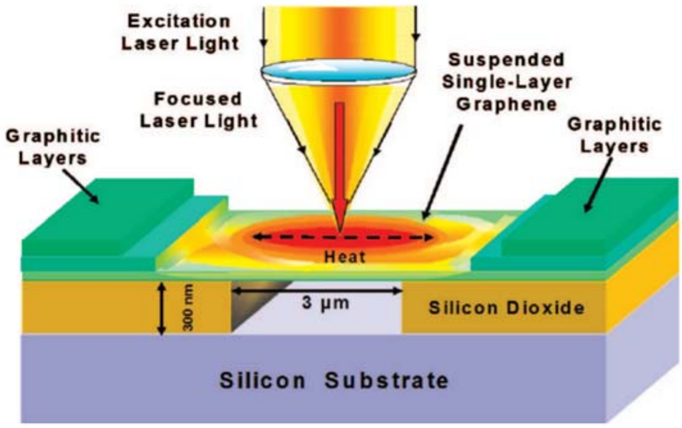


**Fig. 5.** Schematic of the steady-state Raman method for measuring the thermal conductivity of graphene.

The best approach for reducing the Raman spectroscopy measurement uncertainty is to eliminate the influence of the laser absorption coefficient. Therefore, transient Raman methods have been rapidly developed. The most common examples are the flash Raman method and the dual-wavelength flash Raman method (DFT method) developed by the speaker's group and the time-domain Raman (TD-Raman) method and the frequency-domain Raman (FD-Raman) method developed by Xinwei Wang's group.

The flash Raman method was first used to measure the thermal diffusivity of single graphene fibers and multi-walled carbon nanotubes[38-41]. In this method, a continuous laser beam is modulated into a pulsed laser beam that heats the sample to produce periodic heating and cooling. Since the pulse width is very short and the sample is far from steady state, the average sample temperature rise during the heating stage increases as the pulse width is gradually increased, so the sample thermal diffusivity is obtained from the relationship between the average temperature rise and the pulse width. In the flash Raman method, normalization of the temperature rise eliminates the effect of the laser absorption coefficient which greatly improves the measurement accuracy compared to the steady-state Raman method. However, the minimum pulse width of the flash Raman method is limited by the rising edge of the signal generator, which is usually longer than 20 ns which limits measurements of nanomaterials with high thermal diffusivities. The temporal resolution was further improved by developing the DFR method[42-49]. The measurement principle is shown in Fig. 6, where one pulsed laser beam is used to heat the sample and the other pulsed laser beam is used to detect the transient temperature variations. With the two pulses, complete temperature rise and fall curves were measured by varying the time interval between the two pulses with a temporal resolution of 100 ps. Furthermore, the relative positions of the two laser beams incident on the sample were precisely controlled by a 2D scanning galvanometer with a spatial resolution of 50 nm. A phase processing method was developed to analyse the spatial temperature information to further improve the measurement accuracy. The DFR method has been successfully applied to measure the thermophysical properties of suspended and supported nanoparticles, one-dimensional (1D) nanomaterials and 2D isotropic and 2D anisotropic nanomaterials with measurement uncertainties within ±5%.

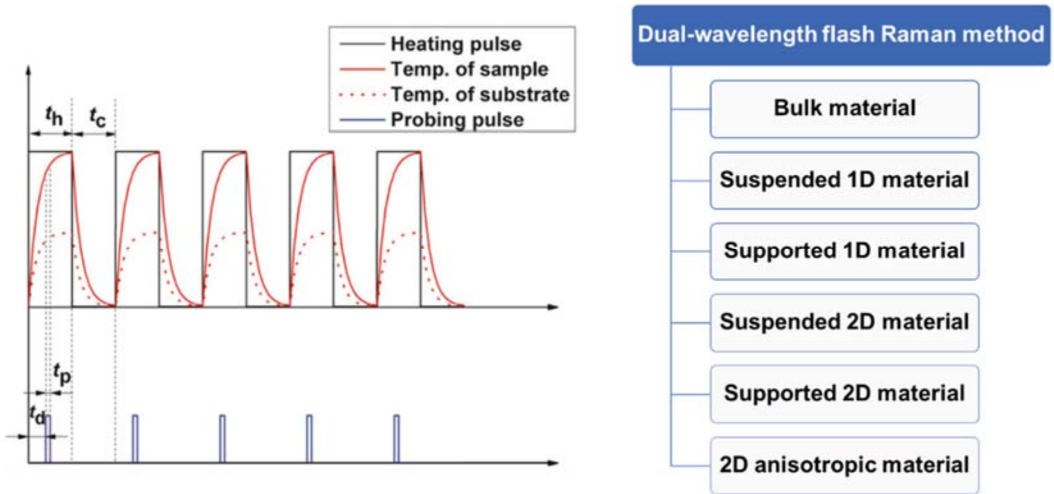


**Fig. 6.** Dual-wavelength flash Raman method measurement principle and applications

The TD-Raman method was developed by Wang's group during the same period[50]. This measurement principle is similar to that of the flash Raman method and measurement results of cantilevered silicon probes show that the measurement uncertainty of this method is <±10%. However, the long pulse interval due to the need to ensure that the sample can cool sufficiently after pulse heating makes the method more time consuming than the steady-state Raman method, especially with small pulse widths. To solve this problem, Wang's group further developed the FD-Raman method to use the same pulse width and pulse interval[51]. The sample reaches a quasi-steady state with high pulse frequencies and the average sample temperature rise is half of the steady state temperature rise. Although the FD-Raman method measurement sensitivity is relatively low, the measurement efficiency is substantially improved. Wang's group then combined the continuous wave Raman method with the picosecond Raman method to develop the energy transport state resolved Raman method (ET-Raman) to characterize photon, electron and phonon interactions[52].

## 4. MULTIDISCIPLINARY CROSSOVER PROJECTS

In recent years, multidisciplinary research has become more and more important for further science and technology development, which has provided new opportunities for the traditional thermal sciences. Thermal measurements, as an applied branch of the heat transfer field, are based on universal measurement principles, so they can be applied in other micro and nano fields. Raman spectroscopy provides a fingerprint spectrum of the specimen that reflects the essential lattice vibration information. Therefore, the variations of the peak position, peak intensity and full width at half maximum of the Raman peaks in Raman spectroscopy not only reflect changes in the temperature, but can also be used for stress measurements, carrier concentration measurements, material component identification and even structural analyses. Thus, the DFR method has been further developed by the speaker's group to measure and optimize the temperature and stress distributions in electronic devices, to detect the interfacial characteristics of all-solid-state lithium batteries, and even in life science research. Here, the speaker will share some of these promising applications.

### 4.1 Opto-electric flash Raman method for temperature measurements in power devices

Power devices are widely used in many fields including energy conversion, electronic manufacturing, information systems and communication systems. The miniaturization of highly integrated electronic products affects the heat dissipation and increases the heat fluxes. High temperatures and heat fluxes can result in current leakage, acceleration of doping element diffusion, and significantly shortening of the device life. Therefore, accurate in-situ measurements and accurate temperature control to maintain operational reliability has emerged as the primary concern for the ongoing development of power devices. The speaker's group developed an in-situ, high temporal resolution opto-electric flash Raman method to accurately measure the temperature fluctuations of power devices caused by modulated driving voltages (Fig. 7)[53]. Synchronous modulation enabled the pulsed laser to maintain the same frequency as the driving voltage of the power device so that the device working temperature during the laser pulse could be determine from the excited Raman spectrum. The time delay between the pulsed laser and the electric signal was then varied with 100 ps resolution to accurately determine the temperature variations throughout the entire cycle. This method was successfully used to measure the temperature changes of GaN high electron mobility transistor devices with a square wave driving signal with various frequencies. The experimental results show that, with the 100 Hz amplitude modulation mode, the maximum temperature change through each driving cycle was more than 20 K. This illustrates the significance of high temporal resolution measurements in determining the peak temperatures of hot spots in power devices. In addition, two samples mounted in different ways had very different transient temperature fluctuations for the same driving frequency, which shows that transient temperature variation measurements are a promising way to gauge how well a device dissipates heat. The temperature variations caused by a complex driving signal were also determined. This transient opto-electric flash Raman method is promising method for measuring in situ temperature fluctuations in various kinds of power devices to evaluate and optimize device designs.

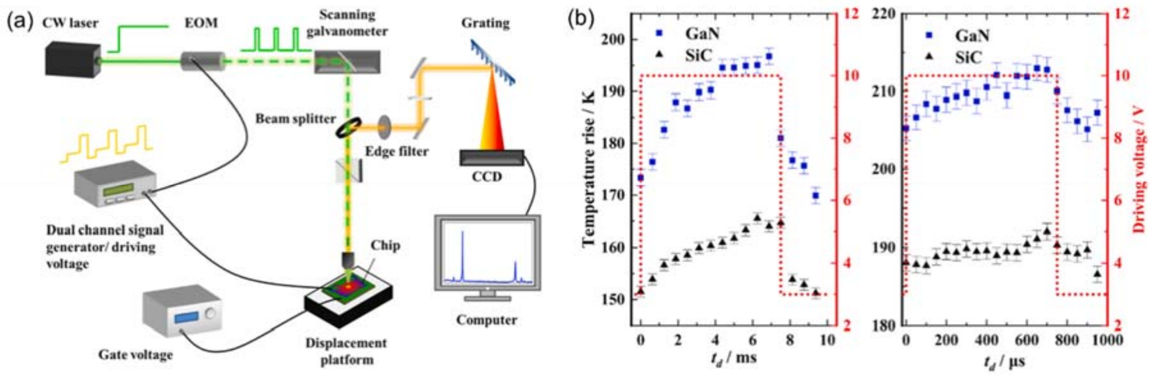


**Fig. 7** (a) Schematic of the opto-electric flash Raman method measurement system and (b) temperature measurement results for GaN and SiC with 100 Hz and 1000 Hz modulated signals.

### 4.2 Dynamic monitoring of interfacial chemical reactions of all-solid-state lithium batteries

All-solid-state lithium metal batteries using non-flammable solid electrolytes are promising options for electric vehicles and portable electronic devices due to their significantly better safety characteristics and higher energy densities. A stable electrode-electrolyte interface is the key to high energy density all-solid-state lithium metal batteries, but the nanoscale behavior of the interface is not well understood. The dynamic evolution of the interphase layer composition was studied by the speaker's group using Raman spectroscopy to detect the cross-sectional Li-LPSCl interface at various temperatures (Fig. 8)[54]. The line-scanning Raman spectra indicated a new peak at ~372 $cm^{-1}$ at the Li-LPSCl interface at 25°C and 60°C, suggesting the formation of a new material. Comparison of the characteristic Raman peak with those of standard materials showed that new material was $Li_2S$. In contrast, only a weak $Li_2S$ signal was captured at -20°C which indicated that although the ion conductivity of $Li_2S$ is much lower than that of the LPSCl electrolyte, $Li_2S$ is thermodynamically stable toward the Li metal, which may act as a protective layer to passivate the interface. This finding provides new insight into the nanoscale interphase composition of the Li-SE interface as valuable guidance for future interface designs.

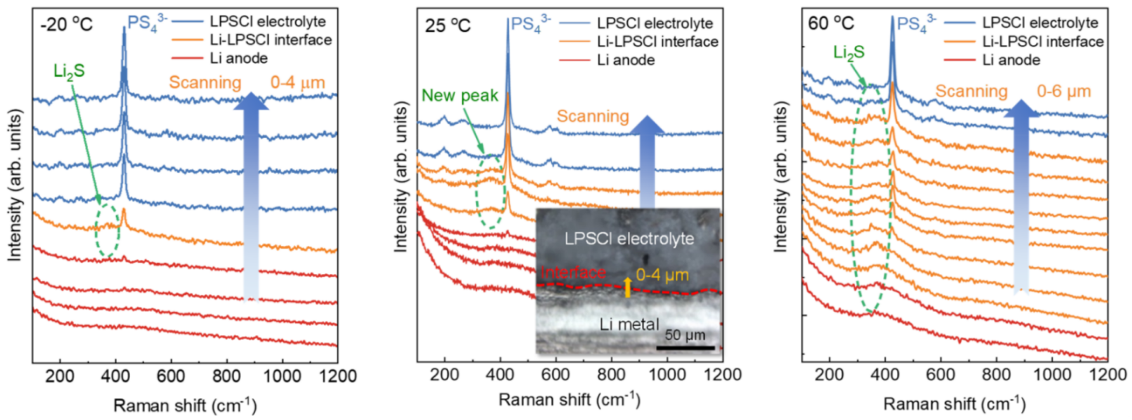


**Fig. 8.** Line-scanning Raman spectra of a Li anode, Li-LPSCl interface and LPSCl electrolyte for cells resting at -20°C, 25°C, and 60°C for 120 h.

### 4.3 Liquid analyses for serum-based cancer diagnoses

Liquid analyses are important in many fields, especially as a disease screening tool, for example for early cancer diagnoses by detecting tumor-derived components in bodily fluids, referred to as "liquid biopsies." Indeed, cancer can be diagnosed before any symptoms appear by detecting tumor biomarkers, circulating tumor cells, DNA methylation, exosomes, and other subtle changes in bodily fluids. Liquid biopsies are rapid, nondestructive, sensitive, and convenient. However, liquid biopsy-based cancer diagnoses are not yet widely used in clinical applications because of their low accuracy, which mainly depends on the sensitivity and specificity. To improve the detection efficiency, accuracy and reproducibility, the speaker's group developed a label-free method to analyze bodily fluids based on surface-enhanced Raman scattering (SERS) with large laser spot-swift mapping involving electrochemistry preparation of silver nanoparticle substrates[55]. This method can analyze the overall properties of multicomponent liquids and identify low-concentration components. A large laser spot formed by a scanning galvanometer is used to obtain an average spectrum from different samples, while swift mapping detects low-concentration components such as tumor biomarkers (Fig. 9). The silver nanoparticle substrates exhibit strong SERS activity and wettability which improves adsorption and avoids sample cluster formation. This method has been applied for serum-based cancer diagnoses. The large spot method accuracy was evaluated by comparison with mass spectrometry results, while the swift mapping sensitivity was evaluated by detection of carcinoembryonic antigens in early colorectal cancer serums. Several cancer-related Raman peaks may be used as predictors, like the peak at 710 $cm^{-1}$ which may represent an increase in circulating tumor DNA and metabolic disorders. This method is sensitive and reproducible and is expected to play an important role in analyses of complex component liquids and mechanism studies, especially for body liquids with subtle changes.

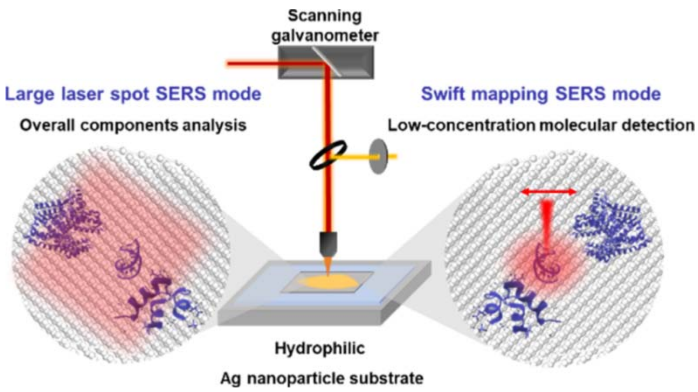


**Fig. 9.** Schematic of the large laser spot SERS mode and the swift mapping SERS mode.

## 5. CONCLUSIONS

This review of nanoscale thermal measurement methods has shown even after 200 years, the heat conduction equation derived by Fourier still directly guides measurements of thermophysical properties for nanomaterials. The thermophysical properties, such as the thermal conductivity, defined by Fourier's law are still the most direct and effective parameters for describing the heat transfer in nanomaterials. Therefore, one objective of the Fourier lecture is to review and commemorate previous respected heat transfer researchers. I hope their achievements will motivate us to continue the history of heat transfer research and make more far-reaching results in the heat transfer field.

This Fourier lecture reviewed the development of nanoscale thermal measurement techniques. Advanced processing methods have led to the development of many excellent new nanoscale thermal measurement methods. This summary of past research shows that all measurement methods are developing towards simpler measurement processes, fewer interfering factors, and more integration and comprehensiveness. For instance, many non-contact measurement methods have been developed in recent years which has significantly simplified sample preparation. The microfabricated suspended device method and the H-type method use similar simplified structures, which significantly reduce the radiation influence. Several methods, such as the T-type method and the Raman method, have developed into comprehensive approaches which are not limited to only thermal detection. In fact, in our fast-developing world, more and more new issues have made researchers realize the importance of multidisciplinary studies. In addition to exploring traditional heat transfer research areas, we should further consider how we can better serve society and how our research can make this world a better place. The speaker has used Raman detection methods for multidisciplinary research in various fields and hopes this experience will inspire heat transfer researchers to continue to explore and achieve greater breakthroughs in a broader range of disciplines.

## ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Nos. 51827807 and 52130602). The author thanks Dr. Aoran Fan and Dr. Yufeng Zhang for their help with this work.

## REFERENCES

[1] Iijima, S., "Helical microtubules of graphitic carbon," *Nature*, 354(6348), pp. 56-58, (1991).
[2] Boiko, B.T., Pugachev, A.T., Bratsychin, V.M., "Method for the determination of the thermophysical properties of evaporated thin films," *Thin Solid Films*, 17(2), pp. 157-161, (1973).

[3] Cahill, D.G., "Thermal conductivity measurement from 30 to 750 K - the 3-omega method," *Rev Sci Instrum*, 61(2), pp. 802-808, (1990).
[4] Kim, P., Shi, L., Majumdar, A., McEuen, P.L., "Thermal transport measurements of individual multiwalled nanotubes," *Physical review letters*, 87(21), pp. 215502, (2001).
[5] Chen, R., Hochbaum, A.I., Murphy, P., Moore, J., Yang, P.D., Majumdar, A., "Thermal conductance of thin silicon nanowires," *Physical Review Letters*, 101, pp. 105501, (2008).
[6] Xu, X.F., Pereira, L.F.C., Wang, Y., Wu, J., Zhang, K.W., Zhao, X.M., Bae, S., Bui, C.T., Xie, R.G., Thong, J.T.L., Hong, B.H., Loh, K.P., Donadio, D., Li, B.W., Ozyilmaz, B., "Length-dependent thermal conductivity in suspended single-layer graphene," *Nat Commun*, 5, pp. 3689, (2014).
[7] Lee, S., Yang, F., Suh, J., Yang, S.J., Lee, Y., Li, G., Choe, H.S., Suslu, A., Chen, Y.B., Ko, C., Park, J., Liu, K., Li, J.B., Hippalgaonkar, K., Urban, J.J., Tongay, S., Wu, J.Q., "Anisotropic in-plane thermal conductivity of black phosphorus nanoribbons at temperatures higher than 100 k," *Nat Commun*, 6, pp. (2015).
[8] Chang, C.W., Okawa, D., Majumdar, A., Zettl, A., "Solid-state thermal rectifier," *Science*, 314(5802), pp. 1121-1124, (2006).
[9] Shrestha, R., Luan, Y.X., Luo, X., Shin, S.M., Zhang, T., Smith, P., Gong, W., Bockstaller, M., Luo, T.F., Chen, R.K., Hippalgaonkar, K., Shen, S., "Dual-mode solid-state thermal rectification," *Nat Commun*, 11(1), pp. 1-7, (2020).
[10] Moore, A.L., Shi, L., "On errors in thermal conductivity measurements of suspended and supported nanowires using micro-thermometer devices from low to high temperatures," *Meas Sci Technol*, 22, pp. 015103, (2011).
[11] Zhang, X., Fujiwara, S., Fujii, M., "Short-hot-wire method for measuring thermal conductivity of a fine fiber (the 1st report: Theoretical analysis of measurement method)," *Reports-Institute of Advanced Material Study Kyushu University*, 12, pp. 29-36, (1998).
[12] Zhang, X., Fujiwara, S., Fujii, M., "Measurements of thermal conductivity and electrical conductivity of a single carbon fiber," *Int J Thermophys*, 21(4), pp. 965-980, (2000).
[13] Fujii, M., Zhang, X., Xie, H.Q., Ago, H., Takahashi, K., Ikuta, T., Abe, H., Shimizu, T., "Measuring the thermal conductivity of a single carbon nanotube," *Physical review letters*, 95(6), pp. 065502, (2005).
[14] Wang, J.L., Gu, M., Zhang, X., Song, Y., "Thermal conductivity measurement of an individual fibre using a t type probe method," *J Phys D Appl Phys*, 42, pp. 105502, (2009).
[15] Wang, J.L., Gu, M., Zhang, X., Wu, G.P., "Measurements of thermal effusivity of a fine wire and contact resistance of a junction using a t type probe," *Rev Sci Instrum*, 80, pp. 076107, (2009).
[16] Miao, T.T., Ma, W.G., Zhang, X., Wei, J.Q., Sun, J.L., "Significantly enhanced thermoelectric properties of ultralong double-walled carbon nanotube bundle," *Appl Phys Lett*, 102(5), pp. 053105, (2013).
[17] Miao, T.T., Shi, S.Y., Yan, S., Ma, W.G., Zhang, X., Takahashi, K., Ikuta, T., "Integrative characterization of the thermoelectric performance of an individual multiwalled carbon nanotube," *J Appl Phys*, 120(12), pp. 124302, (2016).
[18] Ma, W.G., Miao, T.T., Zhang, X., Takahashi, K., Ikuta, T., Zhang, B.P., Ge, Z.H., "A t-type method for characterization of the thermoelectric performance of an individual free-standing single crystal $Bi_2S_3$ nanowire," *Nanoscale*, 8(5), pp. 2704-2710, (2016).
[19] Ma, W.G., Liu, Y.J., Yan, S., Miao, T.T., Shi, S.Y., Xu, Z., Zhang, X., Gao, C., "Chemically doped macroscopic graphene fibers with significantly enhanced thermoelectric properties," *Nano Res*, 11(2), pp. 741-750, (2018).
[20] Fujiwara, S., Zhang, X., Fujii, M., "Short-hot-wire method for measuring total hemispherical emissivity of a fine fiber," *Reports-Institute of Advanced Material Study Kyushu University*, 12, pp. 99-106, (1998).
[21] Wang, H.D., Hu, S.Q., Takahashi, K., Zhang, X., Takamatsu, H., Chen, J., "Experimental study of thermal rectification in suspended monolayer graphene," *Nat Commun*, 8(1), pp. 1-8, (2017).
[22] Zhang, Y., Lv, Q., Wang, H., Zhao, S., Xiong, Q., Lv, R., Zhang, X., "Simultaneous electrical and thermal rectification in a monolayer lateral heterojunction," *Science*, 378(6616), pp. 169-175, (2022).
[23] Rosencwaig, A., Gersho, A., "Theory of the photoacoustic effect with solids," *J Appl Phys*, 47(1), pp. 64-69, (1976).
[24] Paddock, C.A., Eesley, G.L., "Transient thermoreflectance from thin metal-films," *J Appl Phys*, 60(1), pp. 285-290, (1986).
[25] Eesley, G.L., "Generation of nonequilibrium electron and lattice temperatures in copper by picosecond laser-pulses," *Phys Rev B*, 33(4), pp. 2144-2151, (1986).
[26] Schmidt, A.J., Cheaito, R., Chiesa, M., "A frequency-domain thermoreflectance method for the characterization of thermal properties," *Rev Sci Instrum*, 80(9), pp. 094901, (2009).
[27] Liu, J., Choi, G.M., Cahill, D.G., "Measurement of the anisotropic thermal conductivity of molybdenum disulfide by the time-resolved magneto-optic kerr effect," *J Appl Phys*, 116(23), pp. 233107, (2014).
[28] Elzinga, P.A., Lytle, F.E., Jian, Y., King, G.B., Laurendeau, N.M., "Pump probe spectroscopy by asynchronous optical-sampling," *Appl Spectrosc*, 41(1), pp. 2-4, (1987).
[29] Ma, W.G., Miao, T.T., Zhang, X., Kohno, M., Takata, Y., "Comprehensive study of thermal transport and coherent acoustic-phonon wave propagation in thin metal film-substrate by applying picosecond laser pump-probe method," *J Phys Chem C*, 119(9), pp. 5152-5159, (2015).
[30] Dong, C., Ma, W.G., Zhang, X., "Modulation of the time-domain reflectance signal induced by thermal transport and acoustic waves in multilayered structure," *Int J Heat Mass Tran*, 114, pp. 915-922, (2017).

[31] Yan, S., Dong, C., Miao, T.T., Wang, W., Ma, W.G., Zhang, X., Kohno, M., Takata, Y., "Long delay time study of thermal transport and thermal stress in thin pt film-glass substrate system by time-domain thermoreflectance measurements," *Applied Thermal Engineering*, 111, pp. 1433-1440, (2017).

[32] Lu, Y., Tan, X., Du, Y., Ma, D., Ma, W., "Direct observation of ultrafast carrier coupling dynamics in monolayer graphene/metal system," *Int. J. Heat Mass Transfer*, 197, pp. 123322, (2022).

[33] Novoselov, K.S., Jiang, D., Schedin, F., Booth, T.J., Khotkevich, V.V., Morozov, S.V., Geim, A.K., "Two-dimensional atomic crystals," *P Natl Acad Sci USA*, 102(30), pp. 10451-10453, (2005).

[34] Balandin, A.A., Ghosh, S., Bao, W.Z., Calizo, I., Teweldebrhan, D., Miao, F., Lau, C.N., "Superior thermal conductivity of single-layer graphene," *Nano Lett*, 8(3), pp. 902-907, (2008).

[35] Yan, R.S., Simpson, J.R., Bertolazzi, S., Brivio, J., Watson, M., Wu, X.F., Kis, A., Luo, T.F., Walker, A.R.H., Xing, H.G., "Thermal conductivity of monolayer molybdenum disulfide obtained from temperature-dependent raman spectroscopy," *Acs Nano*, 8(1), pp. 986-993, (2014).

[36] Peimyoo, N., Shang, J.Z., Yang, W.H., Wang, Y.L., Cong, C.X., Yu, T., "Thermal conductivity determination of suspended mono- and bilayer $WS_2$ by raman spectroscopy," *Nano Res*, 8(4), pp. 1210-1221, (2015).

[37] Luo, Z., Maassen, J., Deng, Y.X., Du, Y.C., Garrelts, R.P., Lundstrom, M.S., Ye, P.D., Xu, X.F., "Anisotropic in-plane thermal conductivity observed in few-layer black phosphorus," *Nat Commun*, 6(1), pp. 1-8, (2015).

[38] Li, Q.Y., Xia, K.L., Zhang, J., Zhang, Y.Y., Li, Q.Y., Takahashi, K., Zhang, X., "Measurement of specific heat and thermal conductivity of supported and suspended graphene by a comprehensive Raman optothermal method," *Nanoscale*, 9(30), pp. 10784-10793, (2017).

[39] Liu, J.H., Wang, H.D., Hu, Y.D., Ma, W.G., Zhang, X., "Laser flash-Raman spectroscopy method for the measurement of the thermal properties of micro/nano wires," *Rev Sci Instrum*, 86(1), pp. (2015).

[40] Li, Q.Y., Ma, W.G., Zhang, X., "Laser flash Raman spectroscopy method for characterizing thermal diffusivity of supported 2D nanomaterials," *Int J Heat Mass Tran*, 95, pp. 956-963, (2016).

[41] Li, Q.Y., Katakami, K., Ikuta, T., Kohno, M., Zhang, X., Takahashi, K., "Measurement of thermal contact resistance between individual carbon fibers using a laser-flash Raman mapping method," *Carbon*, 141, pp. 92-98, (2019).

[42] Fan, A.R., Hu, Y.D., Ma, W.G., Wang, H.D., Zhang, X., "Dual-wavelength laser flash Raman spectroscopy method for in-situ measurements of the thermal diffusivity: Principle and experimental verification," *J Therm Sci*, 28(2), pp. 159-168, (2019).

[43] Hu, Y.D., Fan, A.R., Liu, J.H., Wang, H.D., Ma, W.G., Zhang, X., "A dual-wavelength flash Raman method for simultaneously measuring thermal diffusivity and line thermal contact resistance of an individual supported nanowire," *Thermochim Acta*, 683, pp. 178473, (2020).

[44] Hu, Y.D., Fan, A.R., Wang, H.D., Ma, W.G., Zhang, X., "Dual-wavelength flash Raman mapping method for measuring thermal diffusivity of the suspended nanowire," *Sci China Technol Sc*, 63(5), pp. 748-754 (2019).

[45] Fan, A.R., Hu, Y.D., Wang, H.D., Ma, W.G., Zhang, X., "Dual-wavelength flash Raman mapping method for measuring thermal diffusivity of suspended 2D nanomaterials," *Int J Heat Mass Tran*, 143, pp. 118460, (2019).

[46] Fan, A.R., Wang, H.D., Ma, W.G., Zhang, X., "Two-step dual-wavelength flash Raman mapping method for measuring thermophysical properties of supported two-dimensional nanomaterials," *Heat Trans Eng*, 43(19), pp. 1627-1638 (2022).

[47] Luo, S.T., Fan, A.R., Zhang, Y.F., Wang, H.D., Ma, W.G., Zhang, X., "Dual-wavelength flash Raman mapping method for measuring the thermal diffusivity of a single supported nanowire," *Int J Heat Mass Tran*, 184, pp. 122271, (2022).

[48] Zhang, Y.F., Fan, A.R., Luo, S.T., Wang, H.D., Ma, W.G., Zhang, X., "Suspended 2D anisotropic materials thermal diffusivity measurements using dual-wavelength flash raman mapping method," *Int J Heat Mass Tran*, 145, pp. 118795, (2019).

[49] Xu, S., Wang, T.Y., Hurley, D., Yue, Y.N., Wang, X.W., "Development of time-domain differential Raman for transient thermal probing of materials," *Opt Express*, 23(8), pp. 10040-10056, (2015).

[50] Zhang, Y.F., Lv, Q., Fan, A.R., Yu, L.X., Wang, H.D., Ma, W.G., Lv, R.T., Zhang, X., "Reduction in thermal conductivity of monolayer $WS_2$ caused by substrate effect," *Nano Res*, 15(10), pp. 9578-9587, (2022)

[51] Wang, T.Y., Xu, S., Hurley, D.H., Yue, Y.N., Wang, X.W., "Frequency-resolved Raman for transient thermal probing and thermal diffusivity measurement," *Opt Lett*, 41(1), pp. 80-83, (2016).

[52] Wang, R.D., Zobeiri, H., Xie, Y.S., Wang, X.W., Zhang, X., Yue, Y.N., "Distinguishing optical and acoustic phonon temperatures and their energy coupling factor under photon excitation in nm 2D materials," *Adv Sci*, 7(13), pp. 2000097, (2020).

[53] Fan, A.R., Li, Y.P., Ma, W.G., Wang, H.D., Zhang, X., "Opto-electric flash Raman method for in situ measuring temperature variation of power device with a high temporal resolution," *Appl Therm Eng*, 217, pp. 119190, (2022).

[54] Luo, S.T., Liu, X.Y., Zhang, X., Wang, X.F., Wang, Z.Y., Zhang, Y.F., Wang, H.D., Ma, W.G., Zhu, L.Y., Zhang, X., "Nanostructure of the interphase layer between a single Li dendrite and sulfide electrolyte in all-solid-state Li batteries," *Acs Energy Lett*, 7(9), pp. 3064-3071, (2022).

[55] Zhang, X.Y., Fan, A.R., Pan, Y.M., Liu, X.Q., Zhao, Z.T., Song, Y.M., Zhang, X., "Large laser spot-swift mapping surface-enhanced Raman scattering on ag nanoparticle substrates for liquid analysis in serum-based cancer diagnosis," *Acs Appl Nano Mater*, 5(10), pp. 15738-15747, (2022).