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Yingtao Wang ; Mona Savalia ; Xian Zhang

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Yingtao Wang, Mona Savalia, and Xian Zhang[a)]

AFFILIATIONS

Stevens Institute of Technology, The Schaefer School of Engineering and Science, Department of Mechanical Engineering, Edwin A. Stevens Hall, Hoboken, New Jersey 07030

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[a)] **Author to whom correspondence should be addressed:** xzhang4@stevens.edu

ABSTRACT

With the rise of two-dimensional (2D) materials, their excellent optical, electronic, and thermal properties different from bulk materials make them increasingly widely studied and commercialized. 2D materials' exceptional physical properties and unique structures make them an ideal candidate for next-generation flexible and wearable devices. In this work, we created a manufacturing method to successfully transfer monolayer, bilayer, and trilayer graphene onto the flexible substrate, with trenches of micron size to suspend graphene. Thermal transport measurements have been characterized to prove the suspended region. The achievement of manufacturing 2D materials in suspended condition will allow us to study their intrinsic physical properties at a mechanical strain, as well as contribute to novel flexible and wearable electronic devices and sensors.

I. INTRODUCTION

2D materials have gained significant attention in the scientific community due to their unique physical properties.[1–3] The 2D material family consists of transition metal dichalcogenides (TMDs), hexagonal boron nitride (hBN), black phosphorus (BP), oxides and carbides,[4–6] etc. Among them, graphene stands out as a remarkable material with exceptional physical properties such as high electrical conductivity, mechanical strength, and thermal conductivity.[7–9] Graphene, a one-atom-thick layer of graphite, has been consistently explored for fundamental scientific properties and applications in electronics, energy storage, sensing, and biomedicine.[10–12]

2D material-based wearable electronic devices promise to revolutionize modern microelectronics by enabling high flexibility, thinness, and unprecedented device performance. While significant progress has been made in this field over the past decade, the bottleneck to improving device performance remains the heating issues caused by the reduced thermal conductivity when the 2D material is under a large mechanical deformation, thus exploring and understanding the thermal conductivities of graphene under a mechanical strain is critical. To understand the intrinsic thermal properties of graphene when it is stretched, a reliable manufacturing method to transfer 2D materials onto the flexible substrate, in both supported and suspended conditions is needed. However, the existing published manufacturing methods can only transfer 2D materials to the solid substrates.[13–18]

In this research, for the first time, we developed a novel manufacturing method to transfer 2D materials onto a flexible substrate, to produce suspended and supported flexible 2D material devices. Specifically, we transferred the monolayer (1L), bilayer (2L), and trilayer (3L) graphene samples to the flexible polydimethylsiloxane (PDMS) substrate and placed them on a ~10 μm wide trench in a suspended condition. This approach involves the use of hard plastic as a transfer stamp and polyvinyl alcohol (PVA) as a sacrificial layer due to its water solubility, which enables the separation between the support the poly (methyl methacrylate) (PMMA) layer and the Si chip. Through the successful implementation of this methodology, the transfer of 1L-3L graphene has been achieved with high precision and efficiency.

II. EXPERIMENTAL

A. Preparation of graphene/PMMA/PVA/Si

PVA (Aldrich, Average Mw 13 000–23 000) was employed as a sacrificial layer to enable the transfer process. A PVA solution of 4% by weight was prepared by dissolving 2 g of PVA in 50 g of de-ionized water. The solution was spin-coated onto a 1.1×1.1 cm^2 silicon chip using a spinning coater (Model WS-650MZ-23NPP/LITE), operating at 2000 rpm speed, and 1000 rpm/s acceleration for 1 min. Subsequently, a film of PMMA (PMMA950 A2, Micro CHEM) was spin-coated onto the PVA-coated Si chip, operating at 3000 rpm and 1000 rpm/s acceleration for 1 min. The chip was later baked at 130 °C for 5 min. The purple or pink color of the surface of the PMMA/PVA/Si wafer facilitates the identification of the graphene flakes by an optical microscope. 1L-3L graphene samples were obtained by the scotch tape mechanical exfoliation method.

B. Preparation of PDMS with trenches

PDMS (SYLGARDTM 184 Silicone Elastomer Kit) was produced by mixing the base and agent in a 10:1 mass ratio and was cured at 65 °C. When PDMS was partially solidified, filaments with a diameter of ~10 μm were delicately placed on the surface of PDMS in floating status. After curing was complete, the filaments were removed using a tape, resulting in a semicircular trench with a diameter of approximately 10 μm and a depth of 5 μm.

C. Transfer of graphene onto PDMS

The target 1L-3L graphene flakes were found and located in the optical microscope. By floating the graphene/PMMA/PVA/Si chips on the surface of water and letting water dissolve PVA, the graphene/PMMA and the Si chip will separate, with Si chip sinking down, and the graphene/PMMA film floating on the. A plastic (polystyrene) substrate of 1.1×1.1 cm, obtained by cutting from a Petri dish or similar smooth plastic products, can serve to scoop the graphene/PMMA film. The PMMA film, being nonadhesive to the plastic substrate, facilitates the ease of transfer of the graphene/PMMA film from plastic to PDMS at room temperature. To ensure a precise transfer of the target 1L-3L graphene flakes onto the micron-sized trench, a transfer station [Fig. 2(e)] is used. The transfer process involves the utilization of a microscope to achieve precise positioning of the target flake and the trench with a precision of 0.1 μm. Graphene's adhesion to PDMS was improved by exposing the substrate to a vacuum desiccator at room temperature for an overnight duration. Finally, acetone was used to remove PMMA.

D. Thermal transport measurements of flexible graphene

Thermal transport measurements were performed using opto-thermal Raman technique,[16–18] using a RENISHAW InVia Raman Microscope system with a 514 nm laser. Temperature-dependent and power-dependent measurements were specifically performed in the opto-thermal Raman technique. In temperature-dependent measurements, a heating platform (Linkam Stage THMS 600) was used in and it provides heat to the sample from 295 to 495 K. In power-dependent measurements, Raman laser is passing through a neutral density filter to have its power tuned. Through these two groups of measurements, the relation between temperature and laser power is obtained.

III. RESULTS AND DISCUSSION

A. Manufacturing

As shown in Fig. 1, 1L-3L graphene/PDMS samples were produced through a sequence of six steps. The initial step is the preparation of a PMMA/PVA/Si wafer, where PMMA functions as a support layer for graphene, and PVA serves as a sacrificial layer to isolate the PMMA and the Si chip.[19] The thickness of the PVA and PMMA layers is controlled by adjusting the spinning speed during their coating. For instance, by applying a coating speed of 2000 rpm for PVA and 3000 rpm for PMMA, the color of the surface is purple or pink, facilitating the observation and identification of 1L, 2L, 3L, and bulk graphene. However, if a lower coating speed is employed, the PVA and PMMA layer would become thicker and exhibit a blue or green color, thereby rendering the identification of graphene challenging.

The mechanical exfoliation technique is employed to synthesis graphene on PMMA/PVA/Si chips.[20] The process entails placing a 2×2 mm graphite crystal onto the adhesive side of Scotch tape, which is then folded several times to allow the crystal to attach to the empty area. The thickness can be gradually reduced during this process. Following this, a small piece of tape containing graphene flakes is cut and attached to the PMMA/PVA/Si wafer. After massaging the tape for 2 min, the 1L-3L graphene samples are transferred to the PMMA/PVA/Si wafer. It is recommended to use a moderate temperature of 40 °C if PMMA is detached from the PMMA/PVA/Si wafer by tape attachment.

B. Transfer process

Figure 2 presents the photos of the transfer process. In order to achieve a more effective separation of PMMA and the Si chip, four edges of the PMMA film on Si substrate are cut to prevent any potential attachment between the PMMA film and the Si substrate. One corner of the PMMA film is cut in order to indicate the sample orientation during the following floating and scooping steps. Figure 2(a) presents the photo of the graphene/PMMA/PVA/Si sample before edge and corner cutting, and Fig. 2(b) presents the photo of it after edge and corner cutting. The cut corner serves as the starting point for the separation process by immersing it into water, and water starts to touch the PVA layer to dissolve it at this point.

Following the separation between the PMMA film and Si chip, the graphene/PMMA layer is scooped using a hard plastic, as shown in Fig. 2(d). The conventional transfer method is using PDMS or other soft polymers as scoop[17,21,22] and transfer the 2D materials onto the target hard substrate. However, this method does not work when the target substrate is soft and flexible, because the PMMA film does not come off from the scoop. Several materials for scoop have been tested, including silicon, copper, aluminum, hard plastic, etc. It has been discovered that clear hard plastic is the ideal material

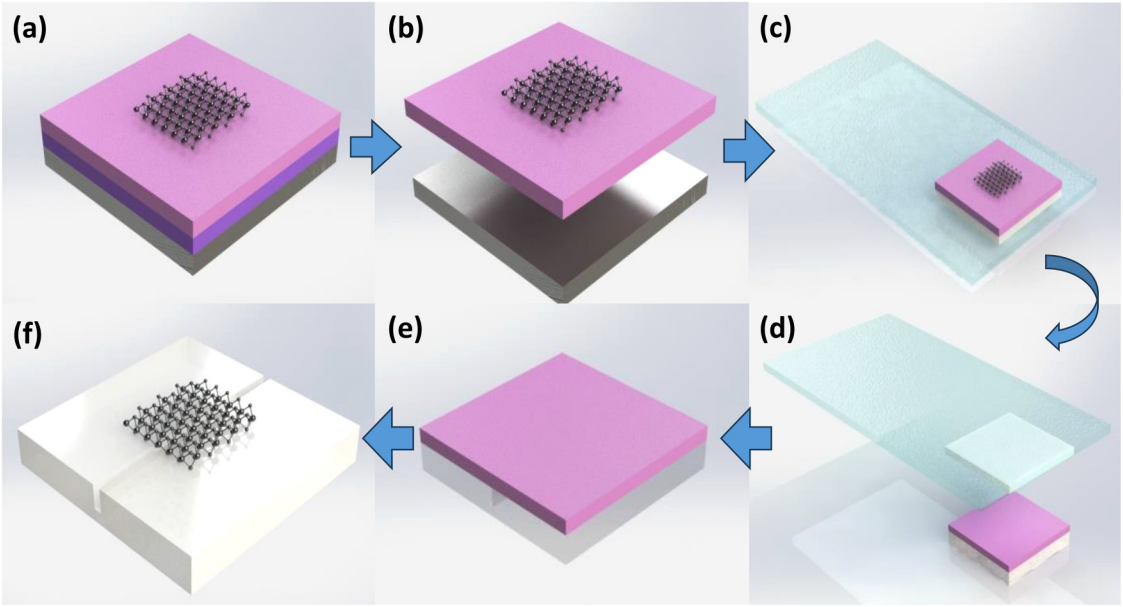

FIG. 1. Schematics of the manufacturing process of (a) Si/PVA/PMMA/graphene sample, (b) immersion of the sample in water for the dissolution of the PVA layer, (c) transfer of the graphene/PMMA layer onto the PDMS substrate using a plastic sheet, (d) facilitating graphene attachment to the PDMS substrate, (e) removal of residual moisture between the graphene layer and PDMS inside a desiccator, and (f) removal of the PMMA layer, resulting in the fabrication of the graphene suspended on the micron size groove on a PDMS substrate.

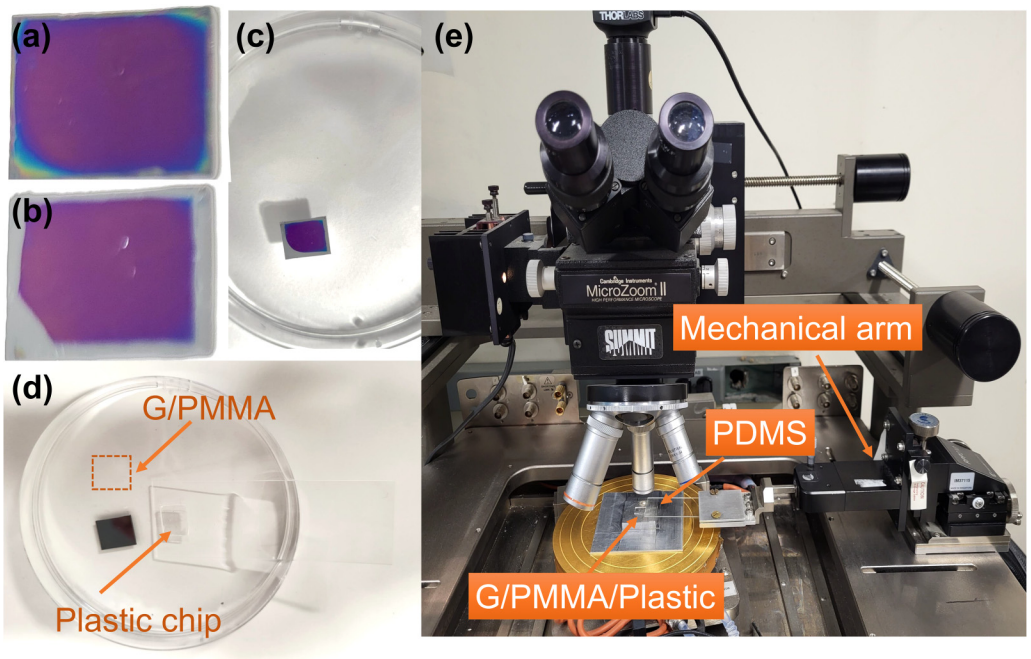

FIG. 2. Photos of the transfer process. (a) Graphene/PMMA/PVA/Si substrate. (b) Graphene/PMMA/PVA/Si substrate after cutting the four sides and a corner. (c) Graphene/PMMA/PVA/Si substrate floating on the water surface to separate graphene/PMMA from Si. (d) The scooping step of graphene/PMMA from the water surface to the scoop which is a hard plastic chip fixed on a glass slide. (e) The transfer station to achieve a precise transfer process, with a resolution of 0.1 μm.

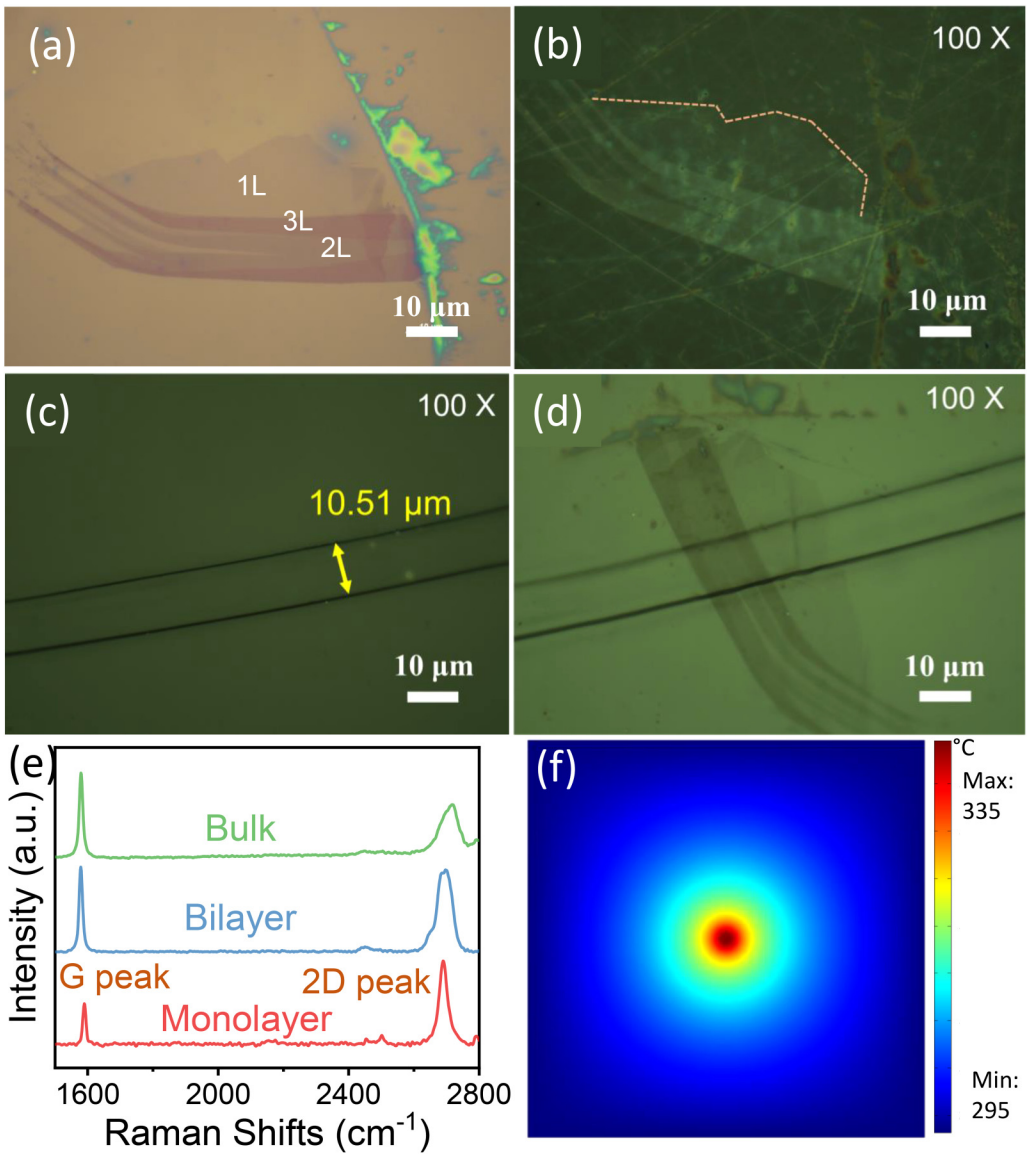

FIG. 3. Microscope characterizations of the transfer process. 100× optical microscope images of (a) monolayer, bilayer and trilayer graphene on the SiO_2/Si substrate, (b) graphene transferred on a hard plastic scoop, (c) the PDMS substrate with a ~10 μm wide trench, and (d) graphene transferred on the trench on PDMS. (e) The Raman spectra of 1L, 2L, and bulk graphene. (f) Finite-element simulation of temperature distribution in suspended 1L graphene with the given geometry used to extract the thermal conductivity.

for scoop. It is made from MilliporeSigma Petri dishes, with polystyrene as the material. It allows a smooth transfer of PMMA/graphene from the scoop to the flexible PDMS substrate.

To facilitate the transfer process, a transfer station as shown in Fig. 2(e) is utilized. The target 2D materials and the trenches on PDMS will be observed through the optical microscope. The mechanical arm is used to move the trenches to the top of target flakes with a special resolution of ~0.1 μm in x, y, and z directions.

C. Characterization of the transfer process by microscopes

Figures 3(a)–3(d) present the optical microscope images of graphene flakes in the 1L, 2L and 3L forms at three different stages in the manufacturing process. Figure 3(a) shows the image of 1L-3L graphene exfoliated on the SiO_2/Si substrate. After the floating and scooping steps [Figs. 3(a)–3(d)], the graphene/PMMA/plastic substrate will stand for 10 min for the water evaporation and sample

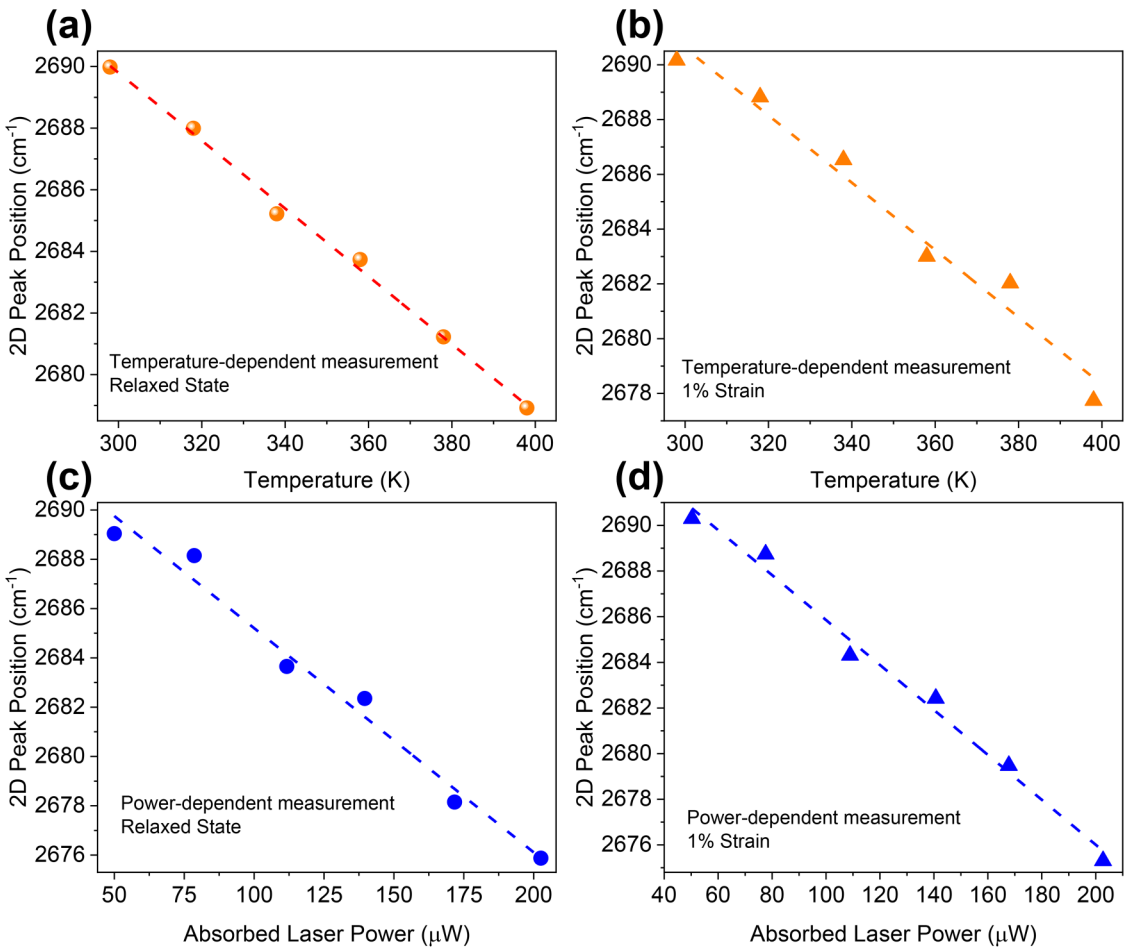

FIG. 4. Temperature-dependent 2D peak position of suspended 1L graphene (a) in relaxed state and (b) with a 1% strain, and power-dependent 2D peak position of suspended 1L graphene (c) in relaxed state and (d) with a 1% strain.

flatness which will enable the target graphene flakes to be located for the second time using an optical microscope, as illustrated in Fig. 3(b). A PDMS substrate featuring a suitably sized trench (~10 μm), as depicted in Fig. 3(c), is then carefully positioned, and placed on the control arm in the downward-facing position [Fig. 2(e)]. Trench is for suspending the graphene flakes. Precise transfer of the flake is achieved by accurately overlapping and touching the target flake and the trench position. The transfer station and control arm are shown in Fig. 2(e). The graphene/PMMA film is subsequently transferred onto the trench on PDMS substrate to form a

TABLE I. First-order temperature coefficients, absorption coefficients, and power shift rates of supported and suspended.

		Power coefficient ($cm^{-1}/\mu W$)	
Sample	Temperature coefficient (cm^{-1}/K)	0.19 μm spot	0.31 μm spot
Suspended 1L graphene in relaxed state	−0.1235 ± 0.0147	−0.0912 ± 0.0101	
Supported1L graphene in relaxed state	−0.1074 ± 0.0125	−0.0229 ± 0.0026	−0.0112 ± 0.0013
Suspended 1L graphene with a 1% strain	−0.1097 ± 0.0121	−0.0938 ± 0.0110	
Supported 1L graphene with a 1% strain	−0.0964 ± 0.0109	−0.0246 ± 0.00026	−0.0119 ± 0.0012

PMMA/graphene/PDMS sandwich structure. Then, a vacuum treatment is applied to remove excessive moisture and facilitate the attachment between graphene and PDMS. The sample is later sprayed by acetone to remove PMMA. PDMS does not swell and does not have impacts on graphene when it is placed in acetone for less than 1 h. The final graphene/PDMS sample is illustrated in Fig. 3(d) in which 1L-3L graphene flakes are suspended on a 10 μm wide trench on the PDMS.

In addition, characterization and verification of 1L-3L graphene flakes' thickness are performed via a confocal Raman spectrometer, as shown in Fig. 3(e), the peak difference between 1L graphene and thicker graphene flakes is presented. By examining the peak intensity ratio between the 2D peak (~2680 cm^{-1}) and the G peak (~1580 cm^{-1}), the thickness of graphene will be determined.[23] Specifically, 1L graphene exhibits a higher 2D peak and a lower G peak. Graphene is classified as 1L when the 2D peak is significantly higher than the G peak and can be fitted with a single clear curve. In contrast, 2L graphene flakes display G and 2D peaks of almost equal height intensity, and the 2D peak is not sharp because it contains multiple peaks. Bulk graphene, on the other hand, shows a much higher G peak than the 2D peak, which is not as distinct and intense as that observed in 1L graphene. In the following sections, graphene samples in 1L, 2L, and 3L forms that are exfoliated on PMMA/PVA/Si samples will be utilized to complete the transfer process will be presented and discussed.

Finite-element simulation [Fig. 3(f)] of temperature distribution in 1L graphene with the given geometry in experiments is conducted to ensure that the temperature at the edge of the flake is at room temperature.

D. Thermal transport measurements of flexible graphene

Thermal transport measurements were performed using opto-thermal Raman technique,[16–18] in order to prove the graphene sample has been successfully suspended. This is based on the fact that suspended graphene and other common 2D materials (such as MoS_2) has a significantly higher thermal conductivity than the supported status, due to the phonon–phonon scattering.[17,24,25]

Thermal conductivities were measured on the suspended 1L graphene, supported 1L graphene, stretched suspended 1L graphene, and stretched supported 1L graphene samples. Figure 4 presents the temperature-dependent and power-dependent Raman 2D peak position shifts for suspended 1L graphene in relaxed status and with a 1% strain.

Table I presents the first-order temperature coefficients and absorbed power shift rates of supported and suspended 1L graphene. Differential equation models in cylindrical coordinates[17,25] are used to calculate and obtain the thermal conductivities. Table II presents the measurement results of these samples.

TABLE II. Thermal transport measurement results of graphene samples.

Sample	Thermal conductivity (W/m K)
Suspended graphene	1946 ± 511
Supported graphene	674 ± 78
Suspended graphene with a 1% strain	1672 ± 445
Supported graphene with a 1% strain	539 ± 71

Suspended graphene has a higher thermal conductivity than the supported graphene which is due to the phonon–phonon scattering in supported samples.[24] For stretched graphene, the carbon–carbon bonds are highly stretched which results in a significant decrease in thermal conductivity due to the softened phonon mode.[26,27] In addition, the measurements confirm the suspended condition in graphene and the success in stretching after the transfer.

IV. SUMMARY AND CONCLUSIONS

We have demonstrated a novel manufacturing process of transferring graphene onto flexible and suspended substrates without the participation of chemical etchant. After separating graphene/PMMA and Si in water, several materials have been tested and a hard plastic sheet has been found to successfully transfer graphene onto the suspended and flexible substrate. This method applies to the large-scale graphene from 1L to bulk form to the top of a trench with micron-sized trenches, and graphene synthesized in other methods, and this high-quality transfer result helps to achieve robust and high-performance wearable electronic devices and sensors.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yingtao Wang: Data curation (equal); Investigation (equal); Writing – original draft (equal). **Mona Savalia:** Data curation (equal); Formal analysis (lead); Investigation (lead); Writing – review & editing (equal). **Xian Zhang:** Conceptualization (lead); Data curation (equal); Investigation (lead); Project administration (lead); Supervision (lead); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1]X. Liu and M. C. Hersam, Nat. Rev. Mater. **4**, 669 (2019).
[2]N. R. Glavin, R. Rao, V. Varshney, E. Bianco, A. Apte, A. Roy, E. Ringe, and P. M. Ajayan, Adv. Mater. **32**, 1904302 (2020).
[3]F. R. Fan, R. Wang, H. Zhang, and W. Wu, Chem. Soc. Rev. **50**, 10983 (2021).
[4]S. Liu, J. Wang, J. Shao, D. Ouyang, W. Zhang, S. Liu, Y. Li, and T. Zhai, Adv. Mater. **34**, 2200734 (2022).

[5]L. Jia, J. Wu, Y. Zhang, Y. Qu, B. Jia, Z. Chen, and D. J. Moss, Small Methods **6**, 2101435 (2022).
[6]X. Xu, T. Guo, H. Kim, M. K. Hota, R. S. Alsaadi, M. Lanza, X. Zhang, and H. N. Alshareef, Adv. Mater. **34**, 2108258 (2022).
[7]X. Huang, C. Zhi, Y. Lin, H. Bao, G. Wu, P. Jiang, and Y.-W. Mai, Mater. Sci. Eng., R Rep. **142**, 100577 (2020).
[8]P. Govindaraj, A. Sokolova, N. Salim, S. Juodkazis, F. K. Fuss, B. Fox, and N. Hameed, Compos. Part B Eng. **226**, 109353 (2021).
[9]J. Miao and T. Fan, Carbon **202**, 495 (2023).
[10]A. G. Olabi, M. A. Abdelkareem, T. Wilberforce, and E. T. Sayed, Renewa. Sust. Energy Rev. **135**, 110026 (2021).
[11]S. Korkmaz and İA Kariper, J. Energy Storage **27**, 101038 (2020).
[12]M. Hoseini-Ghahfarokhi, S. Mirkiani, N. Mozaffari, M. A. Abdolahi Sadatlu, A. Ghasemi, S. Abbaspour, M. Akbarian, F. Farjadian, and M. Karimi, Int. J. Nanomed. **15**, 9469 (2020).
[13]L. Wang *et al.*, Science **342**, 614, (2013).
[14]Y. Cao, "Study of electronic correlation and superconductivity in twisted graphene superlattices," Master thesis (Massachusetts Institute of Technology Department of Electrical Engineering and Computer Science, 2016).
[15]S. Son *et al.*, 2D Mater. **7**, 041005 (2020).
[16]F. Ye, Q. Liu, B. Xu, P. X. L. Feng, and X. Zhang, Small **19**, 2205726 (2023).
[17]X. Zhang, D. Sun, Y. Li, G.-H. Lee, X. Cui, D. Chenet, Y. You, T. F. Heinz, and J. C. Hone, ACS Appl. Mater. Interfaces **7**, 25923 (2015).
[18]E. Easy, Y. Gao, Y. Wang, D. Yan, S. M. Goushehgir, E.-H. Yang, B. Xu, and X. Zhang, ACS Appl. Mater. Interfaces **13**, 13063 (2021).
[19]H. Van Ngoc, Y. Qian, S. K. Han, and D. J. Kang, Sci. Rep. **6**, 33096 (2016).
[20]Y. Yang, Y. Wei, Z. Guo, W. Hou, Y. Liu, H. Tian, and T.-L. Ren, Small Methods **6**, 2200671 (2022).
[21]G.-H. Lee *et al.*, ACS Nano **7**, 7931 (2013).
[22]A. M. van der Zande *et al.*, Nat. Mater. **12**, 554 (2013).
[23]Y. Liu, Z. Liu, W. S. Lew, and Q. J. Wang, Nanoscale Res. Lett. **8**, 335 (2013).
[24]S. Ghosh, W. Bao, D. L. Nika, S. Subrina, E. P. Pokatilov, C. N. Lau, and A. A. Balandin, Nat. Mater. **9**, 555 (2010).
[25]W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi, and R. S. Ruoff, Nano Lett. **10**, 1645 (2010).
[26]Y. Gao, W. Yang, and B. Xu, Carbon **96**, 513 (2016).
[27]N. Wei, L. Xu, H.-Q. Wang, and J.-C. Zheng, Nanotechnology **22**, 105705 (2011).