

Hierarchically Structured Laser-Induced Graphene for Enhanced Boiling on Flexible Substrates

Daeyoung Kong, Minsoo Kang, Kyung Yeun Kim, Jina Jang, Jungwan Cho, Jung Bin In,* and Hyounghoon Lee*



Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 37784–37792



Read Online

ACCESS |



Metrics & More



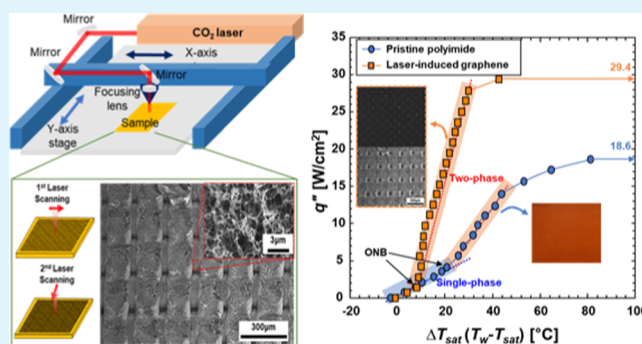
Article Recommendations



Supporting Information

ABSTRACT: Thermal management problems in high-power flexible electronics are exacerbated by the design complexity and requirement of stringent temperature control to prevent skin burns. Thus, effective heat dissipation methods applicable to flexible electronics on polymer substrates are an essential device design component. Accordingly, this study investigates the pool boiling heat transfer characteristics and potential enhancements, enabled by laser-induced graphene (LIG), which is both highly porous and bendable. Patterned LIG with a mesh spacing of 200 μm was formed on flexible polyimide substrates by laser direct writing, and the resulting surfaces exhibited enhanced heat transfer characteristics. Pool boiling experiments were conducted with an FC-72 working fluid to investigate the heat removal capability of LIG, and its performance was further improved by separating the liquid supply passages from the vapor escape routes. Overall, the inclusion of LIG resulted in a 2- to 3-fold increase in both the critical heat flux (33.6 W/cm^2) and heat transfer coefficient (7.6 $\text{kW}/(\text{m}^2\cdot\text{K})$), compared to pristine polyimide films.

KEYWORDS: laser-induced graphene, porous carbon, hierarchical structure, flexible electronics, critical heat flux, thermal management



1. INTRODUCTION

Recent advancements in flexible electronic components have enabled the development of high-performance flexible electronics for a variety of emerging applications such as the mobile health technology, wearable systems, smart cities, and Internet of Things (IoT).¹ As the processing capabilities continue to increase exponentially, so does the importance of thermal management because the increased power consumption inevitably generates excess heat. The operating temperature of wearable electronics operated in close proximity to the human body must be relatively low to prevent skin burn or device malfunctions.² Moreover, the polymers that provide an essential platform for flexible electronic devices have the disadvantage of low thermal conductivity, which hinders effective thermal management. Over the past few decades, the development of thermally conductive materials with excellent flexibility has been a primary research hotspot; however, the enhancements achieved, compared to conventional polymers, is still fairly limited.³ Conventional thermal management techniques, such as heat sinks with fans, heat pipes, and vapor chamber, could be used to address these problems, but they are relatively difficult to apply to flexible substrates. Researchers have also attempted to remove heat using ultrathin heat pipes or flexible vapor chambers; these techniques incur high costs with only moderate performance

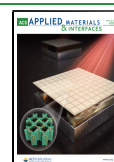
improvements because they use thermal interfacial materials (TIMs) for thermal contact.

Modern microfabrication and advanced coating technologies have enabled material surface properties to be manipulated for enhanced boiling heat transfer capabilities.^{4–7} For instance, Wang et al.⁸ fabricated copper dendrite micro-pin fin arrays for enhanced boiling performance with increased surface roughness. Lu et al.⁹ grew silicon nanowires to achieve a maximum critical heat flux (CHF) enhancement that was ~ 3 times higher than that of smooth surfaces. In addition, Liter and Kaviani¹⁰ fabricated heterogeneous boiling surfaces by adjusting the contact angle and improved the boiling heat transfer by separating liquid and vapor paths. These studies present multiple mechanisms and avenues for improving the boiling performance; however, most of them rely on metal-based materials, making them inherently difficult to be adopted in systems utilizing flexible polymer substrates.¹¹

Received: June 23, 2020

Accepted: July 24, 2020

Published: July 24, 2020



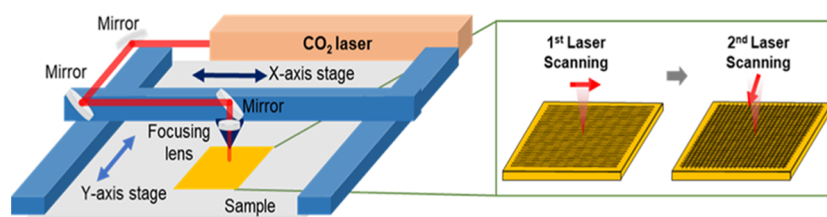


Figure 1. Schematic of the laser-induced graphene fabrication setup and scanning scheme.

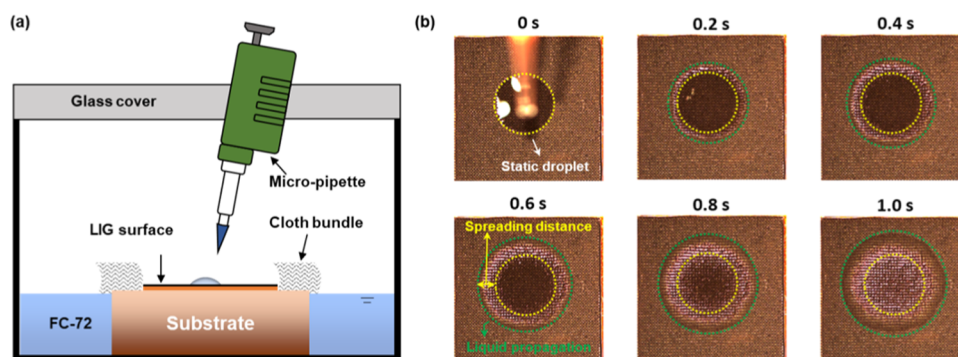


Figure 2. (a) Schematic of the experimental setup used to measure the liquid spreading velocity and (b) sequential high-speed optical images of liquid spreading on a sample LIG surface. The dotted circles represent the droplet boundary (yellow) and wetting front (green).

Graphene, a carbon nanoallotrope, can play an important role in thermal management because of its superior mechanical, electrical, and thermal properties. Furthermore, it can be readily used in flexible electronics because its two-dimensional (2D) structure and inherent flexibility render its implementation in flexible systems very easy.^{12–17} Many studies have been conducted to investigate the techniques to improve the thermal characteristics of flexible materials by graphene synthesis. For example, Li et al.¹⁸ and Cui et al.¹⁹ achieved higher thermal conductivities of 6.6 and 21.8 W/(m·K) with vertically aligned graphene aerogel and a graphene-polymer film, respectively. Unfortunately, several promising methods of realizing improved heat transfer have practical limitations because their synthesis and fabrication are relatively complex and expensive for scale-up, selective-area patterning, and fast fabrication.^{20,21}

Accordingly, laser-induced graphene (LIG) has recently drawn significant research attention in various fields. In general, laser irradiation of polymers has been shown to generate three-dimensional (3D) porous carbonaceous materials via pyrolysis.^{22,23} When polyimide, a common substrate for flexible electronics,²² is used as a precursor, the resulting carbon material is specifically identified as graphene and is thus termed as LIG.^{24–27} Conventional pyrolysis methods require bulk heating by a furnace system, whereas laser irradiation can induce a localized temperature in polyimide that is sufficiently high to instantly convert it to LIG. This laser pyrolysis process is a facile and highly efficient fabrication method that bodes well for large-scale production. Moreover, LIG exhibits excellent mechanical flexibility,²⁸ a large surface area-to-volume ratio,²⁹ and high electrical³⁰ and thermal conductivities^{31,32} (see Supporting Information for flexibility test details, S1). Because of this unique combination of properties, LIG on polyimide has been widely studied for use in supercapacitors, batteries, electrocatalysts, and sensors,³³ but its application in thermal management systems has rarely been studied, despite

it having similar thermal properties to those of graphene films.³⁴

Therefore, this study investigates the pool boiling heat transfer enhancement achieved by fabricating an LIG surface on a flexible polyimide substrate. Direct laser-induced pyrolysis was performed to produce a porous carbonized surface, which was then patterned into a mesh with 200 μm spacing over a total area of $12 \times 12 \text{ mm}^2$. The pool boiling heat transfer performance of the LIG surfaces was evaluated experimentally and compared to the performance of smooth polyimide surfaces as a control. In addition, the porous surface design was optimized to maximize the heat transfer dissipation through the LIG surface. This work is an important step forward toward utilizing the unique and valuable heat transfer properties of LIG in flexible electronics and other emerging applications.

2. EXPERIMENTAL METHODS

2.1. Laser-Induced Graphene Fabrication and Visualization.

To prepare LIG-patterned polymer surfaces, a commercial polyimide, Kapton ($w_{\text{film}} = 125 \mu\text{m}$), was irradiated with a continuous-wave (CW) CO_2 laser (Coryart, Inc., model C40; wavelength: 10.6 μm). The focused laser beam ($1/e^2$ spot diameter = 260 μm) was scanned over the film surface at a scanning speed of 200 mm/s and power of 5.3 W (corresponding power density = 20.3 kW/cm^2) under ambient conditions. The scanning path was programmed to obtain a mesh-like pattern with 200 μm spacing. These parameters ensured that no significant thermal damage occurred in the polyimide bulk, while laser pyrolysis was confined to a limited depth from the film surface. Figure 1 presents a schematic of the laser irradiation system and the laser scanning scheme. The optical penetration depth of the infrared (IR) light into Kapton is shallow; thus, light absorption occurs near the film surface. As a result, the temperature of the irradiated polyimide is instantly increased over its pyrolysis point, transforming the polyimide at the surface into an LIG layer. The presence of graphene in the LIG was confirmed by Raman spectroscopy (see Supporting Information Figure S2) and our previous report.³³

The pore size and quantity were analyzed using an open image processing program, ImageJ, and the surface properties were

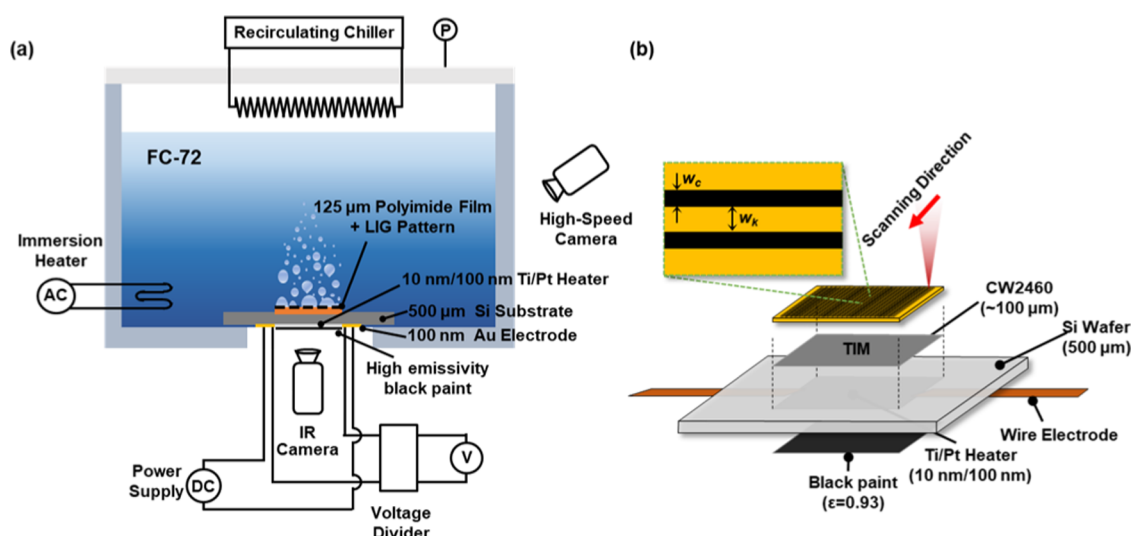


Figure 3. Schematic of (a) pool boiling apparatus and (b) test module used for thermal performance characterizations.

characterized using 3M Fluorinert FC-72 as a dielectric working fluid. The LIG surface was visualized by scanning electron microscopy (SEM) (S-3400N, Hitachi, Japan) and 3D confocal microscopy (OLS4100-SWF, Olympus Co., Ltd., Japan).

2.2. Measurement of Surface Properties. Figure 2a presents a schematic of the glass chamber used to measure the spreading characterization of the working fluid on the LIG surface. A sample, either smooth polyimide or LIG, was placed at the center of the chamber on the top surface of the copper substrate and was wrapped with a bundle of cloth to increase the relative humidity and prevent errors caused by evaporation during the experiment. Next, the working fluid (3M Fluorinert FC-72) was added, which filled the chamber to a level just below the substrate surface. The chamber was then left undisturbed until it became saturated by evaporation (approximately 20 min). A single droplet of FC-72 was then dispensed at the center of the sample, and optical images were recorded at 250 fps with a high-speed camera (Photron FastCAM Mini UX100). A droplet volume of 2 μL was used so that the bond number (Bo), defined as the ratio of gravity to capillary force, would be less than 1, thereby minimizing gravitational effects.³⁵ Figure 2b shows the sequential optical images of the spreading area of an LIG sample used to measure the spreading rate.

2.3. Pool Boiling Experimental Setup and Procedure. Once the wetting characteristics of polyimide and the LIG samples were examined, the heat transfer characteristics were determined using a pool boiling test setup (Figure 3a). This setup consisted of a stainless steel (SUS304) chamber with transparent polycarbonate (PC) windows on the front and the back, enabling bubble formation to be observed during boiling tests. An immersion heater (up to 1.1 kW) was installed on the side wall of the chamber, which was used for both degassing noncondensable gases before the test and maintaining the working fluid at the saturated condition during the test. Vaporized working fluid was condensed and returned to the liquid bulk by a coiled condenser at the top cover of the chamber, which was connected to a circulating chiller (Jeio Tech Co., HH20). The temperature and pressure inside the chamber were monitored by a K-type thermocouple and an OMEGA absolute pressure transducer, which were controlled through the NI Compact DAQ modular data acquisition system using LabVIEW code. The boiling images were captured by a Photron FastCAM Mini UX100 high-speed camera with an ARRI 2000 plus light source.

The structure of the test module is illustrated in Figure 3b. First, the polyimide film was ultrasonically cleaned sequentially with ethyl alcohol, acetone, and isopropyl alcohol for 5 min each and then rinsed with DI water. Then, the film was attached to the top surface of a silicon substrate (525 μm) with a thermal interfacial material (TIM, Chemtronics, Inc., CW2460, $k = 1.6 \text{ W/(m·K)}$) to minimize thermal

resistance during the thermal tests. The thickness of the TIM layer (w_{tim}) was determined by subtracting the known thicknesses of the polyimide film (w_{film}) and the silicon substrate (w_{si}) from the total thickness of the test module (w_{tot})

$$w_{\text{tim}} = w_{\text{tot}} - w_{\text{film}} - w_{\text{si}} \quad (1)$$

A titanium/platinum (10/100 nm) thin-film resistive heater with an area of $10 \times 10 \text{ mm}^2$ was deposited by electron-beam evaporation on the bottom surface of the silicon substrate. The test module was then cured in a vacuum oven for 1 h at 60 °C to prevent any surface deformation during LIG formation and thermal testing. Then, the LIG pattern was formed on the top surface of the polyimide film through the process described in Section 2.1.

During the boiling experiment, the test module was placed at the bottom of the chamber and sealed with high-temperature silicone (Permatex, High-Temp. Red RTV) to prevent leakage. The FC-72 working fluid was poured into the chamber and vaporized for 30 min by the immersion heater with simultaneous condensing, while any noncondensable gases were allowed to escape to the ambient surroundings. Then, DC power (HP 6030A power supply) was supplied to the thin-film heater. The total power input to the heater was measured with a customized voltage dividing circuit, consisting of $0.05 \Omega \pm 1.0\%$ and $5 \text{ k} \Omega \pm 0.1\%$ resistors, to prevent the DAQ system from being damaged by high voltages during the measurements. The heated surface temperature was measured by an IR thermal imaging camera (FLIR E75). The thin metal film heater was black-painted with a high-emissivity surface ($\epsilon = 0.93$) before the measurement, and the IR measurement was precalibrated using a K-type thermocouple (see Supporting Information S3 for the detailed calibration procedure and results). Once the heater surface reached a quasi-steady temperature (fluctuations less than 2 °C for 1 min), the dataset—including the voltage, current supplied to the heater, heated surface temperature, chamber temperature, and chamber pressure—was obtained for 30 s using the DAQ system. Then, the applied heater power was increased in steps of 2 W, and the procedure was repeated with each step until CHF occurred.

Uncertainties in the heater surface temperature and heat flux were determined based on the methodology proposed by Coleman and Steele.³⁶ The temperature of the polyimide film in contact with TIM was calculated by assuming one-dimensional (1D) heat transfer

$$T_s = T_h - q'' \left(\frac{w_{\text{si}}}{k_{\text{si}}} + \frac{w_{\text{tim}}}{k_{\text{tim}}} + \frac{w_{\text{film}}}{k_{\text{film}}} \right) \quad (2)$$

The thickness of w_{film} is detailed in Supporting Figure S4.

The temperature was measured by an IR thermal camera with an accuracy of $\pm 2\%$. The accuracy of the heater power input was ± 0.3

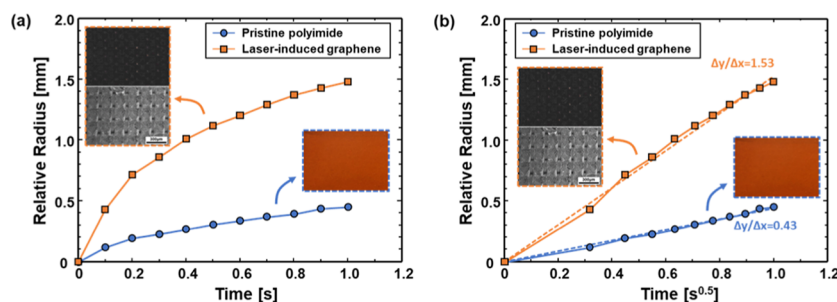


Figure 4. Liquid spreading distance of the pristine polyimide film and LIG surface over (a) time and (b) square root of time.

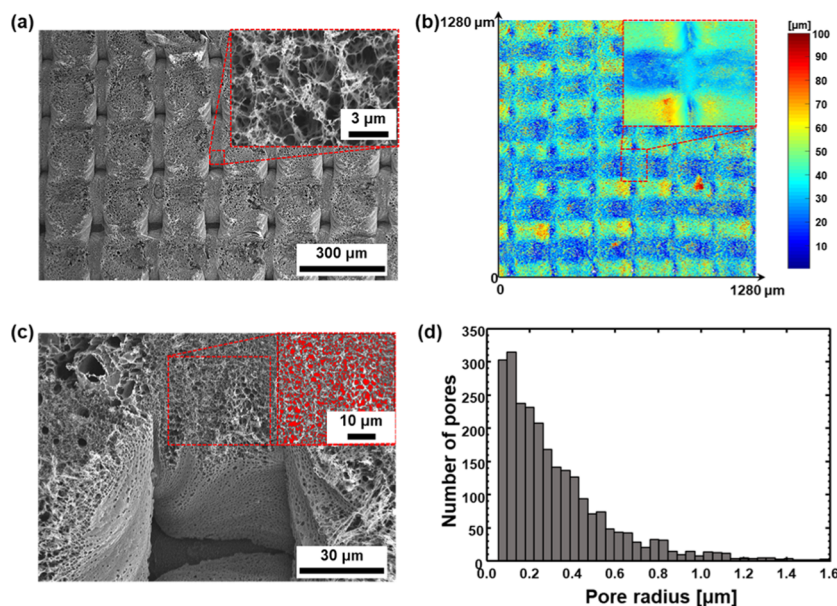


Figure 5. Images of the LIG pattern obtained by (a) scanning electron microscopy (SEM) and (b) confocal microscopy topology. The insets in (a) and (b) show magnified images of the LIG pattern near an intersection. (c) Image processing on the magnified SEM image of the effective area of nucleation cavities, with the inset showing image processing analysis results from ImageJ. (d) Distribution of pores with respect to pore radius.

W, and the errors of the recorded voltage and the current obtained from the voltage divider were ± 0.1 and $\pm 1\%$, respectively. The effective heat flux, based on the bottom polyimide film, was calculated by considering natural convective heat loss from the bottom of the silicon substrate with an assumed convective heat transfer coefficient (HTC) of $5 \text{ W}/(\text{m}^2 \cdot \text{K})$,³⁷ and the accumulated uncertainty was estimated to be 1.2–15.0%.

3. RESULTS AND DISCUSSION

3.1. Surface Characterization. The manner in which fluids spread on porous media is closely related to their boiling performance, and it is well known that higher spreading velocities provide an increased supply of liquid to the heated area, resulting in enhanced boiling heat transfer and CHF.^{38–40} Therefore, we characterized the liquid spreading on the LIG surface to analyze its relationship with the boiling heat transfer. We first optimized the operating conditions of the laser, especially power and scanning speed, to prevent any film puncturing or surface roughening during the fabrication process. Figure 4 shows the spreading distance of FC-72 droplets over 100 ms plotted against both time (Figure 4a) and square root of time (Figure 4b). Clearly, incorporating the LIG on the polyimide surface increased the spreading distance by 3–4 times. In this case, the spreading rate can be quantitatively expressed as the wetting distance, d_r , based on the Washburn model, as follows^{41,42}

$$d_r = \sqrt{\frac{2P_{\text{cap}}}{K}}t = W\sqrt{t} \quad (3)$$

where P_{cap} , K , t , and W denote the capillary pressure (Pa) in the porous medium, viscous resistance ($(\text{Pa} \cdot \text{s})/\text{m}^2$), time (s), and wetting coefficient, respectively. These wetting coefficients, estimated by simple linear regressions, were 1.53 and 0.44 $\text{mm}/\text{s}^{0.5}$ for the LIG and pristine polyimide surfaces, respectively.

Figure 5a shows the scanning electron microscopy (SEM) image of the mesh-like patterned LIG, which features a foam-like structure covered with entangled nanowires, as shown more clearly in the inset. Figure 5b shows the topological image of the LIG-patterned surface obtained using a 3D confocal microscope. The root-mean-square roughness (R_{rms}) and roughness factor ($r = A_{\text{tot}}/A_p$, where A_{tot} is the total surface area and A_p is the projected heating area) were 6.9 and 7.1 μm , respectively. Notably, these values were calculated as averages found by analyzing five local spots in the 3D confocal microscopy image. As shown in Figure 5c, pores capable of facilitating boiling nucleation were created in the laser-pyrolyzed portions of the polyimide film. The size and quantity of these pores directly influence the boiling characteristics and the heat transfer performance of the films in the nucleate boiling region. Therefore, we selected five distinct

regions of the laser-carbonized surface and analyzed the pore size distribution and the pore quantity using ImageJ. The results are presented in Figure 5d, which plots the pore quantity against the pore radius (r_c) using the data obtained from all five selected regions. Most of the pores (approximately 81%) have small radii of less than $0.5 \mu\text{m}$, but several larger pores of r_c up to $15 \mu\text{m}$ were observed near the areas where laser paths intersected. If the pore size is larger than the size of active nucleation sites at the given heat flux, the required superheat for bubble nucleation should be increased until the liquid temperature at the bubble interface exceeds the equilibrium bubble temperature. Therefore, the corresponding heat flux required to initiate boiling should be increased with the pore size (relatively larger than the size of the active nucleation sites).^{43,44} Thus, pore radii larger than $1.3 \mu\text{m}$ are intentionally excluded from the analysis because they require either a saturated heat flux $q'' > 6 \text{ W/cm}^2$ or a superheated temperature $\Delta T_{\text{sat}} > 30 \text{ }^\circ\text{C}$ for boiling incipience. The smallest pore size on the LIG surface was $r_c = 0.025 \mu\text{m}$; however, this was also excluded because the superheating required to initiate boiling was impractically large.⁴³

3.2. Onset of Boiling Criterion. As the heat flux in the system increases, vapor embryos that have been captured in the pores start to grow. Then, once the buoyancy force of the vapor bubble overcomes the surface tension force, they detach from the wall; this is called the onset of boiling (ONB). Accurately determining the heat flux required for ONB is difficult because it is closely related to multiple properties of both the fluid and the surface, including pore size, pore density, surface roughness, and surface wettability.^{45,46} Here, we estimated the pore radius and the corresponding required wall superheat temperature so that we could predict the ONB on the LIG surface using the Hsu model⁴³

$$\{r_{c,\min}, r_{c,\max}\} = \frac{\delta \left(\frac{\sin \beta}{1 + \cos \beta} \right)}{\left(1 \pm \sqrt{1 - \frac{8\sigma(1 + \cos \beta)T_{\text{sat}}}{h_{\text{fg}}\rho_g \Delta T_{\text{sat}} \delta}} \right)} \quad (4)$$

where β is the contact angle; h_{fg} , ρ , and σ are the latent heat, density, and surface tension of FC-72 at $P_{\text{atm}} = 1 \text{ bar}$, respectively; δ is the thermal boundary layer thickness, which is determined from the ratio between the thermal conductivity of the liquid (k_l) and the HTC in single-phase natural convection. The required superheat temperature, ΔT_{sat} , is defined as the difference between the surface temperature (T_s) and the saturated temperature (T_{sat}) of the working fluid. Hsu postulated in his model that ONB occurs when the liquid temperature at r_c surrounding the top surface of the bubble, exceeds T_{sat} at the vapor pressure P_g . Because ΔT_{sat} is inversely proportional to pore size and the available fluid temperature T_f decreases with the distance from the heated wall, only certain pore sizes will be activated for boiling.

Figure 6 shows the estimated ΔT_{sat} value for ONB obtained by the Hsu model in eq 4. In the figure, the LIG surface pore size is highlighted with two background colors, blue and red, corresponding to activated and nonactivated boiling sites. A contact angle of 6° and a natural convective HTC of $2 \text{ kW/(m}^2\cdot\text{K)}$ were used in this prediction.⁴⁷ Based on the surface characterization results from Section 3.1, $\Delta T_{\text{sat}} = 1.3\text{--}8.6 \text{ }^\circ\text{C}$ is required for ONB on the LIG surface.

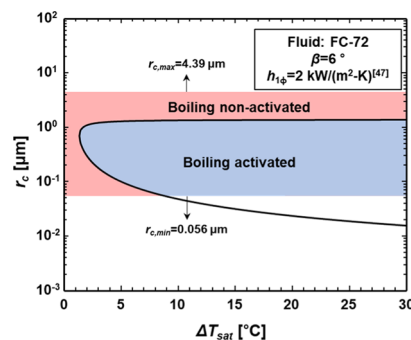


Figure 6. Wall superheat temperature with respect to the active nucleation radius obtained using the Hsu model.

3.3. Critical Heat Flux. Figure 7a,b shows the pool boiling curves and HTC, respectively, of the LIG surface and pristine polyimide film. Note that we used $\Delta T_{\text{sat}} = (T_w - T_{\text{sat}})$ as the x axis in Figure 7a because it is difficult to accurately measure the true temperature of the boiling surface, T_s . T_w is an interface temperature between the PI film and LIG, which is determined from 1D heat transfer (see Supporting Information Figure S4 for detailed vertical temperature distribution). As shown in the figure, both HTC and CHF are significantly enhanced on the LIG surfaces, compared to the pristine polyimide films. Interestingly, the LIG surface exhibited an early ONB at a relatively low heat flux of $q'' = 1.4 \text{ W/cm}^2$ owing to the larger pore sizes and higher thermal conductivity, while single-phase cooling is maintained on the pristine polyimide surface until q'' reaches a value of approximately 4 W/cm^2 . The required superheat temperature for boiling also decreased from approximately 24 to $9.3 \text{ }^\circ\text{C}$ for the pristine polyimide and LIG surfaces, respectively. Boiling heat transfer was significantly increased on the LIG surface, compared to the polyimide, enabling the LIG to maintain significantly lower superheat temperatures. The measured ONB corresponds well to the results obtained from the Hsu model, which predicted a q''_{ONB} of 1.4 W/cm^2 for the LIG surface. Boiling HTC, h , was obtained using eq 5 given subsequently. As shown in Figure 7b, the LIG surface achieved a 3-fold increase in the boiling HTC, compared to pristine polyimide, with values of $8.3\text{--}9.3$ within a range of normalized heat flux $q''/q''_{\text{CHF}} = 0.3\text{--}0.95$.

$$h = q'' / (T_w - T_{\text{sat}}) \quad (5)$$

The CHF itself also substantially increased from 18.6 W/cm^2 on pristine polyimide to 29.4 W/cm^2 on the LIG surface because the LIG provided more activated nucleation sites and an enhanced liquid supply. Further, the corresponding wall superheat temperature at the CHF was considerably lower for the LIG surface than for the pristine polyimide surface, with values of approximately 42.6 and $81.1 \text{ }^\circ\text{C}$, respectively.

Figure 8 presents the optical images of bubble formation on both the polyimide and LIG surfaces, arranged by increasing the heat flux. At a low heat flux of 3 W/cm^2 , the polyimide surface remains in the single-phase regime, but multiple nucleation sites were activated on the LIG surface, and small bubbles were continuously released from these sites. At a larger heat flux, 10 W/cm^2 , the nucleate boiling was vigorously active on both surfaces. However, boiling on the LIG surface is distributed better across many nucleation sites, resulting in smaller and larger number of bubbles, compared to those produced on the pristine polyimide surface. As the heat flux was increased to 18 W/cm^2 , large vapor columns were

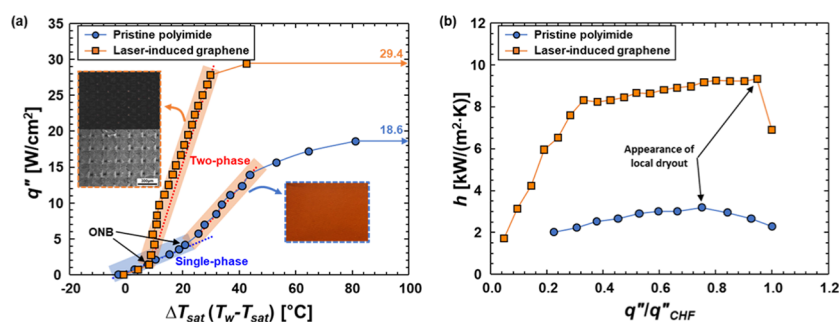


Figure 7. (a) Boiling curves and (b) HTC of the pristine polyimide and the LIG surface. The experimental results show that both CHF and HTC are significantly enhanced on the LIG surface compared to the pristine polyimide film.

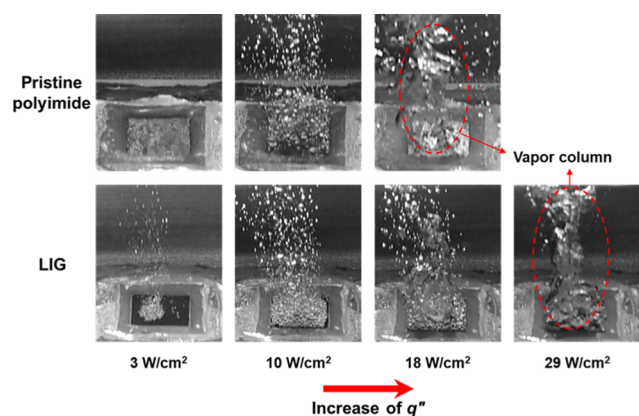


Figure 8. Visualization of pool boiling on pristine polyimide and LIG surfaces, arranged according to the increasing heat flux. Early boiling incipience was observed on the LIG surface compared to the pristine polyimide film. The nucleate boiling regime was maintained for a significantly longer period on the LIG surface, whereas disruptive vapor columns were observed on the pristine polyimide film.

generated on the pristine polyimide surface by bubble coalescence, which blocked the inflow of fresh liquid and resulted in local dry-out. Contrarily, the nucleate boiling regime was maintained on the LIG surface under this condition, and similar disruptive vapor columns were not observed until the heat flux was increased to nearly 30 W/cm².

3.4. Influence of Laser Surface Patterning. In these systems, CHF occurs when there is an insufficient supply of liquid to the heated surface. This happens when the evaporation rate exceeds the liquid supply rate or when nearly generated vapor columns prevent liquid replenishment. To address this problem, we aligned the vapor columns via laser surface texturing so that the physical pathways of the liquid supply and vapor escape could be separated, and the CHF could thus be enhanced (Figure 9a).^{48,49} The vapor column spacings were determined using the capillary length λ_{cap} of 736 μm , calculated by eq 6, for FC-72 as a reference because the bubble departure and liquid supply are both related to the gravitational and surface tension forces.

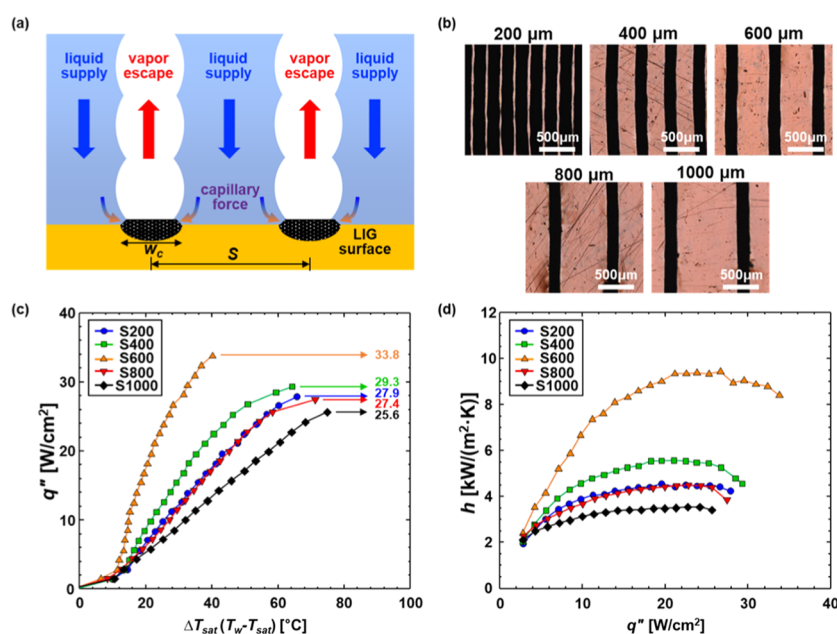


Figure 9. (a) Enhancement of the critical heat flux and the heat transfer coefficient by separating the liquid supply from the bubble flow path, where spacing variations promote boiling heat transfer. (b) Microscopic images of LIG patterns with S varying from 200 to 1000 μm . (c, d) Pool boiling curves and heat transfer coefficients with $S = 200$ –1000 μm . Both CHF and HTC increased with increasing spacing for up to 600 μm , and trends of sharp decrease were observed for any further increase in the spacing beyond 600 μm .

$$\lambda_{\text{cap}} = \sqrt{\frac{\sigma}{g(\rho_g - \rho_f)}} \quad (6)$$

A total of seven different LIG patterns with spacing values of $S = 200, 400, 500, 600, 700, 800$, and $1000 \mu\text{m}$ were fabricated and evaluated to investigate the effect of surface patterning on CHF. The optical microscopy images of these patterns obtained by a confocal microscope (OLS4100-SWF, Olympus Co., Ltd., Japan) are presented in Figure 9b. The size of the laser-carbonized and pristine polyimide area was measured from the confocal images, and the exact size and boiling data are summarized in Table 1.

Table 1. Test Matrix and Boiling Results with the Increased Liquid Pathway

sample	$w_c [\mu\text{m}]$	$S [\mu\text{m}]$	S/λ_{cap}	HTC [kW/(m ² ·K)]	CHF [W/cm ²]
S200	163.4	200	0.3	4.0	27.9
S400		400	0.5	4.7	29.2
S500		500	0.7	5.2	30.5
S600		600	0.8	7.6	33.7
S700		700	0.9	4.9	29.2
S800		800	1.1	3.9	26.7
S1000		1000	1.4	3.2	25.1

Figure 9c,d shows the pool boiling curves and HTC obtained for the various laser-patterned samples presented in Figure 9b. Figure 9c compares the boiling curves for patterns with $S = 200, 400, 600, 800$, and $1000 \mu\text{m}$, denoted herein as S200, S400, S600, S800, and S1000, respectively. Clearly, ONBs were observed at almost the same heat flux (approximately 3 W/cm^2) for all five patterns, and the wall superheat at ONB was also fairly similar. These similarities exist because the surface morphologies of the nucleation sites were fairly similar as they were all prepared by the same LIG fabrication process. Interestingly, with the increasing heat flux, distinctions in the heat transfer performance for patterns with different spacings emerged. As the heat flux increased, the wall superheat increase was weakened as the spacing increased from S200 to S600. However, the trend is reversed at larger spacing S600–S1000, and the wall superheat increased rapidly. Interestingly, CHF gradually increased from 27.8 to 29.2 W/cm² and then to 33.6 W/cm² as the spacing was correspondingly increased from S200 to S400 and then to S600 even though the total LIG area and the number of

nucleation sites decreased along the same trend. The CHF enhancement in this case is attributed to the separation of nucleate sites from the liquid supply route. The alignment of the liquid supply and vapor escape routes enabled the generation of vapor bubbles at the designated sites, which delayed bubble coalescence and large vapor column formation. However, a sharp decrease in CHF was observed for any further increase in the spacing beyond S600 as the effective heat transfer area, and the number of activated nucleation sites was reduced. For S800 and S1000, the CHF values were 26.7 and 25.1 W/cm², respectively, which were 20.2 and 25.1% lower than those for S600, and 9.0 and 14.6% lower than those obtained on the mesh-like pattern used in Figure 7, respectively. These results indicate that the boiling enhancement provided by the porous patterning diminishes when the spacing is larger than the capillary length of FC-72 ($736 \mu\text{m}$).

Figure 9d compares the HTCs for the same five patterns with respect to heat flux. Near the ONB, the HTCs were fairly similar for all of the samples. However, similar to the CHF trends, they increased as the spacing increased, with S200 and S600 samples exhibiting $h = 1.9$ – 4.5 and $h = 2.4$ – $9.3 \text{ kW/(m}^2 \cdot \text{K)}$, respectively, and then decreased as the spacing was further increased beyond S600. The corresponding wall superheat near the CHF decreased from 60.1 to 40.2 °C when the spacing was increased from S200 to S600, respectively, and then increased to 74.8 °C when the spacing was further increased to S1000.

Figure 10a,b shows the variations in CHF and HTCs, respectively, for different LIG pattern spacings. In addition to the spacings shown in Figure 9b and those evaluated in Figure 9c,d, two additional spacings of 500 and 700 μm , denoted as S500 and S700, respectively, were included to more accurately capture the heat transfer performance trends with respect to pattern spacing. The maximum CHF of 33.6 W/cm² was attained for S600, which is slightly smaller than the capillary length of FC-72 ($\lambda_{\text{cap}} = 736 \mu\text{m}$). This is probably because the CHF is related to various other parameters other than pattern spacing (e.g., surface wettability,⁵⁰ porous material thickness,⁵¹ and surface roughness⁵²). Thus, further studies are required to investigate each of these parameters to clearly understand the way the heat transfer performance can be optimized through surface patterning.

4. SUMMARY AND CONCLUSIONS

For effective cooling of flexible substrates, patterned LIG surfaces were fabricated on polyimide sheets by direct laser-induced pyrolysis. The boiling heat transfer performance was

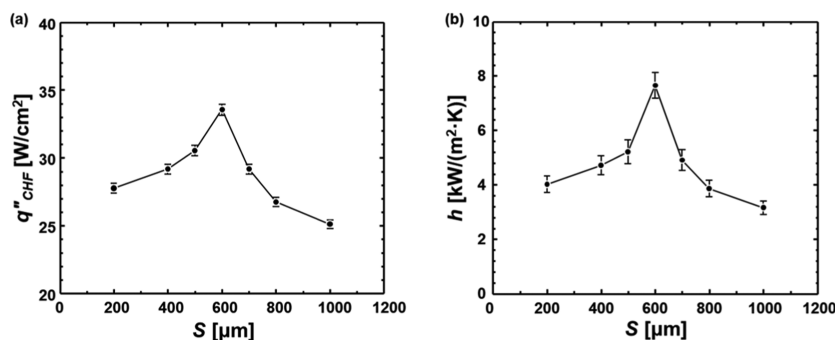


Figure 10. Enhancement of (a) CHF and (b) HTC due to the liquid pathway effect. Enhancement of both CHF and HTC was improved by separating the liquid supply and vapor escape paths, and the maximum values were achieved at a spacing of 600 μm , with corresponding enhancements of 81 and 140% compared to the pristine polyimide surface.

evaluated and found to have improved primarily because of higher thermal conductivity and superior liquid spreading provided by the LIG. Notably, the LIG surface was porous with relatively large pores that facilitated nucleation for boiling heat transfer. The LIG-patterned surface was fabricated on a commercial polyimide film using a CO₂ laser. Laser irradiation at a power of 5.3 W and a scanning speed of 200 mm/s produced a 41 μm thick porous carbon on the polyimide substrate. The droplet spreading characteristics and pore distribution of the LIG surface were investigated, and the wetting distance of the working fluid FC-72 was found to have increased 3–4 times with LIG inclusion, compared to the bare polyimide surface. Pores with radii in the range of 0.06–15 μm were produced on the LIG surface, with most pores having radii $r_c < 0.5$ μm. The maximum heat flux of 29.4 W/cm² was attained with a mesh-like LIG pattern, which represents an enhancement of approximately 60% over the CHF obtained using the pristine polyimide surface ($q''_{CHF} = 18.6$ W/cm²). The effective HTC also significantly improved, exhibiting a 2- to 3-fold increase from 1.9–3.2 to 3.1–9.3 kW/(m²·K) for the pristine polyimide and mesh-like LIG surfaces, respectively. The heat transfer performance optimization was investigated using laser patterning to separate the liquid supply and vapor escape paths. Both the CHF and HTC increased by 81 and 189%, respectively, compared to the pristine polyimide surface. The maximum CHF was observed at a spacing of 600 μm, where $S/\lambda_{cap} = 0.83$. Further studies are required for optimizing the heat transfer performance using surface patterning because various other surface properties influence this performance.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c11402>.

Bending test of PI-LIG film, Raman spectra of LIG, IR thermometer calibration, and cross-sectional SEM image of LIG (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Jung Bin In – School of Mechanical Engineering, Chung-Ang University, Seoul 06974, South Korea; orcid.org/0000-0002-9418-9873; Phone: +82-2-820-5971; Email: jbin@cau.ac.kr

Hyungsoon Lee – School of Mechanical Engineering, Chung-Ang University, Seoul 06974, South Korea; orcid.org/0000-0001-5961-6393; Phone: +82-2-820-5993; Email: leeh@cau.ac.kr; <http://atsla.cau.ac.kr>

Authors

Daeyoung Kong – School of Mechanical Engineering, Chung-Ang University, Seoul 06974, South Korea; orcid.org/0000-0003-4887-050X

Minsoo Kang – School of Mechanical Engineering, Chung-Ang University, Seoul 06974, South Korea

Kyung Yeun Kim – School of Mechanical Engineering, Chung-Ang University, Seoul 06974, South Korea

Jina Jang – School of Mechanical Engineering, Chung-Ang University, Seoul 06974, South Korea

Jungwan Cho – School of Mechanical Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do 16419, South Korea

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsami.0c11402>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by Samsung Research Funding & Incubation Center of Samsung Electronics under project number SRFC-TA1903–06 and the Chung-Ang University Graduate Research Scholarship in 2018.

■ REFERENCES

- (1) Gupta, S.; Navaraj, W. T.; Lorenzelli, L.; Dahiya, R. Ultra-Thin Chips for High-Performance Flexible Electronics. *npj Flexible Electron.* **2018**, *2*, No. 8.
- (2) Vörös, J. Trends in Epidermal Stretchable Electronics for Noninvasive Long-Term Healthcare Applications. *Int. J. Autom. Smart Technol.* **2017**, *7*, 37–52.
- (3) Al-Saleh, M. H.; Sundararaj, U. A Review of Vapor Grown Carbon Nanofiber/Polymer Conductive Composites. *Carbon* **2009**, *47*, 2–22.
- (4) Chu, K.-H.; Enright, R.; Wang, E. N. Structured Surfaces for Enhanced Pool Boiling Heat Transfer. *Appl. Phys. Lett.* **2012**, *100*, No. 241603.
- (5) Tang, Y.; Tang, B.; Qing, J.; Li, Q.; Lu, L. Nanoporous Metallic Surface: Facile Fabrication and Enhancement of Boiling Heat Transfer. *Appl. Surf. Sci.* **2012**, *258*, 8747–8751.
- (6) Kumar, U.; Suresh, S.; Thansekhar, M. R.; Babu, D. Effect of Diameter of Metal Nanowires on Pool Boiling Heat Transfer with FC-72. *Appl. Surf. Sci.* **2017**, *423*, 509–520.
- (7) Zhang, W.; Chai, Y.; Xu, J.; Liu, G.; Sun, Y. 3D Heterogeneous Wetting Microchannel Surfaces for Boiling Heat Transfer Enhancement. *Appl. Surf. Sci.* **2018**, *457*, 891–901.
- (8) Wang, Y.-Q.; Lyu, S.-S.; Luo, J.-L.; Luo, Z.-Y.; Fu, Y.-X.; Heng, Y.; Zhang, J.-H.; Mo, D.-C. Copper Vertical Micro Dendrite Fin Arrays and Their Superior Boiling Heat Transfer Capability. *Appl. Surf. Sci.* **2017**, *422*, 388–393.
- (9) Lu, M.-C.; Chen, R.; Srinivasan, V.; Carey, V. P.; Majumdar, A. Critical Heat Flux of Pool Boiling on Si Nanowire Array-Coated Surfaces. *Int. J. Heat Mass Transfer* **2011**, *54*, 5359–5367.
- (10) Liter, S. G.; Kaviani, M. Pool-Boiling CHF Enhancement by Modulated Porous-Layer Coating: Theory and Experiment. *Int. J. Heat Mass Transfer* **2001**, *44*, 4287–4311.
- (11) Wong, W. S.; Salleo, A. *Flexible Electronics: Materials and Applications*; Springer, 2009; p 481.
- (12) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* **2008**, *321*, 385–388.
- (13) Balandin, A. A.; Ghosh, S.; Bao, W.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Lett.* **2008**, *8*, 902–907.
- (14) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. Large-Scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. *Nature* **2009**, *457*, 706–710.
- (15) Wu, T.; Zhang, X.; Yuan, Q.; Xue, J.; Lu, G.; Liu, Z.; Wang, H.; Wang, H.; Ding, F.; Yu, Q.; Xie, X.; Jiang, M. Fast Growth of Inch-Sized Single-Crystalline Graphene from a Controlled Single Nucleus on Cu–Ni Alloys. *Nat. Mater.* **2016**, *15*, 43–47.
- (16) Choi, H.; Nguyen, P. T.; In, J. B. Laser Transmission Welding and Surface Modification of Graphene Film for Flexible Supercapacitor Applications. *Appl. Surf. Sci.* **2019**, *483*, 481–488.

- (17) Su, C.-Y.; Yang, C.-Y.; Jhang, B.-W.; Hsieh, Y.-L.; Sin, Y.-Y.; Huang, C.-C. Pool Boiling Heat Transfer Enhanced by Fluorinated Graphene as Atomic Layered Modifiers. *ACS Appl. Mater. Interfaces* **2020**, *12*, 10233–10239.
- (18) Li, X.-H.; Liu, P.; Li, X.; An, F.; Min, P.; Liao, K.-N.; Yu, Z.-Z. Vertically Aligned, Ultralight and Highly Compressive All-Graphitized Graphene Aerogels for Highly Thermally Conductive Polymer Composites. *Carbon* **2018**, *140*, 624–633.
- (19) Cui, S.; Jiang, F.; Song, N.; Shi, L.; Ding, P. Flexible Films for Smart Thermal Management: Influence of Structure Construction of a Two-Dimensional Graphene Network on Active Heat Dissipation Response Behavior. *ACS Appl. Mater. Interfaces* **2019**, *11*, 30352–30359.
- (20) Xu, Y.; Sheng, K.; Li, C.; Shi, G. Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process. *ACS Nano* **2010**, *4*, 4324–4330.
- (21) Chen, Z.; Ren, W.; Gao, L.; Liu, B.; Pei, S.; Cheng, H.-M. Three-Dimensional Flexible and Conductive Interconnected Graphene Networks Grown by Chemical Vapour Deposition. *Nat. Mater.* **2011**, *10*, 424–428.
- (22) Lin, J.; Peng, Z.; Liu, Y.; Ruiz-Zepeda, F.; Ye, R.; Samuel, E. L. G.; Yacamán, M. J.; Jakobson, B. I.; Tour, J. M. Laser-Induced Porous Graphene Films from Commercial Polymers. *Nature Commun.* **2014**, *5*, No. 5714.
- (23) In, J. B.; Hsia, B.; Yoo, J.-H.; Hyun, S.; Carraro, C.; Maboudian, R.; Grigoropoulos, C. P. Facile Fabrication of Flexible All Solid-State Micro-Supercapacitor by Direct Laser Writing of Porous Carbon in Polyimide. *Carbon* **2015**, *83*, 144–151.
- (24) Kumar, R.; Singh, R. K.; Singh, D. P.; Joanni, E.; Yadav, R. M.; Moshkalev, S. A. Laser-Assisted Synthesis, Reduction and Micro-Patterning of Graphene: Recent Progress and Applications. *Coord. Chem. Rev.* **2017**, *342*, 34–79.
- (25) Duy, L. X.; Peng, Z.; Li, Y.; Zhang, J.; Ji, Y.; Tour, J. M. Laser-Induced Graphene Fibers. *Carbon* **2018**, *126*, 472–479.
- (26) Ye, R.; James, D. K.; Tour, J. M. Laser-Induced Graphene. *Acc. Chem. Res.* **2018**, *51*, 1609–1620.
- (27) Ye, R.; James, D. K.; Tour, J. M. Laser-Induced Graphene: From Discovery to Translation. *Adv. Mater.* **2019**, *31*, No. 1803621.
- (28) Peng, Z.; Lin, J.; Ye, R.; Samuel, E. L. G.; Tour, J. M. Flexible and Stackable Laser-Induced Graphene Supercapacitors. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3414–3419.
- (29) Yu, Y.; Bai, S.; Wang, S.; Hu, A. Ultra-Short Pulsed Laser Manufacturing and Surface Processing of Microdevices. *Engineering* **2018**, *4*, 779–786.
- (30) Peng, Z.; Ye, R.; Mann, J. A.; Zakhidov, D.; Li, Y.; Smalley, P. R.; Lin, J.; Tour, J. M. Flexible Boron-Doped Laser-Induced Graphene Microsupercapacitors. *ACS Nano* **2015**, *9*, 5868–5875.
- (31) Smith, M. K.; Luong, D. X.; Bougher, T. L.; Kalaitzidou, K.; Tour, J. M.; Cola, B. A. Thermal Conductivity Enhancement of Laser Induced Graphene Foam upon P3HT Infiltration. *Appl. Phys. Lett.* **2016**, *109*, No. 253107.
- (32) Venkatachalam, S.; Depriester, M.; Sahraoui, A. H.; Capoen, B.; Ammar, M. R.; Hourlier, D. Thermal Conductivity of Kapton-Derived Carbon. *Carbon* **2017**, *114*, 134–140.
- (33) Kim, K. Y.; Choi, H.; Tran, C. V.; In, J. B. Simultaneous Densification and Nitrogen Doping of Laser-Induced Graphene by Duplicated Pyrolysis for Supercapacitor Applications. *J. Power Sources* **2019**, *441*, No. 227199.
- (34) Han, G. H.; Chae, S. J.; Kim, E. S.; Güneş, F.; Lee, I. H.; Lee, S. W.; Lee, S. Y.; Lim, S. C.; Jeong, H. K.; Jeong, M. S.; Lee, Y. H. Laser Thinning for Monolayer Graphene Formation: Heat Sink and Interference Effect. *ACS Nano* **2011**, *5*, 263–268.
- (35) Ehrhard, P.; Davis, S. H. Non-Isothermal Spreading of Liquid Drops on Horizontal Plates. *J. Fluid Mech.* **1991**, *229*, 365–388.
- (36) Coleman, H. W.; Steele, W. G. Engineering Application of Experimental Uncertainty Analysis. *AIAA J.* **1995**, *33*, 1888–1896.
- (37) Kong, D.; Jung, K. W.; Jung, S.; Jung, D.; Schaadt, J.; Iyengar, M.; Malone, C.; Kharangate, C. R.; Asheghi, M.; Goodson, K. E.; Lee, H. Single-Phase Thermal and Hydraulic Performance of Embedded Silicon Micro-Pin Fin Heat Sinks Using R245fa. *Int. J. Heat Mass Transfer* **2019**, *141*, 145–155.
- (38) Ahn, H. S.; Lee, C.; Kim, J.; Kim, M. H. The Effect of Capillary Wicking Action of Micro/Nano Structures on Pool Boiling Critical Heat Flux. *Int. J. Heat Mass Transfer* **2012**, *55*, 89–92.
- (39) Kim, B. S.; Lee, H.; Shin, S.; Choi, G.; Cho, H. H. Interfacial Wicking Dynamics and Its Impact on Critical Heat Flux of Boiling Heat Transfer. *Appl. Phys. Lett.* **2014**, *105*, No. 191601.
- (40) Shim, D. I.; Choi, G.; Lee, N.; Kim, T.; Kim, B. S.; Cho, H. H. Enhancement of Pool Boiling Heat Transfer Using Aligned Silicon Nanowire Arrays. *ACS Appl. Mater. Interfaces* **2017**, *9*, 17595–17602.
- (41) Washburn, E. W. The Dynamics of Capillary Flow. *Phys. Rev.* **1921**, *17*, 273–283.
- (42) Xiao, R.; Enright, R.; Wang, E. N. Prediction and Optimization of Liquid Propagation in Micropillar Arrays. *Langmuir* **2010**, *26*, 15070–15075.
- (43) Hsu, Y. Y. On the size range of active nucleation cavities on a heating surface. *Int. J. Heat Mass Transfer* **1962**, *84*, 207–213.
- (44) John, G.; Collier, J. R. T. *Convective Boiling and Condensation*, 3rd ed.; Oxford, 1996.
- (45) Chi-Yeh, H.; Griffith, P. The Mechanism of Heat Transfer in Nucleate Pool Boiling—Part I. *Int. J. Heat Mass Transfer* **1965**, *8*, 887–904.
- (46) Li, C.; Wang, Z.; Wang, P.-I.; Peles, Y.; Koratkar, N.; Peterson, G. P. Nanostructured Copper Interfaces for Enhanced Boiling. *Small* **2008**, *4*, 1084–1088.
- (47) Zupančič, M.; Može, M.; Gregorčič, P.; Golobič, I. Nanosecond Laser Texturing of Uniformly and Non-Uniformly Wettable Micro Structured Metal Surfaces for Enhanced Boiling Heat Transfer. *Appl. Surf. Sci.* **2017**, *399*, 480–490.
- (48) Rahman, M. M.; Pollack, J.; McCarthy, M. Increasing Boiling Heat Transfer Using Low Conductivity Materials. *Sci. Rep.* **2015**, *5*, No. 13145.
- (49) Jaikumar, A.; Kandlikar, S. G. Pool Boiling Enhancement through Bubble Induced Convective Liquid Flow in Feeder Microchannels. *Appl. Phys. Lett.* **2016**, *108*, No. 041604.
- (50) O'Hanley, H.; Coyle, C.; Buongiorno, J.; McKrell, T.; Hu, L.-W.; Rubner, M.; Cohen, R. Separate Effects of Surface Roughness, Wettability, and Porosity on the Boiling Critical Heat Flux. *Appl. Phys. Lett.* **2013**, *103*, No. 024102.
- (51) Zou, A.; Maroo, S. C. Critical Height of Micro/Nano Structures for Pool Boiling Heat Transfer Enhancement. *Appl. Phys. Lett.* **2013**, *103*, No. 221602.
- (52) Kim, J.; Jun, S.; Laksnarain, R.; You, S. M. Effect of Surface Roughness on Pool Boiling Heat Transfer at a Heated Surface Having Moderate Wettability. *Int. J. Heat Mass Transfer* **2016**, *101*, 992–1002.