A modified spin-casting approach for scalable preparation of ultra-thick reduced graphene oxide films with high thermal conductivity

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Abstract

With the fast development of high-power electronic devices in recent years, the demand for high-performance thermal dissipation films with high thermal conductivity and large thickness has dramatically increased. Graphene has shown great potential in thermal management due to its extremely high thermal conductivity. However, it remains a significant challenge to achieve high thermal conductivity in thick graphene films ($\geq 100 \mu m$). Herein, a scalable strategy combining a modified layer-by-layer ‘spin-casting’ solution deposition method and multi-step annealing post treatment was adopted for preparing ultra-thick, highly thermal conductive graphene films. The properties of the graphene films were characterized by SEM, XRD, Raman, and XPS, exhibiting excellent graphitic crystallinity, well aligned and dense packing assembly structure. These nearly ideal structural features endow the graphene films with high in-plane thermal conductivity of $1265 \pm 46 \ W \ m^{-1} K^{-1}$ at a large thickness of $100 \mu m$. The ultra-thick graphene films show superior thermal dissipation performance as compared with traditional Cu/Al foil, demonstrating their great potential in the field of highly-efficient heat spreader films for the next generation of high-power devices.

Introduction

In recent years, the rapid progress of miniaturization and integration level of microelectronic devices leads to the considerable heat generation per unit area, resulting in great challenges for the performance stability and long-term reliability of the electronic products, such as smartphone, 5G communication equipment [1, 2]. Common commercial thermal management materials mainly include metallic materials (Ag, Cu, Al, etc.) and pyrolysis graphite film. However, the formers have relatively low thermal conductivity (200–500 W m$^{-1}$ K$^{-1}$) and high density, making them unsuitable for high-performance heat dissipation applications [3]. While for the latter, the thermal conductivity will decrease significantly with increasing the thickness of pyrolysis graphite film, as the orientation and crystallinity of pyrolysis graphite will decrease with film thickness [4]. Considering this heat dissipation problem for large heat flux, more efficient thermal management materials with high thermal conductivity and large film thickness are urgently demanded.

Due to the intrinsic nature of $\text{sp}^2$ hybridized carbon and 2D honeycomb lattice of the graphene, phonon transmission inside graphene layers can be highly efficient, endowing the monolayer graphene with ultra-high in-plane thermal conductivity (2000–5000 W m$^{-1}$ K$^{-1}$), far beyond that of bulk graphite ($\sim 2000 \ W \ m^{-1} K^{-1}$) [5–7]. Ascribed to such extraordinary thermal property, together with high mechanical property and
lightweight, graphene materials are recognized as an ideal candidate for the high-performance thermal management materials [8–13]. Several approaches have been exploited to realize the practical utilization of graphene in heat dissipation, such as graphene/polymer composite thermal interface materials (TIMs) and graphene film lateral heat spreaders [14–17]. For the graphene/polymer composite approach, although the addition of graphene into polymer matrix can notably improve the thermal properties of the composites, the thermal conductivity is still too low (1 ~ 2 orders of magnitude lower than monolayer graphene) for high-performance thermal management materials, because of the high interface thermal resistance between the graphene and the matrix [18–20].

Recently, owing to the outstanding thermal, mechanical, and electrical properties, many efforts have been devoted to preparing graphene films for heat dissipation [13, 21–24]. The fabrication methods of graphene films mainly include solution-based deposition and chemical vapor deposition (CVD) [11, 13, 25]. Generally, the growth efficiency of CVD-derived graphene films is relatively low and it is difficult to acquire large film thickness, limiting the large-scale heat dissipation application of high heat flux. In comparison, the solution-based deposition methods show unique advantages in preparation of graphene films. The graphene oxide (GO) is extensively used to form the homogeneous solution precursor due to the good dispersity of GO in water and polar organic solvents [26, 27]. Several solution deposition techniques have been developed for fabricating GO films with a wide range of thickness, including vacuum filtration, doctor blade coating, centrifugal casting, and so on [8, 13, 28–32]. Solution-derived GO films usually have a layered structure, and reduced GO (rGO) films can be obtained by reduction the GO films through chemical or thermal treatment [13, 17, 33–36], endowing rGO films with high in-plane thermal conductivity. By carbonizing at 1300 °C and graphitizing at 3000 °C, as well as compressing at 50–300 MPa, the obtained rGO films showed a high thermal conductivity of 1940 ± 113 W m−1 K−1 [10]. This is probably resulted from the reduction of functional groups on graphene, and the healing of defect sites of graphene (transforming the sp3 hybridized carbon of GO to the sp2 hybridized carbon of graphene) [8, 37]. By engineering the structures of graphene films in the aspects of grain size, film alignment and thickness, and interlayer binding energy, Wang et al reported an ultra-high thermal conductivity for rGO films, up to 3200 W m−1 K−1 [33]. However, these reported high thermal conductivity data are almost from rGO films with small film thickness of a few microns. Because it is relatively easy to achieve high orientation of GO/rGO sheets in thin films [38–40]. Until now, it is still challenging to realize large film thickness yet good orientation in a reduced/graphitized GO film for high-performance heat dissipation applications [41, 42]. As the volume or concentration of GO solution increases, the evaporation of the external solvent may lead to a shell layer which will inhibit the uniform evaporation of internal solvent and limit the orientation of inner GO sheets [10]. For instance, Zhang et al prepared graphene films of different thicknesses by controlling filtration volume or GO concentration during the vacuum filtration process. As the film thickness increased from 20 μm to 60 μm, the in-plane thermal conductivity reduced from 1642 W m−1 K−1 to 675 W m−1 K−1, due to an increase in the structural defect number within the thicker films [12].

According to several related research works, the excellent thermal conductivity of graphene films might be closely associated with the low defect content in the graphene sheets and the highly oriented layer-by-layer compact-stacking microstructure, both of which are beneficial to the phonon transmission [31, 33, 43]. As for the GO films, an ultra-high temperature graphitization (>2800 °C) post-annealing is necessary to fully remove the defect and restore the crystalline structure of the graphene sheets [10, 34, 41, 44]. However, when the GO films are thermally reduced/graphitized, the interstitial water and oxygen-containing groups in the GO sheets will release in gaseous form, leading to lots of voids/micro-bubbles between graphene layers and significant expansion of the graphene films [31, 45–47]. These expanded layer-spacing will serve as scattering sites for phonons, severely deteriorating thermal conductivity of graphene films. A simple mechanical pressing method is often used to improve the packing density of the graphitized graphene films [31, 48, 49].

This work reports a layer-by-layer spin-casting method to prepare large-scale thick GO films for high-performance thermal dissipation applications, inspired by the previously reported centrifugal casting and spin-casting techniques [29, 38]. A highly oriented thick GO film was prepared by the well-assembled GO sheets in each spin-casting cycle. Subsequently, a modified multi-step carbonization/graphitization process was carried out on the as-prepared thick GO films, including a hot-pressing carbonization step at 1800 °C and a graphitization step at 2800 °C. The structure evolution of the graphene films was systematically investigated by SEM, XRD, XPS, and Raman spectroscopy. The obtained graphene film with a large thickness of 100 μm has a thermal conductivity of 1265 ± 46 W m−1 K−1, due to the excellent graphitic crystallinity, well aligned and densely packed structure within the ultra-thick films. These graphene films can be used as highly efficient heat spreader film with high heat flux carrying capacity for the thermal dissipation of various high power-density electronics.
Experimental

Preparation of ultra-thick GO films
A well-dispersed GO aqueous solution with a moderate concentration of 5 mg mL\(^{-1}\) was prepared using modified Hummers’ method\(^{[50, 51]}\). A custom-designed equipment with a rotatable hollow drum was utilized to fabricate the ultra-thick GO films, schematically shown in figure 1(a). A certain amount of GO solution (20 ml) was first dropped uniformly into the bottom of the drum, followed by rotating the drum with a speed of 2000 rpm. At the same time, infrared heating was applied to promote the solvent evaporation of GO solution. After continuous curing of rotating and heating for 45 min, a thin GO layer with an average thickness of \(\sim 0.8\ \mu m\) was obtained. Subsequently, several process cycles including solution dropping, drum rotating and infrared heating were carried out to fabricate GO films with various thicknesses up to \(\sim 300\ \mu m\) (figure 1(b)).

Preparation of graphene films
The as-prepared GO films were reduced and graphitized through multi-step thermal annealing to fabricate the fully restored graphene films, as schematically shown in figure 1(c). For the reduction and carbonization annealing steps, a vacuum hot-press furnace (BTF-2300-VP-120, Anhui BEQ) was utilized, with a base pressure of \(2 \times 10^{-3}\) Pa and a maximum temperature of 1800°C. First, GO films were heat-treated at 500°C for 0.5 h under a pressure of 1 kPa, with a ramp rate of 1 °C min\(^{-1}\) (room temperature to 500°C). Most of the oxygen-containing groups in the GO sheets were removed as small-molecule gas\(^{[36]}\), with the film thickness increased by a factor of 2–3. Then, the reduced GO films were further carbonized at 1800°C for 1 h under a pressure of 20 MPa, with the ramp rate of 5 °C min\(^{-1}\) (500°C to 1800°C) to obtain the densely packed graphene film. The third annealing step was conducted on a graphitization furnace (customized model, Shanghai Chenhua). The hot-pressed graphene films were graphitized at 2800°C for 1 h, under the protection of Ar atmosphere. During this annealing step, the remaining defects in the graphene sheets were fully restored, and the residual oxygen impurity atoms were released as small molecule gas\(^{[10]}\). Finally, each graphene film was compressed by a roller press (MSK-HRP-04 UL, Hefei Kejing) at a speed of 10 cm min\(^{-1}\) for 3 times, to diminish the expansion of the graphene films generated in the third annealing step. In the following discussion, the graphene films after different annealing steps were named GO-500, GO-1800, and GO-2800, respectively.

Characterization
The surface and cross-section morphologies of the graphene films were characterized using a field emission scanning electron microscope (SEM, Apero C HiVac, THERMO SCIENTIFIC) at 15 kV. X-ray diffraction (XRD, D8 Discover, Bruker, Cu Kα line with wavelength of 1.5406 Å) patterns, X-ray photoelectron spectroscopies (XPS, ESCALAB 250XI, THERMO SCIENTIFIC), and Raman spectroscopies (LabRAM HR,
Horiba-JY, excitation wavelength of 532 nm were recorded to investigate the structure evolution of the GO/graphene films during the different annealing steps. Mechanical property tests were performed on MTS Exceed E43 equipped with a 10 N detector at a tensile rate of 1 mm min$^{-1}$. The graphene films were cut into 3 mm-width strips to prepare the mechanical test samples, and the gauge length was 10 mm. Electrical conductivity measurements were carried out with four-probe experimental set-up using an RTS-8, 4 probes TECH. Thermal conductivity tests were conducted on a laser flash apparatus (LFA-447, Netzsch). Infrared thermal images were captured using an infrared imager (T1480 pro, FLUKE) for the demonstrative thermal dissipation application of the graphene films.

**Results and discussion**

Figure 2(a) shows the photograph of an as-prepared GO film with a size of 10 cm \times 25 cm, demonstrating the scalability of the modified ‘spin-casting’ method. The detailed fabrication process of the ultra-thick GO films is schematically illustrated in figure 1(a). A film-forming procedure similar to spin-casting occurs during the preparation of GO films. Once the GO solution is dropped into the bottom of the rotatable drum and spread out, the drum starts to rotate at high speed. A thin GO solution film forms under the impact of centrifugal force, like the film formation mechanisms of spin coating/spin casting. The water in the GO solution film evaporates under high-speed rotating and infrared heating, and an ultra-thin GO layer is acquired with a mono-layer thickness of \(\sim 0.8 \mu m\). The small thickness of GO solution film results in an excellent stacking order of the ultra-thin GO layer, as illustrated in figure 2(b). A second solution ‘spin-casting’ cycle is then carried out on the previously obtained GO film. By adjusting the cycle number of the solution deposition process, different GO film thicknesses can be obtained through a ‘layer-by-layer’ manner. An ultra-thick GO film with a maximum thickness of 300 \(\mu m\) is assembled after \(\sim 380\) ‘spin-casting’ cycles, and the interfaces among GO layers are fused together and indistinguishable, as shown in figures 2(b), (c).
Annealing process, as schematically shown in Figure 1(c). During the first vacuum hot-pressing step at a temperature below 500 °C, a large portion of oxygen-containing groups on the GO sheets are removed as gas [36, 46, 52], as evidenced by Thermogravimetric (TG) results in Figure S1 (available online at stacks.iop.org/MRX/9/036405/mmedia). As the released gas may cause structure damage to the GO films, a small pressure of 1 kPa was applied to the GO films to ensure the integrity of the assembly structure. Despite the applied small pressure during annealing, the thickness of the GO-500 film has almost doubled. For a detailed investigation of the morphology variation during the multi-step annealing, relatively thin GO films are used for cross-sectional SEM characterization (Figures 2(c)–(g)). The highly oriented structure is maintained in GO-500 film as compared with as-received GO films (Figure 2(c)), while expanded layer gaps with dimension of a few microns can be observed, resulting from the released gas during the first annealing step (Figure 2(d)) [36]. In the second vacuum hot-pressing step at 1800 °C, some of the defects in the GO-500 films are removed, and small molecular gas is still released with a relatively low speed (Figure S1) [36, 53]. Meanwhile, the thickness of the GO-1800 film dramatically decreases to about one-sixth of GO-500 film under the high-pressure of 20 MPa. Figure 2(e) shows a highly-oriented and densely-packed structure of the GO-1800 film after the second vacuum hot-pressing step. In the third annealing step, the GO-1800 films are treated at an ultra-high temperature of 2800 °C with the protection of Ar atmosphere, a typical condition for the graphitization of graphene films [46]. The defects (atomic vacancies) in the graphene sheets are expected to shift to the border of graphene crystalline domains and be annihilated, resulting in fully restoration of sp² graphitic lattice during this annealing step [41]. However, a small amount of gas is still released upon the graphitization step, leading to a mass loss of about 3%. The released gas introduces some micro-gasbags between graphene sheets, causing expansion of the GO-2800 films, as illustrated in Figure 2(f). To eliminate the gasbags in the graphene films, a roller-pressing treatment is carried out on the GO-2800 films at room temperature. By adjusting the roller gaps and rolling speed, typical features of excellent orientation and dense packing for the graphene layers can be observed in Figure 3(g). The maximum thickness of the GO-2800 film decreases to ∼100 μm after roller-pressing for 3 times, as shown in Figure S2.

Finally, an ultra-thick compact graphene film is obtained without delamination, with a high density (2.1 g cm⁻³) close to the graphite block.

In a graphene film, the thermal conduction is mainly dominated by the phonon (lattice vibration) propagating in the individual graphene sheets and phonon transferring through the interfaces between adjacent sheets [5, 13, 54]. As in the case of this work, multi-step high temperature annealing resulted in the removal of functional groups and defects in the graphene sheets, as well as restore of sp² from sp³ hybridized structure by carbon atomic reorganization [37, 55]. These structural features may be considered as the first factor responsible for high thermal conductivity of the graphene films in this work, and can also be verified by XRD and Raman characterizations in the following section. As previously reported, phonons show a relatively long mean free path (MFP) of ∼28 μm in a high crystallinity CVD-derived graphene sheet with a near ballistic transporting.
mechanism, which is the main cause of the high thermal conductivity [7]. The defective sp³ hybridized carbon can serve as scattering sites for the phonons, which will lead to fast attenuation of energy transmitted by the phonons [54]. Once the content of the sp³ defect decreases within the graphene sheets by multi-step annealing, the probability of ballistic transporting for phonons can be enhanced and the MFP will increase significantly, leading to higher efficiency for thermal conduction. Moreover, the well-aligned and densely-packed micro-structures may be considered as the second factor responsible for the high-thermal conductivity. As can be seen in figure 2(g), the graphene sheets mostly align along the film, and when phonons propagate within the film, the transporting routes will be the shortest, as compared with the misaligned situation (figure 3(f)). The shorter phonon transporting route, the lower phonon scattering probability of defects within the graphene sheets or at the interfaces, which will certainly lead to higher thermal conductivity [13, 33]. On the other hand, the dense packing of graphene sheets can eliminate the interface defects such as gasbags and provide additional interface transmission paths for phonons within the film, leading to further enhancement of thermal conductivity [10, 13]. Therefore, by combining modified layer-by-layer ‘spin-casting’ and multi-step annealing, the as-received ultra-thick graphene films are composed of high-crystallinity graphene sheets with well-aligned and densely-packed micro-structure, endowing the films with high thermal conductivity.

To clarify the effect of high-pressure hot-pressing treatment on the assembly structure of the graphene films, the 1800 °C annealing without applying any pressure was also carried out on the as-received GO films. Figures 3(a), (d) show the difference in visual appearance between the hot-pressed and non-hot-pressed graphene films. Apparently, there are more creases on the surface of the sample without hot-pressing. In comparison, the hot-pressed sample exhibits a smooth surface with a metallic texture. The SEM surface morphologies in figures 3(b), (e) also demonstrate a significant difference between the hot-pressed and non-hot-pressed samples. A lot of micro-wrinkles uniformly distribute over the whole surface of the non-hot-pressed graphene film, while the surface morphology of the hot-pressed one is comparatively smooth with only a few flattened folds. Moreover, the non-hot-pressed graphene film shows larger layer gaps and more micro-voids than the hot-pressed one, indicating a more loosely packed structure (figure 3(f)). These structural defects (large layer gaps, micro-voids, and micro-wrinkles) are regarded as phonon scattering centers, increasing thermal resistance between graphene layers/sheets [5, 13]. As a result, the hot-pressing treatment at 20 MPa is crucial to achieve high thermal conductivity for the graphene films.

Systematically characterizations of structure features are conducted for reduced GO/graphene films at different annealing steps. Figure 4(a) shows XRD patterns of the as-received GO, GO-500, GO-1800, and GO-2800 graphene films, detailed peak parameters are summarized in table S1. The XRD d-spacing (002) decreases from 8.00 Å (θ = 10.99°) in as-received GO film to 3.35 Å (θ = 26.55°) in graphitized GO-2800 graphene film (closer to the value in graphite block) [37], indicating the complete removing of the oxygen-containing groups and full repairing of the graphitic lattice of the graphene sheets. Moreover, the full width at half maximum (FWHM) of the diffraction peak decreases significantly from 2.41° for as-received GO film to 0.14° for graphitized GO-2800 graphene film, meanwhile the peak intensity also increases dramatically. All the features...
consistent with the results of TG in gradually removed with the increase of annealing temperature in the subsequent annealing steps, which is four peaks, representing four types of C atoms, namely, the sp² C atoms of graphitic lattice showing a similar trend to the survey curves. For the as-received GO, high crystallinity of the graphene mentioned above of XRD patterns indicate the effectiveness of the multi-step annealing treatment on acquiring high crystallinity of the graphene films. The evolution of the defect content in the graphene sheets upon multi-step annealing treatments is characterized by Raman spectra, as shown in figure 4(b). In a Raman spectrum of graphene materials, the G peak (∼1580 cm⁻¹) represents the sp² carbon of well-ordered graphitic structures on graphene sheets, while the D band (∼1346 cm⁻¹) represents the sp³ carbon of the defects on graphene sheets [17]. Generally, the intensity ratio (I_D/I_G) can be used to indicate the defect content of the graphene films, which is a critical factor determining phonon scattering and thermal conductivity in the graphene films [56–58]. The I_D/I_G ratios for the as-received GO film, GO-500, and GO-1800 graphene films are all over 1 (table S2), indicating relatively high defect content on these graphene films. In comparison, the D band almost vanishes for the 2800 °C graphitized graphene film, leading to an extremely low I_D/I_G ratio of ∼0.07. This result indicates that the ultra-high temperature graphitization can effectively restore the defect in the graphene sheets. The XPS measurements are also carried out to verify the variation of the oxygen-containing groups by comparing survey curves and C 1s spectra of graphene films at different annealing steps. The XPS survey curves (figure 5(c)) demonstrate that the oxygen content decreases significantly upon multi-step annealing. Particularly, most of the oxygen atoms are removed in the first annealing step at 500 °C. Meanwhile, the residual oxygen atoms are then gradually removed with the increase of annealing temperature in the subsequent annealing steps, which is consistent with the results of TG in figure S1. The C 1s XPS spectra of GO and GO-2800 films (figure S3) also show a similar trend to the survey curves. For the asreceived GO film, C 1s spectrum can be deconvoluted into four peaks, representing four types of C atoms, namely, the sp² C atoms of graphitic lattice (C=C, ∼284.5 eV), sp³ C atoms of defects (C=C, ∼285.1 eV), C atoms single-bonded to oxygen (C=O, ∼287.1 eV), and C atoms double-bonded to oxygen (C=O, ∼288.8 eV) [39]. While for the GO-2800 graphene film, the peaks of C atoms bonded to oxygen completely disappear, owing to the fully removing of oxygen-containing groups. The content of sp³ C atoms (defects) decreases significantly upon graphitization at 2800 °C, as summarized in table S3. Moreover, a wide peak of graphitic lattice C atoms related to π* plasmon arises in the sample, demonstrating the well-ordered structure in the GO-2800 graphene film once again [31].

The mechanical property of the graphene film is derived from the stress-strain curve shown in figure 4(d). The graphene film possesses a high tensile strength of 98 ± 19 MPa and a large elongation at break of ∼4%, both of which are among the highest values for the graphene films ever reported [8, 24, 31, 33, 42]. The average modulus of the graphene films is 4.5 ± 0.5 GPa. The excellent mechanical property of the graphene film originates from the high crystallinity and highly-ordered structure of the film. The effect of thickness on the electrical conductivity of graphene films is illustrated in figure 4(e). The electrical conductivity decreases from ∼8.8 × 10⁵ S cm⁻¹ to 4.3 × 10⁵ S cm⁻¹ with the thickness increasing from 20 μm to 100 μm, indicating that interlayer resistance becomes more predominant with the increase of film thickness. Figure 4(f) shows the effect of film thickness on the in-plane thermal conductivity of graphene films at room temperature. The variation
tendency is almost the same as that of electrical conductivity. Thermal conductivity decreases gently from \( \sim 1565 \ \text{W m}^{-1} \ \text{K}^{-1} \) to \( \sim 1265 \ \text{W m}^{-1} \ \text{K}^{-1} \) when the film thickness increases from 20 \( \mu \text{m} \) to 100 \( \mu \text{m} \). The slight decrease of thermal conductivity in the thicker graphene films is mainly ascribed to the increase of phonon scattering probability at the interface defects between graphene layers, such as gasbags, wrinkles, and interspaces [36]. Generally, thermal conductivity depends on the integrity/crystallinity of individual graphene sheet and the contact between the sheets [30, 33, 34]. The systematically optimized multi-step annealing provides the graphene film with high crystallinity and well-ordered assembly structure. Moreover, the good alignment and dense packing features of the graphene films are beneficial to close contact of graphene sheets, leading to relatively high thermal conductivity (\( > 1200 \ \text{W m}^{-1} \ \text{K}^{-1} \)) for the graphene films even with a high thickness over 100 \( \mu \text{m} \), superior to the thick graphene films ever reported [34, 41, 42]. Notably, the thermal conductivity of such ultra-thick graphene film is also significantly greater than that of pyrolytic PI film with thickness of 100 \( \mu \text{m} \) (622 \( \text{W m}^{-1} \ \text{K}^{-1} \)) [60].

The modified ‘spin-casting’ approach and the multi-step annealing post-treatment provide an opportunity for the large-scale fabrication of high-quality ultra-thick graphene films, which is promising for the thermal dissipation of high-power devices. To further validate the potential of the ultra-thick graphene films to serve as thermal interface membranes, the heat dissipation properties have been compared between high thermal conductive Cu/Al foil and the ultra-thick graphene film by infrared thermography, both films have the same thickness of \( \sim 100 \ \mu \text{m} \). The hot spot is supplied by an electric heating tip with a temperature of 200 °C, as shown in figures 5(a), (c). The heat transfer of the graphene film exhibits a much higher rate than that of Cu and Al foils, spending shorter time interval to reach equilibrium state. Figures 5(d)–(f) show the infrared images at the heating time of 1 min for the three different films, and the brighter heated-regions centered at the hot spot can be clearly observed on the Cu and Al foils. As shown in figure 5(b), the temperature distribution of Cu and Al foils along the line across the hot spot shows a high temperature gradient of \( \sim 40 \) °C and \( \sim 61 \) °C, respectively. In comparison, the temperature profile of the graphene film is much more uniform, with a low temperature gradient of 19 °C (figure 5(b)). Therefore, the fabricated ultra-thick graphene films outperform the traditional Cu and Al foils in terms of heat dissipation.

**Conclusion**

In this work, a novel method is reported for preparing high quality ultra-thick graphene films by a modified layer-by-layer ‘spin-casting’ GO solution depositing method and subsequent multi-step annealing post treatment. The as-prepared graphene films exhibit highly oriented and densely packed assembly structures. The multi-step annealing treatment can endow the ultra-thick graphene films with full restoration of graphitic lattice and highly ordered structure, leading to the high thermal conductivity of 1265 ± 46 \( \text{W m}^{-1} \ \text{K}^{-1} \) even for the film thickness over 100 \( \mu \text{m} \). The thermal dissipation performance of the ultra-thick graphene film is superior to that of traditional Cu/Al thermal management membrane, demonstrating its great potential in heat spreading of the next generation of high-power devices.

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**Data availability statement**

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

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