RGO and Three-Dimensional Graphene Networks Co-modified TIMs with High Performances

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Abstract
With the development of microelectronic devices, the insufficient heat dissipation ability becomes one of the major bottlenecks for further miniaturization. Although graphene-assisted epoxy resin (ER) display promising potential to enhance the thermal performances, some limitations of the reduced graphene oxide (RGO) nanosheets and three-dimensional graphene networks (3DGNs) hinder the further improvement of the resulting thermal interface materials (TIMs). In this study, both the RGO nanosheets and 3DGNs are adopted as co-modifiers to improve the thermal conductivity of the ER. The 3DGNs provide a fast transport network for phonon, while the presence of RGO nanosheets enhances the heat transport at the interface between the graphene basal plane and the ER. The synergy of these two modifiers is achieved by selecting a proper proportion and an optimized reduction degree of the RGO nanosheets. Moreover, both the high stability of the thermal conductivity and well mechanical properties of the resulting TIM indicate the potential application prospect in the practical field.

Keywords: Thermal Interface Materials, Graphene, Thermal Boundary Resistance

Background
Graphene-assisted thermal interface materials (TIMs) have attracted increasing attention because of their high thermal and mechanical performances [1–5]. Kim et al. reported that the resulting thermal conductivity is 1400% higher than the pristine epoxy resin (ER), and Joen’s group found that a 10 wt% additional graphene filler will bring about a high thermal conductivity (~ 2 W/mK) [3, 4]. However, considering the theoretical thermal conductivity of this unique material is as high as 5000 W/mK [6], the reported results are far from satisfactory. Although graphene is expected to act as the fast transport channel for phonon in the TIMs during the thermal transport process, the nano-scaled RGO sheets lack a continuous structure to form the transport network. Moreover, overmuch interfaces of the RGO nanosheets lead to a high total thermal boundary resistance (Kapitza scattering), which results in a strong phonon scattering [7]. At last, the high defect density of the RGO nanosheets due to the violent oxidation-reduction processes also brings about an extra thermal resistance source (shortening the mean free path of phonon, Umklapp scattering) [8].

In order to give full play to the high thermal conductivity of the adopted graphene, high-quality three-dimensional graphene networks (3DGNs) prepared by chemical vapor deposition method have been adopted to hybridize with ER by our group [7]. The better thermal and mechanical properties of the 3DGNs-ER (compared with that of the RGO-based sample) manifest the fatal significance of the low defect density and the continuous construction of the employed graphene [9]. On the other hand, originating from the absence of surface functional groups of the 3DGNs, a bottleneck, a bed contact between the 3DGNs and ER (a poor wettability of the 3DGNs), is revealed with the ongoing study. Based on our recent report, a moderated amount of surface defects of the 3DGNs can play as a positive role to improve the contact between the graphene basal plane and matrix [10, 11]. However, some tedious adjustment processes including a precise CH4 flow and a strict cooling rate of the substrate are needed during the CVD procedure [12]. Therefore, an idea on combining the RGO...
nаношитов и 3DGNs, чтобы использовать их преимущества, естественно представлены.

В этом исследовании, RGO наношиты и 3DGNs являются агентами захвата, которые улучшают термические свойства материала. Определенные функции этих двух модификаторов обсуждаются и доказаны. На одной стороне, 3DGNs обеспечивают быстрый транспортный путь, увеличивая термические свойства. На другой стороне, RGO наношиты загружаются на поверхность 3DGNs, что улучшает термические свойства. Дальнейшее улучшение термических свойств материала достигается за счет синергии RGO наношитов и 3DGNs.

**Methods**

**Materials**

Картофельный каркас с плотностью 300 г/см куб в ареале и плюс 12 мм в толщину, который был приобретен у Haobo Co., Ltd. (Shenzhen, China) и использовался в качестве шаблона для получения 3DGNs. Этиловый спирт, HCl, FeCl3 и полиметилметакрилат (PMMA) были приобретены у Shanghai Chromatography Chemical Reagent Plant (Beijing, China). Этиловый лактат, поли(метилметакрилат) и ацетон были приобретены у Aladdin Co., Ltd. (Suzhou, China). Суперчистая вода (режимом 18 MΩ cm) была использована для приготовления всех водных растворов. Силиконовые смеси были получены у Sanmu Co. Ltd. (Dongguan, China). Методы обработки и восстановления были обсуждены и доказаны. На одной стороне, термические свойства материала улучшаются за счет синергии RGO наношитов и 3DGNs.

**Preparation**

Подготовка RGO наношитов и 3DGNs была проведена нашей группой [12–14], и более подробные сведения приведены в приложении. RGO-3DGNs-ER композит был изготовлен методом две-шаговой методики. Сначала, гидротермальное соединение RGO наношитов и 3DGNs было получено через гидротермальную реакцию, которая является предварительным условием для последующей обработки 3DGNs. Второй шаг, подготовка RGO-3DGNs-ER, аналогична нашей предыдущей работе [7]. Кратко, определенное количество подготовленных RGO-3DGNs было помещено в формочку, и ER включая агент захвата был помещен на круглую поверхность. После этого, ER поднимается в пористой RGO-3DGNs, а затем RGO-3DGNs-ER добавляется снова. Эти два шага повторяются три-четыре раза. Экран ER проникает в пористый RGO-3DGNs. Полученный RGO-3DGNs-ER после фиксации был пропитан, образуя ER-3DGNs-ER с капиллярным эффектом. В конце концов, ER-3DGNs-ER смесь была закреплена при 110 °С в течение 3 ч.

**Characterization**

Морфология TIMs была получена с помощью сканирующего электронного микроскопа (SEM, FEI Sirion 200 Scanning Electron Microscopy, работающего при 5 кВ) и трансмиссионного электронного микроскопа (TEM, JEM-2100F, работающего при ускоряющем напряжении 20 кВ). Атомно-силовую микроскопию (AFM) результаты получены с помощью Nanoscope IIIa (Digital Instrument, USA) и E-Sweep (Seiko, Japan) в режиме отображения. Сканирующие Рaman спектры были получены с помощью LabRam-1B Raman микроскопа (Horiba Jobin Yvon, France). X-лучевая фотоэлектронная спектроскопия (XPS) измерения были проведены на RBD PHI-5000 ESCA системе (Perkin Elmer). Фурье-трансформированная инфракрасная спектроскопия (FTIR) кривые были измерены на IR Prestige-21 системе (PerkinElmer). Механические свойства этих композитов записывались с помощью Triton DMTA (Triton Instrument, UK) прибора. Tg и модуль упругости были измерены при частоте 1 Гц и скорости нагрева 5 °С мин^-1 согласно ASTM1640 и анализировались в тенсиле модели. Длины образцов были 2 x 4 см. Лазерный тест системы и дифференциальная сканирующая калориметрия использовались для анализа термических свойств TIMs.

**Results and Discussion**

AFM и SEM изображения получены RGO наношитов, 3DGNs, RGO-3DGNs, и RGO-3DGNs-ER показаны на рис. 1. Средний размер RGO наношитов составляет 400~600 нм (рис. 1a), который был специально создан для комбинации с 3DGNs при помощи нанесения окисления и реакции уменьшения. Процесс 3D конструкция 3DGNs может быть виден на рис. 1b, и его пористая структура показана. Как для TIM, гладкая поверхность RGO-ER может быть видна на рис. 1c, при помощи нанесения пористой структуры, которое участвует в физическом ядре, инертного ER, ингредиента с объемной наношитой RGO-3DGNs-ER [7]. Было показано, что ER-3DGNs-ER должна быть помещена на поверхность 3DGNs. Синергия гидротермальной реакции, которая является предварительным условием для TIMs, которое улучшает термические свойства, что в свою очередь, помогает улучшить термические свойства материала.
the graphene basal plane and ER) of the RGO nanosheets (more details will be discussed in the following).

Raman curves of the adopted RGO nanosheets and 3DGNs are shown in Fig. 2a. Three major signals, G, 2D, and D peaks, can be seen for the former, while the D peak is difficult to find in the corresponding pattern of the 3DGNs. As for the graphite-like materials, the D peak is aroused from defects. Therefore, the obtained Raman profile implies the high quality of the 3DGNs \[15, 16\]. The G band associates with the \(E_{2g}\) phonon at Brillouin zone center. Moreover, the defect density and average size of the RGO nanosheets can be calculated by the integrated intensity ratio of \(I_G/I_D\) \[15\]. According to Eq. (1) \[17\],

\[
L_a = \frac{43.5}{R} = 43.5 \times \frac{I_G}{I_D}
\]

the average size is \(\sim 500\) nm, which is in line with the result of the AFM image. Two kinds of defects including functional groups and boundaries can be classified for the RGO nanosheets. The amount of boundaries is determined by the average size of the adopted RGO nanosheets, while the amount of the functional group is dependent on the reduction procedure. More details on the reduction degree of the RGO nanosheets by XPS spectra are discussed in our previous reports and the Supplementary materials \[7, 8\]. The enlarged FTIR is a useful tool to observe the chemical bond between various materials according to the intensities and positions of the corresponding signals. The major adsorption peaks and the corresponding functional groups of the ER are marked in Fig. 2b, and the spectra of the RGO nanosheets and 3DGNs are also presented. The similar signals at \(\sim 1600\) cm\(^{-1}\) and 3000–3700 cm\(^{-1}\) are induced from the skeletal vibration of the graphene basal plane and the O–H stretching vibration of adsorbed water \[18–20\]. A remarkable difference between these two

![Fig. 1 Morphologies of the RGO nanosheets, 3DGNs, and resulting TIMs. AFM and SEM images of the prepared RGO nanosheets, 3DGNs, RGO-3DGNs, and RGO-3DGNs-ER are shown in Fig. 1. The average size of the RGO nanosheets is 400–600 nm a, which is elaborately designed to combine with the 3DGNs by adjusting the oxidation and reduction procedures. A continuous 3D construction of the 3DGNs can be seen from b, and its porous structure is clearly shown. As for the resulting TIM, the smooth surface of the RGO-ER can be seen from c, and the absence of tiny pores (compared with that of the pristine ER, inset of c indicates a potential high thermal performance. d The morphology of the RGO-3DGNs-ER, which is similar with that of the RGO-ER. The 3D structure of the 3DGNs is difficult to identify in the SEM image because the 3D interspaces are filled by the ER. However, the 3D phonon transport network (the function of the 3DGNs) still maintains in the TIMs, which has been proven by our previous reports. The RGO nanosheets in the RGO-3DGNs-ER should be loaded on the surface of the 3DGNs because of the hydrothermal reaction, which is the pre-condition to exert the function (enhance the wettability between the graphene basal plane and ER) of the RGO nanosheets.](image-url)
profiles is that an additional obvious peak at 1335 cm\(^{-1}\) arising from the O=C–OH can be seen only for the RGO nanosheets resulting from the surface functional groups [21]. After combining with the ER, the O=C–OH signal disappears absolutely, manifesting that the carboxyl on the surface of the RGO nanosheets reacts with hydroxyl of the ER to form a close chemical contact, which contributes to the phonon fast transport at the interface between them.

The corresponding thermal performances of various samples are shown in Fig. 3. The thermal conductivity of the pristine ER is ~ 0.2 W/mK, which is far from the requirement for the TIMs in the practical application. With the increased mass fractions of various fillers, the resulting thermal performances enhance almost in a linear manner (Fig. 3a). Therein, the RGO nanosheets and 3DGNs co-modified composites display the best performance with identical mass fraction compared with the

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**Fig. 2** Raman and FTIR curves of the various samples. Raman curves of the adopted RGO nanosheets and 3DGNs are shown in a. Three major signals, G, 2D, and D peaks, can be seen for the former, while the D peak is difficult to find in the corresponding pattern of the 3DGNs. As for the graphite-like materials, the D peak is aroused from defects. Therefore, the obtained Raman profile implies the high quality of the 3DGNs. The G band associates with the E\(_{2g}\) phonon at Brillouin zone center. Moreover, the defect density and average size of the RGO nanosheets can be calculated by the integrated intensity ratio of I\(_G\)/I\(_D\). After calculation, the average size is ~ 500 nm, which is in line with the result of the SEM image. The enlarged FTIR is a useful tool to observe the chemical bond between various materials according to the intensities and positions of the corresponding signals. The major adsorption peaks and the corresponding functional groups of the ER are marked in b, and the spectra of the RGO nanosheets and 3DGNs are also presented. The similar signals at ~ 1600 cm\(^{-1}\) and 3000–3700 cm\(^{-1}\) are induced from the skeletal vibration of the graphene basal plane and the O–H stretching vibration of adsorbed water. A remarkable difference between these two profiles is that an additional obvious peak at 1335 cm\(^{-1}\) arising from the O=C–OH can be seen only for the RGO nanosheets resulting from the surface functional groups. After combining with the ER, the O=C–OH signal disappears absolutely, manifesting that the carboxyl on the surface of the RGO nanosheets reacts with hydroxyl of the ER to form a close chemical contact, which contribute to the phonon fast transport at the interface between them.

**Fig. 3** Thermal conductivities of resulting composites with increased mass factions of fillers. The corresponding thermal performances of various samples are shown in Fig. 3. The thermal conductivity of the pristine ER is ~ 0.2 W/mK, which is far from the requirement for the TIMs in the practical application. With the increased mass fractions of various fillers, the resulting thermal performances enhance almost in a linear manner (Fig. 3a). Therein, the RGO nanosheets and 3DGNs co-modified composites display the best performance with identical mass fraction compared with these cases of employing a single filler, and the specific thermal conductivity value is closely related to the proportion of the 3DGNs and RGO nanosheets, demonstrating a synergy between them (b). Although both the RGO nanosheets and 3DGNs are constituted with graphene basal sheets, the distinctions from morphology of these two fillers and chemical state of carbon atoms endow the different functions of them in the TIMs. On the one hand, the high quality and the continuous structure of the 3DGNs make it an excellent fast transport network for phonons, which has been proven in our previous reports. On the other hand, due to the high defect density and the lack of a continuous structure, the phonon transport ability of the RGO filler is weaker than the 3DGNs.
these cases of employing a single filler, and the specific thermal conductivity value is closely related to the proportion of the 3DGNs and RGO nanosheets, demonstrating a synergy between them (Fig. 3b). Although both the RGO nanosheets and 3DGNs are constituted with graphene basal sheets, the distinctions from the morphology of these two fillers and chemical state of carbon atoms endow the different functions of them in the TIMs. On the one hand, the high quality and the continuous structure of the 3DGNs make it an excellent fast transport network for phonons, which has been proven in our previous reports [8]. On the other hand, due to the high defect density and the lack of a continuous structure, the phonon transport ability of the RGO filler is weaker than the 3DGNs [7]. Therefore, the general performances of the RGO nanosheet-assisted TIMs are not as good as these samples of adopting the 3DGNs. However, surface functional groups of the RGO nanosheets bring about a better contact for the interface between the graphene basal plane and ER, which can be confirmed by the reduced thermal boundary resistance. Based on Balandin’s theory, thermal conductivity of graphene-modified ER can be expressed as follows [22]:

\[
K = K_g \left[ \frac{2p(K_g - K_e) + 3K_e}{(3-p)K_g + K_p + \frac{4k_eK_p}{H}} \right] + K_e \left( 1 - \frac{4k_eK_p}{H} \right)
\]

(2)

where \(p\) represents the volume percentage of the graphene filler and \(K, K_p, K_e\), and \(H, \delta\) are thermal conductivities of the resulting composite, graphene, and ER, respectively. \(H\) and \(\delta\) are the thickness of the graphene and the thermal boundary resistance between the graphene and ER. After calculation, the similar \(\delta\) values of the RGO-ER and RGO-3DGNs-ER samples prove that the added RGO nanosheets are loaded on the surface of the 3DGNs (Fig. 4). Based on our previous findings, the \(\delta\) value of the 3DGNs-ER sample is much higher than that of the RGO-ER because of the poor contact between the 3DGNs and ER [7, 8]. The functional groups of the RGO nanosheets bring about a better contact at the interface, which leads to the smaller \(\delta\) compared with that of 3DGNs-ER sample. The further optimization on the reduction degree of the adopted RGO nanosheets is carried out, and the ratio of the element carbon atoms to carbon atoms from functional groups \(\sim 1.7\) is recommended (more details are provided in Additional file 1: Figure S1 and our previous reports [7, 8]).

In order to simulate the practical work condition of electronic devices, the performances of the resulting TIMs under high temperature are detected (Fig. 5a). With increased temperature, the thermal conductivities of all TIMs decrease due to the enhanced Umklapp scattering. Although the Kapitza boundary scattering decreases at the same time (the probability of a phonon across the interface is proportional to \(e^{-\delta T}\)), the decrease cannot remedy the corresponding increase of the Umklapp scattering, leading to the whole decrease of thermal conductivity. Compared with that of the 3DGN-assisted sample, the stability of thermal conductivity of the RGO nanosheets added composites under high temperature is better because of the more sensitive Kapitza boundary scattering (as a result of the more boundaries of the RGO nanosheets). Moreover, no obvious degradation can be found for the thermal performance of the RGO-3DGNs-ER sample after 240 h continuous working (Fig. 5b), indicating the potential promising prospect of this TIM. The stability of the pure ER during a long work time is also recorded in Fig. 5b. The similar stabilities of the pure ER and the resulting composites (all the degradations of their thermal conductivities are less than 10%) indicate that no significant influence on the thermal stability can be found after adding the fillers.

As last, the mechanical properties of these TIMs are also recorded. The corresponding performances including ultimate strengths and stretching limits of them are listed in Additional file 1: Table S1. Both the 3DGNs-ER and RGO-3DGNs-ER samples display the high mechanical strength because the continuous 3D structure of the 3DGNs is beneficial to keeping the outstanding intrinsic mechanical property of the graphene. After comparing the performances of the 3DGNs-ER and RGO-3DGNs-
ER samples, it can be inferred again that the RGO nanosheets are loaded on the surface of the 3DGNs rather than dispersed in the ER matrix because the influence from the added RGO nanosheets can be ignored.

Conclusions
The RGO nanosheets and 3DGNs co-modified ER has been prepared to prepare the TIMs. The advantages of the RGO nanosheets and 3DGNs can give full play to loading the RGO nanosheets on the surface of 3DGNs (by a hydrothermal process) rather than dispersing in the ER matrix. The presence of the 3DGNs not only provides a fast transport network for phonons but also acts as a scaffold for the RGO nanosheets. On the other hand, the surface functional groups of the RGO nanosheets enhance the close contact between the graphene basal plane and ER at their interface, which offsets the poor wettability of the 3DGNs. Therefore, the thermal performance of the resulting TIM is enhanced significantly (a high thermal conductivity ~ 4.6 W/mK is achieved when a 9 wt% 3DGNs and 1 wt% RGO nanosheets are added, which is 10 and 36% higher than those cases of 10 wt% 3DGNs and 10 wt% RGO nanosheet added samples), and a well stability of the thermal performance of the resulting TIM is revealed under high temperature (at 100 °C, the decrease of the thermal conductivity is less than 25%). Moreover, the excellent mechanical properties including high ultimate strength and stretch limits indicate the potential promising prospect of the presented TIM.

Additional file
Additional file 1: Figure S1. XPS curve of RGO after reduction with optimizing time. Table S1. Mechanical performances of the various samples (DOCX 186 kb)

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Authors’ Contributions
This manuscript is written by TB and WH. The preparation of samples is performed by WZ and LS. The characterization of samples and preparing experiments are made by MT, YH, and LX. The analysis and discussion of the obtained results are carried out by TB, WZ, MT, and HW. All authors read and approved the final manuscript.

Competing Interests
The authors declare that they have no competing interests.

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