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Highly compressible graphene aerogel with high thermal conductivity along both in-plane and through-plane directions

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Abstract

Graphene-based thermal interface materials (TIMs), such as horizontal graphene papers and vertical graphene monoliths, commonly possess high thermal conductivity (TC) only along either in-plane or through-plane direction due to their high anisotropy structure. Three-dimensional (3D) graphene monoliths with interconnected network can extend the excellent thermal transport performances of two-dimensional graphene to macro monoliths along multi-directions. However, the high porosity of 3D graphene monoliths usually leads to low TC. Here, highly compressible graphene aerogels (HCGAs) with closely packed cell walls and regularly cellular structure were prepared. The HCGAs can be highly compressed (95% compressive strain) to reduce the porosity while maintaining the continuously thermal transport paths. Significantly increased TC along both in-plane and through-plane directions can be obtained by directly mechanical compression of the aerogels. HCGAs with initial density of 11.5 mg cm$^{-3}$ at 95% compressive strain possess in-plane TC of 167.2 W m$^{-1}$K$^{-1}$ and through-plane TC of 46.8 W m$^{-1}$K$^{-1}$, which outperforms other carbon-based TIMs reported previously.

1. Introduction

Nowadays, modernization, miniaturization, integration and high power in electronics have been considered as the development trends for electronic devices [1]. But the increase in power density emits massive heat and seriously shortens the service life of electronics [2]. Hence, efficient removal of heat is a key technology for electronic components, which cannot be ignored and needs to be cleverly addressed. Thermal interface materials (TIMs) as the substance are inserted between heat producing component and heat sink for heat transport, playing a very important role in solving the interfacial heat transfer problem [3].

Carbon-based materials, such as diamond, graphite, carbon nanotubes (CNTs) and graphene with high thermal conductivity (TC), low thermal expansion, ideal lightweight and high-temperature resistance have been widely studied in the fields of thermal management [4–6]. Among them, graphene, an ultrathin flat membrane from sp$^2$ carbon atoms, has ultra-high in-plane TC (3000 ~ 5000 W m$^{-1}$K$^{-1}$), good flexibility and excellent mechanical properties, making it an ideal material to be used for fabricating TIMs [7].

For evaluating the performances of TIMs, there are two types of TC values depending on the direction of heat flow: in-plane TC and through-plane TC. In-plane thermal conductive materials are excellent heat spreaders to mitigate the problem of hot spots. Through-plane TC is the crucial parameter for efficient transport of heat from the heat producing component to the heat sink [8]. Horizontal graphene papers present high in-plane TC (1100 ~ 3200 W m$^{-1}$K$^{-1}$ [9–13]), which is commonly used as the in-plane thermal spreading materials. However, the through-plane TC of these graphene papers is just 1 ~ 15 W m$^{-1}$K$^{-1}$ [11, 14, 15], which is far from satisfying the requirement in efficient thermal management of power devices. It is attributed to the phonon transmission barrier across the van der Waals interface between the graphene layers [16].
vertical graphene structures based on the transformation of the stacked architecture of graphene paper from a horizontal to a vertical orientation ensures the high through-plane TC ($35.5 \sim 680 \text{ W m}^{-1}\text{K}^{-1}$) [17–20]. However, there are still some drawbacks for vertical aligned graphene as TIMs. The rough surface of the vertically aligned structure results in a high thermal contact resistance [21]. And any deformation under pressure could lead to a reduction in through-plane TC due to the strict structural configuration of vertical graphene [22]. In addition, the significant improvement of through-plane TC commonly comes with the low in-plane TC arising from the high anisotropic [23].

To satisfy the requirements of TIMs with both high in-plane TC and through-plane TC, numerous efforts have been made to fabricate three-dimensional (3D) graphene-based monoliths (such as aerogels, foams and sponges) with honeycomb-like structure, which make them significantly different from the horizontally or vertically oriented graphene materials with high anisotropic structure [24–26]. In 3D graphene monoliths, the heat fluxes conduct along the interconnected graphene network, extending the excellent in-plane TC of the two-dimensional graphene to the macro graphene monoliths along multi-directions [27–29]. However, the TC of 3D graphene monoliths is very low due to the high porosity. Our previous work [30] presented a compressible graphene/CNT aerogel, which can be highly compressed (80% compressive strain) to reduce the porosity while maintaining the continuously thermal transport paths without structure collapse. Significantly increased TC of the hybrid aerogel can be obtained by mechanical compression.

In this work, we fabricated highly compressible graphene aerogels (HCGAs) with regularly arranged porous structure and integrated cell walls. Different from the loose structure of the cell walls in graphene/CNT aerogel, HCGAs possess more closely packed cell walls assembled by only graphene sheets, which is important for decreasing the intrinsic thermal resistance of the network. And the HCGAs can maintain continuous heat transport paths at higher compressive strain (95%) due to the regularly arranged porous structure. Thus, the higher thermal transport performances than that of graphene/CNT aerogels can be achieved by compacting the HCGAs. The high through-plane TC of 46.8 W m$^{-1}$K$^{-1}$ and in-plane TC of 167.2 W m$^{-1}$K$^{-1}$ are obtained when the HCGAs with initial density of 11.5 mg cm$^{-3}$ at 95% compressive strain.

2. Experimental details

2.1. Preparation of HCGAs

Graphene oxide (GO) was prepared by the modified Hummers method from natural graphite and got exfoliated GO sheets in their aqueous dispersions according to the previous process [31]. The HCGAs were prepared by the ice template method described in the previous study [32]. In a typical synthesis procedure, GO aqueous dispersion with 100 mg L-ascorbic acid was poured into a glass vials and heated for 30 min at 90 °C for synthesis of partially reduced GO (Pr-GO) hydrogel. Then the obtained hydrogel was treated by the freeze-thaw process in the refrigerator (−18 °C) and at room temperature. Subsequently, a further reduction process for the freeze-recast hydrogel was carried out for 5 h at 90 °C using the initial reductant (L-ascorbic acid). The hydrogel was subjected to dialysis in deionized water and dried at 60 °C for 48 h to obtain the aerogel. Finally, the completely reduced HCGA was obtained by the high-temperature graphitization at 2800 °C for 2 h in a graphitization furnace with protection of Ar Atmosphere. In addition, HCGAs with various initial densities were also prepared by controlling GO concentrations. The as-prepared aerogels were defined as HCGA-$n$ (n = 1, 2, 3, 4, 5 and 6) based on the GO concentrations of 1, 2, 3, 4, 5 and 6 mg ml$^{-1}$, respectively.

2.2. Characterizations

The microstructure of the HCGAs was observed using a Hitachi S4800 field-emission SEM system with a 5 kV accelerating voltage. Compressive stress/strain measurements were carried out on a single-column system (Instron 5843) equipped with two flat-surface compression stages and 1 KN load cell. The strain rate was controlled to be 10 mm min$^{-1}$ and the cyclic loading was carried out at a displacement of 100 mm min$^{-1}$. The initial density and the compacted density of the HCGAs were calculated as the mass of the HCGAs divided by its corresponding volume without and with compression, respectively.

2.3. Measurement of thermal transport properties

The thermal resistance measurement system was designed in accordance with the standard of American Society for Testing and Materials (ASTM) D5740 [33–35]. The thermal interface resistance of TIMs ($R_{\text{TIM}}$) was measured by the equipment shown in figure 1 according to equation (1).

\[ R_{\text{TIM}} = \frac{\Delta T \cdot A_{\text{contact}}}{Q} \]  \hspace{1cm} (1)
Where $\Delta T$ is the temperature gradient across the HCGAs, $A_{\text{contact}}$ is the contact area between HCGAs and Cu blocks, and $Q$ is the thermal flux through the HCGAs, respectively.

In this work, for testing the through-plane $R_{\text{TIM}}$, the HCGAs were inserted between reference Cu bars and compressed into the thin film with a constant compressive strain (figure 1(a)). For testing the in-plane $R_{\text{TIM}}$, the compressed HCGAs rotated from horizontal to vertical positions while maintaining the constant compressive strain by the horizontal pressure (figure 1(b)). Two fiberglass insulation blocks ($TC = 0.14 \text{ W m}^{-1}\text{K}^{-1}$) were inserted between the compressed HCGAs and the horizontal compression bars in order to minimize the heat losses during the test. The $R_{\text{TIM}}$ is calculated from data obtained by a series of thermocouples embedded within the reference Cu bars. All the measurements were carried out under vacuum condition to reduce the influence of thermal radiation.

Thermal conductivity of TIM ($k$) and thermal contact resistance ($R_c$) across TIM/Cu interface were calculated by the simultaneous linear equations of equation (2) by varying the dimensions of HCGAs along the vertical direction ($l$) [30]. For measuring the through-plane thermal transport performances, $l$ is the thickness of the compressed HCGAs. And for measuring the in-plane thermal transport performances, $l$ is the height of the compressed HCGAs. The detail of the size of HCGA samples for testing thermal transport performances is provided in supporting information (Figure S1 available online at stacks.iop.org/MRX/8/045608/mmedia).

$$R_{\text{TIM}} = 2R_c + \frac{l}{k}$$

3. Results and discussion

Figure 2(a) illustrates the formation process of the cellular structure of HCGAs. At stage of pre-reduction, the reduced GO sheets become hydrophobic due to the removal of their oxygen-containing groups, and the increasing hydrophobicity and $\pi-\pi$ conjugated structure result in the formation of weakly cross-linked hydrogel. In the subsequently freeze-recast step, the growth of ice crystals then can break through the as formed weakly cross-linked network and reject the pr-GO sheets into the neighboring ice crystals to form the tightly packed cell walls. After the further reduction process and subsequent drying process, the ice crystals are sublimated and the cellular structure is left in the aerogel. Dependent on the shape of reactor utilized, arbitrary shapes (such as cylindrical and rectangle shapes) of HCGAs can be fabricated.

Figure 3 shows the microstructure of HCGA-4 with initial density of 8.8 mg cm$^{-3}$. It can be seen that HCGA-4 possesses the macro-porous, honeycomb-like and oriented cellular structure at both cross-section
HCGA-4 presents large pore dimension in the order of hundreds of micrometers (ca. 100 ~ 500 μm) (figure 3(c)). Each cell possesses stretched ligaments in the walls that are joined at nodes or junctions. The cell walls of HCGA-4 are composed by restacked high-quality graphene sheets (figure 2(d)), which is significantly different from the loose structure of cell walls in graphene/CNT aerogels [30]. The compacted cell walls are in favor of decreasing their intrinsic thermal resistance [12] and improving the thermal transport efficiency along the network in HCGAs.

By the reason of 3D graphene monoliths with high porosity generally showing very low TC values, HCGAs should be highly compressed to improve the thermal transport performances. Figure 4(a)–(d) show the micro-morphology change of HCGA-4 during the compress/release process. When the aerogel is under high compression (~80% strain), the void space shrinks and the solid matrix becomes dense (figure 4(b)). The cell walls stack obviously in parallel-aligned arrays perpendicular to the compressive direction. There is no buckling failure or structural collapse of the cellular structure. The zoom-in SEM image (figure 4(c)) indicates that the 3D interconnected structure along the through-plane direction can be well maintained even under high compressive strain. When the applied loads are released, the HCGA-4 can fully recover its original micro-morphology (figure 4(d)). This high compressibility of the HCGAs arises from the mechanical robustness of tightly packed cell walls and regular cellular structure of the aerogel. The HCGAs are particularly effective for tolerating large geometric deformation yet preventing structural damage or collapse. Therefore, the continuous thermal transport paths in HCGAs can be maintained well under highly compacted status.

In horizontal graphene papers and vertical graphene monoliths, the aligned graphene chains provide thermally conductive pathway array only along the horizontal direction or vertical direction [9–13, 17–20] (figure 4(e)). In HCGAs with 3D interconnected structure, the heat fluxes can conduct along the graphene cell walls and come together at their junctions, then continue to transport to adjacent graphene cell walls, which
brings HCGAs continuous thermal transport paths along both in-plane and through-plane directions (figure 4(e)).

In order to study the effect of initial density of HCGAs on their mechanical performances and thermal transport performances, HCGAs with various initial densities were prepared. As shown in figure 5(a), the initial densities of HCGAs increase from 2.7 to 11.5 mg cm$^{-3}$ with the increase of GO concentrations from 1 to 6 mg ml$^{-1}$. Figures 5(b)–(f) and figure 3(a) show the micro-morphology of HCGA-1 ~ 6. There are some vacancies in the cell walls of HCGA-1, indicating that the GO solution with 1 mg ml$^{-1}$ concentration cannot supply sufficient GO sheets to assemble the integrated cell walls. When the GO concentration is higher than 2 mg ml$^{-1}$, there are no vacancies appeared on the cell walls. With increasing GO concentration, the porous structure becomes denser and the average pore size is smaller. And the honeycomb-like and oriented cellular structure of HCGAs maintains very well, even when GO concentration is as high as 6 mg ml$^{-1}$.

Generally, the TC values of 3D graphene monoliths is very low due to ultrahigh porosity and low graphene volume fraction. For achieving high thermal transport performances, HCGAs should be compacted tightly to dramatically decrease the porosity. Meanwhile, the continuous thermal transport paths in HCGAs should be maintained well under highly compressive deformation. The compression tests were performed to evaluate the compressibility of HCGAs. As shown in figure 6(a), the HCGA-4 can be squeezed into a pellet under manual compression. Once the external pressure is removed, the aerogel can almost completely recover to its original shape rapidly. The high compressibility and flexibility of HCGAs are consistent with the in-situ SEM observation of HCGAs during compress/release process discussed above (figures 4(a)–(d)). The stress/strain curves of HCGA-2 ~ 6 are shown in figure 6(b). All HCGAs show high compressibility and can bear the compressive strain as high as 95%, which is close to the highest value of 3D graphene monoliths reported previously [27, 32]. The similarity of these curves verifies that the HCGAs with various densities retain the integrity. The loading
The process of the HCGAs shows the characteristic behavior of porous foam-like materials, with three distinct regions, including the elastic region, plateau region and densification region. The maximum stress at 95% strain increases from 17.6 KPa for HCGA-2 to 125.2 KPa for HCGA-6. The increase of stress is due to the smaller pore size and thicker cell walls of aerogel with higher initial density providing higher stiffness and compressive strength. The cyclic strain-stress curves of HCGA-4 at strain of 95% are shown in figure 6(c). The 1st compression cycle is different from the subsequent ones showing the higher stress at the same strains. The hysteresis loop for the 2nd cycle shrinks significantly compared to the 1st one. Since the 2nd cycle, the shrink of stress-strain curves becomes unremarkable. The decrease of the loading curves is attributed to the irreversible damage occurred in partial region of the porous structure during the 1st compress-release process. In addition, the maximum compressive stress of HCGAs only slightly decreases to 69 ~ 73% of their original values after 1000 compression-release cycles, indicating the structure stabilization of HCGAs (figure 6(d)).

Figure 5. (a) Plot of the initial density of HCGAs versus the GO concentration; SEM images of (b) HCGA-1, (c) HCGA-2, (d) HCGA-3, (e) HCGA-5 and (f) HCGA-6, respectively.

Figure 6. (a) Digital photographs of the compress/release process of HCGA-4; (b) Compressive stress/strain curves of HCGA-2 ~ 6; (c) Stress/strain curves of the 1st, 2nd, 100th and 1000th cycles of HCGA-4; (d) Maximum compressive stress of HCGA-2 ~ 6 at strain of 95% for 1000 compress/release cycles.
The thermal transport performances of HCGAs have been studied. As shown in figures 7(a) and (b), the TC values of HCGA-4 without compression are only 6.5 W m\(^{-1}\)k\(^{-1}\) along the in-plane direction and 4.2 W m\(^{-1}\)k\(^{-1}\) along the through-plane direction. When the HCGA-4 is at 95% compressive strain, the TC values of the compacted aerogel along the in-plane direction is 145.2 W m\(^{-1}\)k\(^{-1}\) and along the through-plane direction reaches 41.3 W m\(^{-1}\)k\(^{-1}\). The dramatical improvement of TC values is attributed to the mechanical press effectively decreases the porosity and increases the density of the aerogels. The compression removes air inside of graphene cells, which is a bad conductor of heat, having a TC of only around 0.22 W m\(^{-1}\)K\(^{-1}\) [6]. The density of HCGA-4 increases from 8.8 mg cm\(^{-3}\) at initial stage to 176.0 mg cm\(^{-3}\) at 95% compressive strain. Previous literatures about horizontal graphene papers or vertical graphene monoliths have also reported that the densification processes can remarkably improve the TC of graphene-based monoliths [7–13, 17, 20].

As mentioned above, the horizontal graphene papers and vertical graphene monoliths possess high TC only along either in-plane or through-plane direction. In this work, HCGAs show high TC values along both in-plane and through-plane directions, which is attributed to 3D interconnected structure and high compressibility of HCGAs.

It is well established that there should be a good contact between TIMs and mating surface for efficient heat removal. Thus, it is also required that TIMs structurally matching the contact surface to decrease the thermal contact resistance. Although the graphene layers assemble as the oriented cellular structure inside the HCGAs, the orientation of the graphene cell walls transform into parallel to the contact surface (insert of figure 7(b)). The parallelly oriented graphene layers seamlessly connected to the cellular graphene can act as the heat spreader, leading to a maximum of contact area at the mating interface to avoid local overheating. In addition, as shown in figure 7(b), the thermal contact resistance of the compacted HCGA-4 along the through-plane direction is only 6.1 K mm\(^2\)W\(^{-1}\), which is much lower than that of HCGA-4 without compression (23.8 K mm\(^2\)W\(^{-1}\)). It is attributed to the high stress corresponding to the 95% compressive strain leads to aerogel matching to mating surface better. The thermal contact resistance of HCGA-4 with and without compression along in-plane direction are similar (figure 7(a)) resulting from no high stress applied at the contact interface when we measured the in-plane thermal transport performances (figure 1(b)).

The effect of the initial density of HCGAs on their thermal transport performances was also studied. As shown in figures 7(c) and (d), both of in-plane TC and through-plane TC are increased with the initial density of HCGAs, which is attributed to higher initial density meaning more graphene layers in unit volume participating.
Table 1 Comparison of thermal transport performances of carbon-based TIMs reported previously (Refs 11, 23, 34–38) with the results in this work.

| Materials                              | In-plane TC (W m⁻¹ K⁻¹) | Through-plane TC (W m⁻¹ K⁻¹) | Anisotropy ratio (high TC/low TC) | References |
|----------------------------------------|--------------------------|-------------------------------|-----------------------------------|-------------|
| Graphene sheets/graphene foam/rubber composite | 11.16                     | 4.05                          | 2.8                               | [36]        |
| Graphene hybrid foam/epoxy composite   | 16.5                      | 35                            | 2.1                               | [23]        |
| Graphene films                         | 3200 ± 330               | 14.8 ± 1.5                    | ~216.2                            | [11]        |
| Graphene/Cellulose nanocrystals        | 1820.4                    | 4.596                         | ~396.1                            | [37]        |
| Expanded graphite/CNTs consolidated hybrid | 233                      | 24.3                          | 9.6                               | [34]        |
| Exfoliated graphite/CNTs consolidated block | 254                      | 38                            | 6.7                               | [38]        |
| HCGA-6 at 95% compressive strain       | 167.2                     | 46.8                          | 3.6                               | Our work    |
in thermal transport. During the measurement of through-plane thermal transport performances, the thermal contact resistance is slightly declined with the increase of initial density of HCGAs, arising from the higher applying compressive stress for HCGAs with higher initial density. HCGA-6 with the compacted density of 230.2 mg cm\(^{-3}\) at 95% strain possesses in-plane TC of 167.2 W m\(^{-1}\)K\(^{-1}\) and through-plane TC of 46.8 W m\(^{-1}\)K\(^{-1}\). And the thermal contact resistance along the through-plane direction is as low as 5.6 K mm\(^{−1}\)W. The effect of graphitization process on the thermal transport performances of HCGA-6 has been discussed. As shown in Figure S3(a), the through-plane TC and in-plane TC of compacted HCGA-6 (95% strain) are 21.5 W m\(^{-1}\)K\(^{-1}\) and 81.4 W m\(^{-1}\)K\(^{-1}\), which is far lower than that of compacted HCGA-6 after graphitization. The improvement of TC values can be analyzed by the structure change. As shown in the Raman spectra (Figure S3(b)), the D-band peak (1300 cm\(^{-1}\)) of HCGA corresponding to the disordered amorphous carbon C–C bonds at the defects or edge boundaries have almost disappeared after graphitization process. And the G-band peak (1580 cm\(^{-1}\)) corresponding to the first-order scattering of E\(_{2g}\) mode of sp\(^{2}\)-hybridized carbon atoms becomes narrow and sharp. It indicates that the graphitization process leads to the further reduction of HCGA. And the defects of reduced-graphene oxide in the cell walls can be repaired, providing an interconnected channel for phonon transportation thus leading the improvement of TC values. The TC values of the HCGA-6 after 1st, 100th and 1000th compress/release processes were also measured. As shown in Figure S2, after 1000 compress/release cycles, the in-plane TC and the through-plane TC of compacted HCGA-6 are 150.5 W m\(^{-1}\)K\(^{-1}\) and 38.8 W m\(^{-1}\)K\(^{-1}\), which is 91% and 83% of that of compacted HCGA-6 after 1st compress/release process. The high retention ratios of TC values after long-term compress/release processes are attributed to the good structure stability of HCGAs. The thermal transport properties of HCGAs with higher initial density (>11.5 mg cm\(^{-3}\)) are not considered in the present work due to the excessively dense structure of the aerogels leading to the losing of high compressibility.

As shown in table 1, there are several literatures have measured TC values along both in-plane and through-plane directions. In comparison with the graphene/polymer foam composites [23, 36], although the TC anisotropy ratio of HCGA-6 is lower, the TC values along both in-plane and through-plane directions are much higher due to the all-carbon components. For the horizontal graphene papers [11, 37], although they have ultra-high in-plane TC, the through-plane TC is much lower than that of HCGA-6. Feng et al[34, 38] reported the graphite/CNT hybrids with 3D interconnected structure and shows high TC along both in-plane and through-plane directions. Although the in-plane TC of compacted HCGA-6 is slightly lower than that of graphite/CNT hybrids, the through-plane TC of HCGA-6 is higher and the TC anisotropy ratio is much lower. These excellent performances suggest the promising potentials of HCGAs in current demanding thermal management systems.

4. Conclusions

HCGAs with interconnected network and honeycomb-like structure were prepared by the ice template method and used as a novel compressible TIM. The mechanical robustness of cell walls and regular cellular structure of the HCGAs bring the aerogel high compressibility. The continuous thermal transport paths in HCGAs can be maintained well even under 95% compressive strain. HCGAs with various initial densities were prepared by controlling GO concentrations. HCGA-6 with initial density of 11.5 mg cm\(^{-3}\) possesses in-plane TC of 167.2 W m\(^{-1}\)K\(^{-1}\) and through-plane TC of 46.8 W m\(^{-1}\)K\(^{-1}\). Comparison with other graphene based TIMs with high TC only along one-dimension direction, HCGAs show high TC along both in-plane and through-plane directions. Our finding providing the insight for the construction of compressible TIMs, which may satisfy the demanding thermal management of next-generation high-power electronics.

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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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