In solid materials, heat is carried by acoustic phonons and electrons.\[1\] The thermal conductivity ($K$) of metals is mainly attributed to high concentration of transport electrons, which in principle defines their maximum $K \approx 429 \text{ W m}^{-1} \text{ K}^{-1}$ for silver at room temperature.\[2\] To reach higher $K$, nonmetallic materials are the only options as their heat conduction is usually dominated by phonons, the particle-core vibrations in a crystal lattice, as in the cases of diamond and semimetallic graphite.\[3\] For a same material, $K$ is mainly scaled with the size of crystal domain ($L$, $\phi(L)$) but limited by the concentration of defects ($D$, $\phi(D)$), such as interfaces, boundaries, impurities, and holes.\[4\] Therefore, a prominent thermal conductive material ($K > 429 \text{ W m}^{-1} \text{ K}^{-1}$; Table S1, Supporting Information) is usually pure, highly crystallized, and defect-free, which in turn inevitably leads to brittleness because of the strong bonding and close-packed 3D structure. A typical example is the diamond film ($K_0 \approx 3230 \text{ W m}^{-1} \text{ K}^{-1}$) with very limited strain (0.4%-0.6%) resulted from their deformation of bond lengths and angles.\[4,5\] Hence, a prominent $K$ and outstanding flexibility are hard to be integrated into one macroscopic material. The large-area multifunctional GFs can be easily integrated into high-power flexible devices for highly efficient thermal management.

Graphene, the most studied 2D carbon allotrope, consists of only one plain layer of conjugated atoms arranged in a honeycomb lattice.\[6–12\] The low atomic mass, strong bonding, simple crystal structure, and low anharmonicity of graphene endow it a distinguished $K \approx 5300 \text{ W m}^{-1} \text{ K}^{-1}$.\[13,14\] Meanwhile, the single-layer structure renders graphene possible flexibility. These unique properties make graphene promising as a kind of alternative building block for fabricating ultrahigh thermal conductive yet superflexible macroscopic material. However, such graphene-based macroscopic materials including graphene film (GF), fiber, and nonwoven fabric have not been accessed yet.\[15–20\] For instance, in 2014, Shen et al. reported a GF with $K \approx 1100 \text{ W m}^{-1} \text{ K}^{-1}$ by direct evaporation of graphene oxide (GO) suspension under mild heating.\[21\] Xin et al. reported a GF fabricated by electrospray deposition of GO with $K \approx 1434 \text{ W m}^{-1} \text{ K}^{-1}$ and electrical conductivity $\rho \approx 10^{-5} \text{ S m}^{-1}$.\[22\] To improve the $K$ of GF, these films were all annealed under extremely high temperature to reduce phonon scattering centers, defects in the lattice structure and functional groups on graphene.\[23,24\] There are also many research efforts so far that have been devoted to reduce the edge effect of graphene and hence improve the performance of graphene-based macroscopic materials by using large graphene sheets.\[17,22,23,25–30\] Lots of edges from small-sized graphene restrain the $K$ and stretched graphene sheets limit the flexibility, the best GF ever reported only shows a $K \leq 1434 \text{ W m}^{-1} \text{ K}^{-1}$ and tensile strain <2%, worse than those of commercial graphitized polyimide film (GPI with $K \approx 1750 \text{ W m}^{-1} \text{ K}^{-1}$ and tensile strain $\approx 3\%$).\[21\] In 2015, Xin et al. reported graphene fibers with a $K \approx 1290 \text{ W m}^{-1} \text{ K}^{-1}$ by combination of large and small-sized GO sheets. The highly ordered arrangement of graphene sheets and dense structure lay a solid foundation for the heat transfer but sacrifice the flexibility of fibers (tensile strain <2%) as well.\[31\] Therefore, despite the superb properties of the individual graphene sheet, to balance the high $K$ and excellent flexibility of its assembled macroscopic material is still a big challenge so far.

Here, we solve the problem by folding atomic thin crystals of neat large-sized graphene into microfolds in macroscopic assembled GFs. The debris-free, giant graphene sheets endow GF with a $K$ of $1940 \pm 113 \text{ W m}^{-1} \text{ K}^{-1}$, due to maximum reductions of phonon-defect and boundary scattering. Simultaneously, the microfolds render GF superflexibility with
a high fracture elongation up to 16%, enabling it more than 100,000 cycles of 180°-bending and 6000 cycles of ultimate folding. The microfolds are formed by mechanical pressing of semifullerene-like microgasbags. The large-area multifunctional GFs can be easily integrated into high-power flexible devices in the real world, spanning from the aerospace industry to smartphones, for highly efficient thermal management.

In our philosophy, for ultrahigh $K$ of GF,\textsuperscript{20,32–34} we take two initiatives: employing debris-free, giant graphene oxide (dfGO) as raw material to reduce defective grain boundaries and using extremely high-temperature annealing process to obtain defect-free (Note: the defects mean the oxygen-containing functional groups, nanocavities and sp$^3$ carbon bonds on the surface of graphene) graphene sheets. For superflexibility, graphene crystals are folded to accommodate large elongation under external tension and provide enough freedom of bending deformation. The microfolds are evolved from the compressing of semifullerene-capped microgasbags.

Preparing dfGO and generating microgasbags are two key steps to fabricate debris-free GO-based graphene film (dfGF).

Large GO, prepared by chemical oxidation of graphite, contains many small pieces of debris, which seriously negative the performance of GF.\textsuperscript{35} In our case, dfGO (average lateral size 108 µm with a narrow relative standard deviation $\sigma_w$, 0.23) and pure GO debris (6 µm on average) are separated from commercial GO (Figures S1a and S2, Supporting Information). Then dfGO and GO debris were mixed with given mass ratios to make GO and GFs from different sized GO (GO-59: 59 µm on average with $\sigma_w$ 57%; GO-35: 35 µm on average with $\sigma_w$ 79%) as control samples.

Figure 1a illustrates our strategy of dfGF preparation (the detailed materials preparation procedure is shown in the Experimental Section and Figure S1 in the Supporting Information). dfGF was fabricated by casting dfGO aqueous dispersions followed by thermal annealing up to 3000 °C. The liquid crystal property of GO ensures a higher orientation of GO sheets align to the plane direction of GO film, much higher than that of GO solution (orientation of GO sheets, 87%) (Figure S1b,c, Supporting Information). During the annealing process, the microgasbags constructed by single or multilayer graphene sheets

![Figure 1](image_url)

Figure 1. Introducing microfolds to GF via microgasbags. a) Schematic illustration for transforming GO film with abundant defects into recovered, defect-free graphene gasbag capped with two giant semifullerenes, and then highly flexible GF composed of folded graphene. b) Top view surface of dfGF. c) Side view cross section of the dfGO film. Foamed dfGF constituted by semifullerene-like chambers from the d) top and e) side view. f) Top view surface of dense dfGF. g) Side view cross section of dense dfGF. Scale bars: 4 µm in (b), (c, up), (d–f), and (g, up); 300 nm in (c, down) and (g, down). More structure images are shown in Figure S4 (Supporting Information).
(Figure S3, Supporting Information) initially sprouted, grew, and matured in the graphitization step from relatively flat dfGO film (Figure 1b,c; Figure S5, Supporting Information), owing to the synergistic effect of gradually defects-healing, graphene sheets stacking, and gases expanding born from undocked dangling groups. The microgasbags with dimensions from several to tens of micrometers are closely packed along the sheet direction, spreading throughout the foamed films (Figure 1d,e). After statistic compression under a pressure of 300 MPa, large area, thickness-controlled dfGFs were produced with silvery color (Figure S1f, Supporting Information) and high density (1.93–2.03 g cm$^{-3}$). The resulting dfGFs are filled by microfolds, which are uniformly distributed in the whole bulk with a typical high surface density up to 471 mm mm$^{-2}$ on the peeled surface (Figure 1f,g).

Infrared imaging visually manifests that the heat-transfer speed of our dfGF is clearly faster than those of the best-GPI and Cu (Figure 2a). The dfGF (10 ± 0.4 μm) shows a $K_{1940} = 113$ W m$^{-1}$ K$^{-1}$, which outperforms the ever best graphene-based macroscopic material (1434 W m$^{-1}$ K$^{-1}$) by 35%, GPI (1750 W m$^{-1}$ K$^{-1}$) by 10%, and copper by 390% (Figure 2b).[2,19,36] and is even comparable to polycrystalline diamond film.[4] Meanwhile, our dfGF is highly flexible. It can keep high surface density up to 471 mm mm$^{-2}$ on the peeled surface (Figure 1f,g).

Normalized properties

<table>
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<tr>
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<th>dfGF</th>
<th>GPI</th>
<th>Cu</th>
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<tbody>
<tr>
<td>Diffusivity</td>
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<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>$K$</td>
<td>0.0</td>
<td>0.2</td>
<td>1.1</td>
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<tr>
<td>Folding times</td>
<td>0.0</td>
<td>0.2</td>
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Figure 2. Combined properties of dfGF. a) Infrared thermal imaging of dfGF, GPI, and copper foil. All of the samples have a thickness of 10 μm, attached vertically on a constant temperature microheater. Scale bar: 1 cm. b) Comparing our dfGFs with copper, GPI, and the previously reported best graphene-based macroscopic material including films/papers and fibers (ever best), in terms of $K$, thermal diffusivity, and folding cycles. All the properties are normalized to the best value of this work. c) The dfGF with the state of bending, curling, enwinding, twisting, and knotting. d) The flexible dfGF can accommodate with the complicated bending of the skin. e) The superfoldable dfGF with the size of 8 cm x 8 cm x 10 μm, which was folded into a crane without breakages left.

The extremely high $K$ of dfGF originates from two main factors: high crystalline and debris-free graphene sheets. Heat conduction of graphene is dominated by phonon diffusion from lattice vibrations of its covalent sp$^2$ bonding network.[23] The defects and grain boundaries of graphene sheets act as thermal resistance for substantial phonon scattering.[37] We employed an extremely high temperature annealing process to heal the defects of GO (Figure 3s).[17,18] With the temperature increasing from 1400 to 3000 °C, the $K$ of dfGF improved from 720 to 1940 W m$^{-1}$ K$^{-1}$ and the electrical conductivity ($σ$) elevated from 19 000 to 1 060 000 S m$^{-1}$. The defects restoration of graphene with conjugated structure is supported by X-ray photoelectron spectroscopy (XPS), elemental analysis, X-ray diffraction (XRD), Raman spectra, and high-resolution transmission electron microscopy (HR-TEM). After graphitization, dfGF had extremely high purity both in carbon element containing and sp$^2$ hybridized carbon structure. Negligible oxygen was detected by elemental analysis (C/O ratio, 443.1), coinciding
with the result from XPS. As shown in Figure S9a,b (Supporting Information), the strong peaks of oxygen-containing groups fade away gradually with the C/O ratio increasing from 2.42 to 96.14, reducing the d-spacing of dfGF from 8.9 to 3.34 Å (Figure 3b). Meanwhile, the dropping intensity of D-band (1350 cm\(^{-1}\), the defect-induced breathing mode) in Raman spectra (Figure 3c) manifests the stepwise healing of sp\(^2\) domains from 18.6 nm (I\(_D\)/I\(_G\) \(\approx\) 1.03, 500 °C) to >3.2 µm (I\(_D\)/I\(_G\) < 0.006, 3000 °C) (Figure S9c, Supporting Information). The undetectable D peak indicates a defect-free structure of graphene, which is more intact than those of commercial highly oriented pyrolytic graphite (HOPG) (961 nm sp\(^2\) domains, I\(_D\)/I\(_G\))
To minimize the grain boundaries of GF, we removed the debris and small-sized GO from the feed. After thermal annealing at 3000 °C, the GF made from the collected debris has an obvious D peak and a relatively high I_D/I_G value 0.07 (Figure S9d, Supporting Information), corresponding to a K of 1021 W m⁻¹ K⁻¹ and a ω of 360 000 S m⁻¹. The increasing of average size weakens the I_D/I_G from 0.03, 0.01, to < 0.006, corresponding to a growing K of 1334, 1625, and 1940 W m⁻¹ K⁻¹ and a σ of 730 000, 870 000, and 1 060 000 S m⁻¹ (Figure 3e). Note that a high temperature (T) can taper the average free range, increase Umklapp scattering of phonons, and finally lower the K, K ∝ 1/T. This effect is amplified by the edges of debris and small-sized graphene sheets. The K of dGF sustains 81% at 500 °C, 1.8 times that of debris-based GF (Figure 3f). To demonstrate the high heat-transfer rate of dGF in real electronics, we used it as the heat-dissipation film in a smartphone to replace the conventional GPI (Figure 3g–l). A particular game program had been worked for 20 min, generating certain energy. Then, the phone was tested having a temperature up to 39 °C. The mobile phone with dGF at game-state shows a peak-temperature of mere 33 °C, 6 °C lower than that of GPI-phone (Figure 3k,l). The average temperature of dGF-phone is lower than that of GPI-phone by about 4 °C, and the temperature distribution of the former is much more uniform than that of the later. The relatively low temperature of dGF in Figure 3k,l means that the dGF has a better thermal transfer rate, homogenizing the heat generated by the CPU.

Apart from the surprising K, dGFs exhibit superb flexibility. As revealed by typical stress–strain curves (Figure 4a–c), the dGF has a large elongation up to 16% and an elastic zone up to 3.2%. The ultimate breakage elongation of GFs is dominated by the linear density of microfolds, which is related to the state of the microgasbags. During the annealing treatment below 1700 °C, the microgasbags sprout and grow gradually with rising temperature (Figure S5, Supporting Information), improving the elongation from 3.0% to 6.7% (Figure S10a,b, Supporting Information). After 2000 °C, the microgasbags bulge rapidly, and the compressed microfolds have an increasing density from 306 to 471 mm mm⁻² (Figure S10c, Supporting Information), arising elongation from 10.6% to 16%. In addition, the abundant edges and holes of small sized GO debris could evolve into cracks that hamper the formation of microgasbag and the subsequent microfolds (Figure S10d–f, Supporting Information), lowering the elongation from 16% to 10% and the tensile strength from 60 to 24 MPa.

The dGF can survive more than 100 000 bending cycles without cracks generated both on surface and interior (Figure 4d; Figure S11a, Supporting Information). At different cycles, the dGF shows a constant electrical resistance and the temperature distribution during the microheater tests, revealing its structural integrity after ultralong bending cycles (Figure 4d,e). Beyond the bending at a relatively large curvature radius, dGF can also survive in repeated folding tests with the ultimately small curvature radius (equal to the thickness of the film; Figure S7, Supporting Information). The dGF still kept its σ and K after 6000 times of recycled folding.
with a repressing process under 300 MPa for every 1000 cycles (Figure 4d,f). This structural stability was further confirmed by the fact that no cracks were observed in the SEM measurements after folding tests (Figure S11b–e, Supporting Information).

It is the microfolds that determine the superflexibility of dfGFs. Owing to the stretchable microfolds, dfGFs possess a widely elastic zone (≈3.2%, Figure 4c) that enables them to fully recover original structures and properties after repeated deformation as well as a semielastic or elastic–plastic range (3.2%–16.0%) that guarantees the excellent retentivity of high K for a whole film even after overstretching. After being stretched to a high strain (e.g., 12.7%), the dfGFs can resize to 7.4% with an elastic zone of 5.3%. Under tension, the randomly dispersed and compacted microfolds (Figure S12a, Supporting Information) can be stretched out or even unfolded and deformed into anisotropic, aligned, and open crumples to adapt large tensile elongation and complex folding, which was confirmed by SEM observations (Figure 5; Figures S12e and S13b, Supporting Information). Notably, two dramatic changes are found at the fracture section after ultimate strain of dfGFs: (1) all of the interconnected microfolds perpendicular to the stressing direction have been unfolded (indicated by the yellow lines in Figure 5a), and (2) the microfolds parallel to the stressing direction have also been partially unfolded and deformed into open crumples orientated to the stretching direction (i.e., the originally isotropic, flat microfolds were deformed into aligned, waved microcrumpled under ultimate straining) (cyan lines in Figure 5a). At the magnified images, the local microfolds were also highly unfolded because of the strong stressing (Figure 5b,c). Figure 5d illustrates the unfolding of microfolds during folding of dfGFs. Such a highly flexible behavior of dfGFs reminds us the similar deformation mechanism of macromolecular chains in semicrystalline polymeric materials or conventional plastics,[44] as exemplified by silkworm silk. The macroscopic appearance of GF or plastic film is smooth, while the corresponding building blocks of monolayer graphene or single polymer chain could be folded. The stretching or unfolding of molecular chains or sheets contributes to the toughness of plastics or GF. Furthermore, microfolds can even tolerate strong twist transformation of GF into the fiber (Figure S13, Supporting Information) without any local damages generated,[45,46] opening an avenue to highly tough inorganic fibers composed of neat 2D nanoparticles. In the control samples of GO films and commercial GPI papers, their flattened lamellar structures without microfolds just provide a low elongation and a poor flexibility, and both the films broke seriously on the outer surface after folding for only once and fractured into pieces after 2–4 folding cycles (Figures S14, S15, and S7, Supporting Information).

The microfolds endow our GF a much higher elongation than that of the film with fewer microfolds (elongation, 2%–4%),[21,22] and they may have an adverse influence on K for introducing pores and lowering the degree of alignment. It was reported that chemical vapor deposition (CVD)-based polycrystalline few-layers graphene film had a high K (>2000 W m⁻¹ K⁻¹).[47] In our case of GFs, the positive effect of large-sized graphene sheets overwhelms the negative effect

Figure 5. Unfolding of microfolds on the fracture surface of dfGF. a) SEM image of unfolded microfolds on the fractured surface of a dfGF. The red arrows stand for the stressing direction. The yellow arrows indicate three unfolded, interconnected microfolds. b,c) The local microfolds were also highly unfolded under strong stressing. The dotted cyan and yellow lines stand for the stretched microfolds parallel and perpendicular to the drawing direction, respectively. d) Schematic stretching and folding mechanism of dfGF. The microfolds are marked in red lines. Scale bars: (a), 20 μm (left), 1.5 μm (right); (b), 2 μm (left), 600 nm (right); (c), 20 μm (left), 5 μm (right).
caused by microfolds, so dfGF shows a higher K than the small-sized GO based graphene film with fewer microfolds.

Apart from the temperature, the foaming process can also be managed by other factors. For instance, the mechanical pressure forcing on the film during the annealing process can inhibit the growth of microgasbags and reduce microfolds (Figure S10g, Supporting Information).[48] A higher pressure lowers the density of microfolds greatly from 410 mm mm$^{-2}$ (5 MPa) to 230 mm mm$^{-2}$ (40 MPa). Fewer microfolds of GF improve its tensile modulus and strength but lower the elongation from 13% to 7.2% (Figure S10h, Supporting Information).

This new model of flexible and thermally conducting material will boost the design of high-performance yet highly flexible materials. Significantly, the glistening surface of GF (insert of Figure S1f, Supporting Information) manifests that such local microfolds of atomic thin graphene do not influence the smoothness of GFs, which favors the fine contact with a substrate in the practical thermal conducting applications. So our approach based on the molecular level of folding is essentially different from the previous ones which created crumple of a whole macroscopic material with stretching elastic substrates.[49–53] As a result, our material surface is still highly smooth, whereas the previous cases are generally rough. Such an exploration resolved the main contradiction between high K and flexibility of a material, and it also triggers many new open questions, such as how to control the density, size, and orientation of microfolds. We believe that the resolution of these questions in the future will set up the precise relationship between molecular folding/unfolding and mechanical/thermal properties for 2D materials beyond graphene.

In conclusion, we have overcome the challenge of integrating high thermal conductivity and superflexibility together into one macroscopic material by folding atomic-thick crystals. The local folds are formed by mechanical pressing of semifullerene like microgasbags. The debris-free, giant graphene sheets endow our films, the small sized graphene sheets (e.g., graphene oxide or few layer graphene) and inhomogeneous stacking of graphene (e.g., multi-layer graphene or graphite particle) for previous graphitic materials limit either K or flexibility. Such scalable, multifunctional graphene films can be developed into novel engineering materials with ultrahigh thermal and electrical conductivity as well as prominent flexibility, which are extremely useful in the next generation of high-frequency flexible/wearable electronics, spanning from aerospace industry and smartphones. We believe that these design concepts and experimental techniques can be extended to other 2D nanomaterials (e.g., BN, MoS$_2$, FeS$_2$, Mo$_2$C, graphdiyne, and black phosphorus) without fundamental obstacles,[34] which would open the door for high-performance yet highly flexible materials and devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords
debris-free graphene oxide, defect-free graphene sheets, flexible graphene films, microfold, thermal conductivity

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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