Thermal Transport in Three-Dimensional Foam Architectures of Few-Layer Graphene and Ultrathin Graphite

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Supporting Information

ABSTRACT: At a very low solid concentration of 0.45±0.09 vol %, the room-temperature thermal conductivity (κGF) of freestanding graphene-based foams (GF), comprised of few-layer graphene (FLG) and ultrathin graphite (UG) synthesized through the use of methane chemical vapor deposition on reticulated nickel foams, was increased from 0.26 to 1.7 W m⁻¹ K⁻¹ after the etchant for the sacrificial nickel support was changed from an aggressive hydrochloric acid solution to a slow ammonium persulfate etchant. In addition, κGF showed a quadratic dependence on temperature between 11 and 75 K and peaked at about 150 K, where the solid thermal conductivity (κS) of the FLG and UG constituents reached about 1600 W m⁻¹ K⁻¹, revealing the benefit of eliminating internal contact thermal resistance in the continuous GF structure.

KEYWORDS: Graphene, graphite, foam, thermal conductivity, thermal management

Owing to the very high thermal conductivity as well as the large surface-to-volume ratio for carbon nanotubes (CNTs)¹ and graphene,² these carbon nanomaterials have been investigated as nanofillers to enhance the thermal conductivity of lightweight polymeric composites,³⁻⁷ as thermal interface materials in electronic packaging⁸⁻¹⁰ and as lateral heat spreaders to reduce the local hot spot temperature in nanoelectronic devices.¹¹,¹² Among several factors including agglomeration, structural deformation, defects, and support or medium interaction¹³,¹⁴ of the nanostructures, one critical issue that has prevented these CNT- and graphene-based networks to reach their full potential is the thermal contact resistance at their interface with both the medium and adjacent nanostructures.¹⁵,¹⁶ In addition, the performance of thermal interface materials based on vertical CNT arrays has been limited by the small fraction of nanotubes making contact to both mating surfaces and the large interface thermal resistance between nanotubes in the array.⁸⁻¹⁰ These problems can potentially be overcome by the recently reported macroscopic graphene-based foam (GF) structures¹⁷ because internal contact thermal resistance may be greatly reduced or eliminated in these continuous, three-dimensional (3D) architectures of covalently bonded two-dimensional (2D) graphene building blocks. In fact, the reported room temperature electrical conductivity of polymeric composites with the graphene foam fillers is 1⁻⁶ orders of magnitude higher than those with individual CNTs,¹⁸ or graphene¹⁹ fillers at a similar volume loading fraction. However, thermal transport properties of the GF structures have not been reported.

In this Letter, we report temperature-dependent electron and phonon transport measurements of 3D GF structures consisting of few-layer graphene (FLG) and ultrathin graphite (UG) synthesized through the use of methane chemical vapor deposition (CVD) on open-celled reticulated nickel foam. Our measurement results show that the structure quality and transport properties of the freestanding GF with a solid concentration of ~0.45 vol % depend much more sensitively on the etching process of the sacrificial Ni foam than on the grain size of the Ni foam. The room temperature effective thermal conductivity of the freestanding GF samples (κGF) with this very low solid concentration was increased 6.6 times after an aggressive Ni etchant was replaced with a gentle one. As the solid concentration was increased a factor of 3.1 by increasing the strut wall thickness, κGF was only increased a factor of 1.3, likely because of higher crystalline defects observed in the thicker strut walls. The obtained solid thermal conductivity, κGF, for all samples can be explained by a theoretical model suggesting that κGF is limited by phonon–phonon and phonon–boundary scatterings, instead of internal contact thermal resistance. Moreover, the theoretical analysis suggests an enhanced phonon–phonon scattering rate in GF and natural graphite (NG),²⁰ both of which contain internal folding, than in heat-treated highly oriented pyrolytic graphite (HT-HOPG).²¹

Six GF samples have been measured in this work, denoted as GF1−6. The GF was synthesized by saturation of carbon in
measurements, annealing the Ni foam at a temperature of 1100 °C before growth increased the grain size by ∼2–3 times and created a noticeably smoother surface (Figure S1, Supporting Information). The Ni was subsequently removed using dilute HCl, Fe(NO3)3, or (NH4)2S2O8. The latter Ni etching processes based on ferric nitrate and ammonium persulfate were found to be much slower and gentler than that based on dilute hydrochloric acid, which caused bubble formation during the etching process. After the Ni support was etched away, the mass density (ρm,GF) and volume fraction (ϕ) for GF1–4 were 0.010±0.002 g cm−3 and 0.45±0.09 vol %, respectively, and were increased to 0.03±0.003 g cm−3 and 1.41±0.10 vol %, respectively for GF5,6 by increasing the growth time by a factor of 3. A summary of synthesis conditions, mass density, and corresponding room temperature thermal properties for each GF sample is given in Table 1. During the entire sample preparation processes, the GF samples were not exposed to polymer, which have been found to scatter electrons22 and phonons14 in graphene.

SEM analysis of the GF is shown in Figure 1. For the thin-walled lower volume fraction samples, GF1–4, the structure quality is seen to increase significantly as the Ni etchant is replaced from dilute HCl (GF1, Figure 1a) to the two slow etchants based on Fe(NO3)3 (GF2,3, Figure 1b,c) and (NH4)2S2O8 (GF4, Figure 1d). For the thick-walled higher volume fraction samples, GF5,6, the structure is noticeably more defective than GF1–4 regardless of the Ni etchant used (Figure 1e,f).

Phase contrast transmission electron microscopy (TEM) images of the freestanding GF samples are shown in Figure 2 and Figure S2 in the Supporting Information. Amorphous carbon was not observed in the TEM analysis, and stacking in the GF was directly observed to be AB ordered. X-ray diffraction (XRD) analysis of the GF is shown in Figure 3a, along with the reflection positions and intensities for SP-1 grade HOPG23 for comparison. The (002) interlayer spacing was measured to be 3.3679 Å, close to the 3.3553 Å reported for high-quality HOPG.23 From the full width at half-maximum of the (002) and (004) reflections, we calculated the average thickness of the GF strut walls at ∼14 nm, or ∼40 layers, for GF1–4. On the basis of the same pore size and different mass densities, we estimated that the strut wall thickness was about 45 nm for GF5,6.

The GF strut wall was additionally characterized with micro-Raman spectroscopy at 488 nm laser excitation with an incident laser power on the order of a few milliwatts. The Raman spectra of the strut walls of the GF is shown in Figure 3b and matched well with those of high-quality graphite,24 with the very low volume fraction GF1–4 showing no observable D peak and the thicker walled GF5,6 exhibiting a D peak to G peak intensity ratio of ∼2%. The 2D peak to G peak intensity ratio for all samples was between 40% and 48%. Edges of voids present in the strut walls of GF1 also yielded characteristics of high-quality single- and few-layer graphene (Figure S3, Supporting Information), with small 2D peak to G peak intensity ratios of 1.6–3.3% likely resulting from edge states25 instead of point defects within the FLG and UG. The GF was further characterized in the spectral width of interest for thermal radiation by Fourier transform infrared (FTIR) spectroscopy (Figure 3c).

The effective thermal conductivity of the GF, κGF was obtained from the electrical resistance measured during electrical self-heating of the GF by a direct current. The thermal conductance of the GF is defined as $G_{GF} = \kappa_{GF}A/L_t$.
where $A = \text{wt}$ and $w, t,$ and $L$ are the width, thickness, and suspended length of the sample, respectively. As its dimensions were much larger than the nominal pore size within the foam, 590 $\mu$m, we can assume that the volumetric heat generation due to Joule heating, $\dot{q}$ is approximately uniform. We then account for heat transfer through both radiation and conduction with the following one-dimensional steady-state heat equation for the suspended GF:

$$\frac{d}{dx} \left( \kappa_{GF} A \frac{dT}{dx} \right) - \frac{h_i P(T - T_0)}{A} + \dot{q} = 0$$  \hspace{1cm} (1)$$

where $P = 2(w + t)$ and $h_i$ is the effective radiation heat transfer coefficient.

We define the temperature rise along the length of the GF as $\theta(x) = T(x) - T_0$, where $x = 0$ is the midpoint and $x = \pm L/2$ are the end-points so that $\theta(x = 0) = \theta_{\text{midpoint}}$ and $\theta(x = \pm L/2) = 0$. For small temperature rises, $\theta(x)$ much smaller than $T_0$, the effective radiation heat transfer coefficient reduces to

$$h_i = 4\varepsilon_{GF}(T_0)\sigma T_0^3$$  \hspace{1cm} (2)$$

where $\varepsilon_{GF}(T)$ is the emissivity and $\sigma$ is the Stefan–Boltzmann constant. The $\varepsilon_{GF}(T)$ calculated from the experimental FTIR result is shown in Figure S8 of the Supporting Information and is close to the upper limit of unity given for a black surface.

An analytical solution for $G_{GF}$ can then be formed as

$$G_{GF} = -\frac{Q}{m^2L^3\bar{\theta}} \left[ \frac{2}{mL} \tanh(mL/2) - 1 \right]$$  \hspace{1cm} (3)$$

where

$$m^2 \equiv \frac{h_i P}{\kappa_{GF} A}$$  \hspace{1cm} (4)$$

and $\bar{\theta}$ is the average temperature rise of the electrically heated suspended GF. We additionally note that if we take the limit of eq 3 as $m \to 0$, i.e., the case where radiation heat transfer becomes negligible compared to conduction, the above solution can be reduced to the following simple form

$$\lim_{m \to 0} G_{GF} = \frac{Q}{12\bar{\theta}}$$  \hspace{1cm} (5)$$

The obtained thermal conductance data of the GF samples is shown in Figure S9 of the Supporting Information and suggests that the radiation loss is not negligible for the low thermal conductance sample GF1 at temperatures above about 300 K and only causes a small error for this sample at lower temperatures and for the high conductance samples GF2–6 over the entire temperature range of measurements.

The total thermal conductivity of the GF is composed of both electronic and lattice contributions, $\kappa_{GF,e}$ and $\kappa_{GF,l}$ respectively. Using the Wiedemann–Franz law, the electronic contribution to the thermal conductivity can be calculated from the electrical resistivity, $\rho_{GF}$, as $\kappa_{GF,e} = LT/\rho_{GF}$ where $L$ is the Lorentz number and $T$ is the temperature. Over the measured temperature range, the maximum value for $\kappa_{GF,e}$ is only 0.2–3.6% of $\kappa_{GF}$. Hence, phonons make the dominant contribution to the thermal conductivity of the GF.

To determine the electrical and thermal properties of the FLG and UG constituents inside the GF, we use the approach of Lemlich and Schuetz and Glicksman, respectively. The solid electrical resistivity ($\rho_S$) and $\kappa_S$ are then

$$\rho_S = \left( \frac{\varphi}{3} \right) \rho_{GF}$$  \hspace{1cm} (6a)$$

and

$$\kappa_S = \left( \frac{3}{\varphi} \right) \kappa_{GF}$$  \hspace{1cm} (6b)$$

Equations 6a and 6b have been reported to be accurate in describing electrical and thermal transport in open-celled metal foams at low $\phi$. Although uncertainty remains in this model, subsequent semiempirical models do not deviate significantly from these original expressions at low $\phi$.30,31

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Figure 2. Transmission electron microscopy of GF1. (a) Low and (b) high resolution phase contrast micrographs near a void in the strut wall. (b, inset) Ordered AB stacking is observed at the folded edge of the 8-layer graphene, oriented close to the [2110] zone axis, and measured interlayer spacing for the (0002), (0111), and (0110) crystallographic planes closely match those determined more accurately through X-ray diffraction. Scale bars are 1 $\mu$m for (a), 5 nm for (b), and 1 nm for the inset in (b).

Figure 3. Optical characterization results. (a) X-ray diffraction spectrum of the GF shown in comparison with the reflection positions of SP-1 grade highly oriented pyrolytic graphite (HOPG) normalized to the (0002) reflection intensity. (b) Raman spectra of the six GF samples normalized to the G peak intensity. The main strut walls of GF1–4 exhibit spectra similar to defect-free bulk graphite with no detectable D peak, while the thicker walled GF5,6 exhibit D peak to G peak intensity ratios of about 2%. (c) Fourier transform infrared (FTIR) spectrum normal to the ~2 mm thick GF.
However, the anisotropic thermal conductivity of the FLG and UG strut walls of the GF considered here may call for future studies to improve the model for GF.

Figure 4 shows the obtained effective and solid thermal conductivity and electrical resistivity values of the GF. The

\[ \kappa_G \] for GF1 to 0.92–0.94 W m\(^{-1}\)K\(^{-1}\) for GF2,3 among the low-density GF, and 3.0–3.2 W m\(^{-1}\)K\(^{-1}\) for the higher density GF5,6. The corresponding peak \( \kappa_G \) values were \( \sim 250 \) W m\(^{-1}\)K\(^{-1}\) for GF1 and \( \sim 650 \) W m\(^{-1}\)K\(^{-1}\) for GF2, 3 and GF5, 6. For sample GF4, with a low mass density and processed with the very slow ammonium persulfate-based Ni etching process, \( \kappa_G \) reached a maximum at about 150 K with a peak value of 2.7 W m\(^{-1}\)K\(^{-1}\), corresponding to a peak \( \kappa_G \) value of \( \sim 1600 \) W m\(^{-1}\)K\(^{-1}\). Both the lower peak temperature and increased peak thermal conductivity are indicators of the decreased crystalline quality of GF4. We note that although samples GF5,6 with thicker FLG/UG strut walls show lower \( \rho \) than the samples with thinner strut walls, the solid thermal conductivity of GF4 is higher than that for GF5,6. The lower solid \( \kappa_G \) of GF5,6 may be attributed to higher crystallographic defects consistent with SEM and Raman observations, which could be a result of thermal expansion mismatch between the Ni support and the precipitated graphitic layers and other factors, whereas the increased defects may possibly increase the charge carrier concentration and reduce the \( \rho \) of GF5,6.

It has been suggested that only well-oriented and well-annealed graphite exhibits a quadratic temperature dependence of the low-temperature thermal conductivity; hence, the approximate \( \kappa_G \propto T^2 \) behavior observed for all GF samples between 11 and 77 K are indicative of well-oriented FLG and UG constituents. Additionally, the decreasing thermal conductivity with increasing temperature observed in the GF samples at \( T > 200 \) K reveals the dominant role of phonon–phonon scattering processes and suggests that the thermal conductivity is limited by phonon–phonon scattering and not internal contact thermal resistance. However, the \( \kappa_G \) values of the GF samples are still lower than the peak basal plane values reported for HT-HOPG and natural graphite, respectively, as shown in Figure 4d.

We have analyzed the measurement results with the following thermal conductivity model\(^27\)

\[ \kappa = \sum_{p=1}^{12} \kappa_p \]

\[ = \frac{1}{8\pi d k_B T^2} \sum_{p=1}^{12} \int \left( \frac{h\nu_p}{k_B T} \right)^2 \nu_p^2 (\hbar \nu_p)^2 \tau_p \left( e^{\hbar \nu_p/k_B T} - 1 \right)^2 k \, dk \]

(7)

where \( \delta \) is the {0002} interplanar spacing, \( k_B \) and \( \hbar \) are the Boltzmann constant and the reduced Planck constant, respectively, \( \tau_p \) is the relaxation time, \( \omega_p \) is the phonon frequency, \( k \) is the wavevector, and \( \nu_p \) is the phonon group velocity. The summation is over the 12 different phonon polarizations \( (p) \) of AB stacked graphite.\(^7\) The crystallographic information obtained by XRD allows us to accurately determine \( \delta \) and the Brillouin zone dimensions for the GF in addition to its AB stacked structure (Figure S9, Supporting Information).

In eq 7, the total polarization-specific relaxation time, \( \tau_{p}^{\delta} \) including contributions from phonon–boundary, phonon–impurity, and umklapp phonon–phonon scattering processes, is calculated using the relaxation time approximation (RTA) of Klemens and Pedraza.\(^8\) Although it has been shown recently that the RTA does not adequately account for the selection rules governing phonon scattering in single- and few-layer graphene,\(^9\) it can still provide important physical insights into thermal transport in graphite and the GF structures. For
example, by fitting the thermal conductivity data at low temperatures where boundary scattering is expected to be dominant, this model suggests that the phonon–boundary scattering mean free path is ≈525 nm for GF1, 1.5 μm for GF2,3 and GF5,6, 4.25 μm for GF4, 9 μm for HT-HOPG,21 and 55 μm for NG.20 We note that the in-plane phonon mean free path is affected more strongly by lateral grain size and the interlayer coupling strength between the 2D graphene sheets in the FLG/UG strut walls, as opposed to scattering by the top and bottom surfaces of the strut wall, with the latter being the case for semiconductor thin films. The much smaller phonon–boundary mean free path value for GF1 than for GF2–6 is in agreement with the SEM observation of a high density of voids in GF1, presumably caused by the aggressive hydrochloric acid-based Ni etching process. However, the similar value found for GF5 and GF6 suggests that the structural integrity of the higher density GF, with correspondingly thicker strut walls, is much less sensitive to the Ni etching conditions than the low-density samples GF1–4. Moreover, the model suggests stronger phonon–boundary scattering in NG20 and GF than in HT-HOPG,21 approximately 6.3, 9.4, 3.9, and 1.1 times higher for NG,20 GF1, GF2,3, and GF5,6, and GF4 at room temperature, respectively. According to a recent TEM study,40 the grain size of the NG samples is larger than a millimeter, much larger than the 6–30 μm grain size for HOPG. Moreover, the TEM results reveal internal folded bands inside NG.40 Similar folded bands can also be observed in the SEMs of our GF samples (Figure S1, Supporting Information). It remains to be investigated whether these folded bands may also lead to enhanced phonon–phonon scattering near the folded regions in addition to reducing the effective boundary scattering mean free path to be smaller than the grain size.

Despite the question on the effect of the folded bands, the continuous GF structure shows clearly superior thermal conductivity than other nanocarbon networks or metal foams. At a very low graphene loading of about 0.5 vol %, the effective room temperature thermal conductivity of 1.7 W m⁻¹ K⁻¹ of the GF is already a factor of 13–53, 2.6, and 8–12 higher than the filler contribution in polymeric composites with randomly oriented CNTs,3,4 magnetically aligned MWCNTs,4 and FLG/UG particle5–7 fillers at similar loadings. Moreover, the GF samples with density 1.3–4.1 times lower than that of the sacrificial Ni foam can achieve a room temperature solid thermal conductivity that is a factor of 5–11 and 1.2–2.5 higher than for Ni and Cu, respectively.

Figure 5 shows an additional comparison between the effective thermal conductivity of GF samples in this work and pitch-derived carbon foams graphitized at 1000 and 2800 °C.41 The mass density of the graphitized carbon foams is much larger than that for all the GF samples, mainly because of much thicker strut walls for the graphitized foams. Table S2 in the Supporting Information summarizes the specific thermal conductivity, defined as the ratio between the effective thermal conductivity and the mass density expressed in specific gravity. Both Figure 5 and Table S2 show that the specific thermal conductivity of the GF samples grown by CVD at a temperature of 1050 °C greatly exceeds that of the carbon foams graphitized at 1000 °C and approaches values reported for those graphitized at a much higher temperature of 2800 °C.

High-temperature annealing of the GF may lead to further enhancement of the specific thermal conductivity. Moreover, the GF structure with nanometer scale strut wall thickness can provide a much larger heat transfer surface area for a given solid volume than existing graphitic foams with micrometer scale strut wall thickness,41 making GF more effective for heat transfer fin and filler applications based on the effective medium theory,42 provided that the pore size of the GF can be reduced to achieve a comparable volume fraction as those of the graphitic foams without increasing the strut wall thickness. These experiments lead to the establishment of the correlation between the transport properties of free-standing GF structures and the processing conditions. It is shown that enhancement in the thermal conductivity of the low-density GF by more than a factor of 6 can be obtained with the use of a slow etching process of the sacrificial Ni support. The thermal transport measurement results further reveal that phonon transport in the GF is only limited by the unfolded crystallite domain size at low temperature and phonon–phonon scattering near room temperature in the FLG/UG building blocks, as opposed to interface phonon transmission that has reduced the effective thermal conductivity of van der Waals-bonded carbon nanomaterial networks. Because the effective thermal conductivity is limited by the very low GF volume fraction instead of internal contact thermal resistance, it is feasible to further increase the effective thermal conductivity of this 3D graphene architecture by more than 1 order of magnitude via an increase in the graphene volume fraction through the reduction of the pore size without increasing the strut wall thickness. Therefore, this 3D graphene-based architecture holds great promise as thermal interface and heat spreading materials that meet the requirements in both the thermal conductivity and mechanical compliance for thermal management of electronic devices as well as thermal storage and electrochemical devices.43

ASSOCIATED CONTENT
Supporting Information
Additional SEM, TEM, and Raman analysis, synthesis and structural characterizations, thermal conductance measurement and analysis, theoretical thermal conductivity modeling, and
comparison with graphitized carbon foams. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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I. Additional scanning and transmission electron microscopy analysis.

**Figure S1.** GF synthesis and effect of annealing of nickel foam. Scanning electron micrographs of (a) as-purchased Ni foam, (b) few-layer graphene (FLG) and ultrathin graphite (UG) on as-purchased Ni foam after 1 hr growth and (c) resultant free-standing graphene-based foam (GF) after Ni etching by Fe(NO₃)₃ and dilute HNO₃. (d) Ni foam annealed at 1100 °C, (e) FLG / UG on annealed Ni foam after 1 hr growth and (f) resultant free-standing GF after Ni etching by Fe(NO₃)₃ and dilute HNO₃. Scale bars in (a–f) are 10 μm.
Figure S2. (a) Transmission electron micrograph near a void in the strut wall of the GF1. High resolution TEM of (b) 1-, (c) 2-, (d) 4-, and (e) 8-layered graphene observed at regions of corresponding color labels in (a). The convoluted structure complicates statistical analysis of grain size within the GF as many overlapping sections are irradiated by the electron beam at varying angles of incidence. Scale bars are 1 μm for (a) and 5 nm for (b–e).

II. Additional micro-Raman spectroscopy analysis.

Figure S3. Raman spectra at different positions on the strut walls of GF1 normalized to the G peak intensity. (i,ii) Main strut walls exhibit spectra similar to defect-free bulk graphite$^{S1}$ with no detectable D peak, while areas at the edges of strut wall voids in GF1 exhibit spectra of (iii,iv) few- and (v) single-layer graphene with D peak to G peak intensity ratios of $I_D / I_G = 1.6$, 2.5, and 3.3 % for (iii), (iv), and (v), respectively, likely arising from edge states.$^{S2}$
III. Synthesis and structural characterizations.

GF was synthesized on Ni foam (INCOFOAM™, Novamet Specialty Products Corp.) with the following specifications: 42×10^{-3} g cm^{-2} foam density, 590 μm nominal pore size, and 1.9 mm thickness. Ni foam used for the GF synthesis was used either as purchased, or annealed for ~ 24 hours at 1100 °C under flowing H_2 (40 sccm, 99.999 %) at ~ 50 Torr and cooled back to room temperature at 0.25 °C min^{-1}. The Ni foam was cut into ~ 2 cm by ~ 5 cm strips and positioned at the center of a 1 inch fused quartz tube in a hot wall furnace (TF55035A-1, Lindburg® BlueM®). The quartz tube was ramped to 1050 °C at atmospheric pressure under flowing Ar (40 sccm, 99.999 %) and H_2 (10 sccm, 99.999 %). The Ni foam was kept under Ar / H_2 for 30 minutes before introducing CH_4 (99.999 %). Ni foam was exposed to 5 sccm CH_4, 5 sccm H_2, and 40 sccm Ar for 60 minutes at 1050 °C for GF1–4 and 3 hours for GF5–6, then cooled at a rate of 10 °C min^{-1} to room temperature. The as-synthesized foam was cut into several-cm long strips, each 3–5 mm wide, and the Ni was subsequently removed in a wet etchant. The Ni was etched in dilute HCl (5 wt %) at 80 °C for ~ 20 hours for GF1 and GF5, in Fe(NO_3)_3 (1 M) at 80 °C for ~ 15 days followed by HNO_3 (5 wt %) at 50 °C for ~ 5 days for GF2–3, or in (NH_4)_2S_2O_8 (1 M) at 80 °C for 1 week followed by HNO_3 (0.5 M) at 80 °C for 3 days for GF4 and GF6. The GF was then placed gently in several baths of deionized H_2O, and finally in isopropyl alcohol before drying under ambient conditions at 50 °C. To determine the mass density, \( \rho_{m,GF} \), and volume fraction, \( \phi \), of the GF, the mass of several pieces of GF from similar furnace positions in the same growth were measured using a high precision electronic balance (XP105DR, Mettler-Toledo International Inc.), and was seen to vary by approximately 10–20 %. This density variation was consistently seen for several growth batches with the same growth parameters and did not show correlation to position in the furnace over the ~ 5 cm length of Ni foam from each growth batch.

Scanning electron microscopy was conducted at 30 kV accelerating voltage (Quanta 600 FEG, FEI Company and Supra 40 VP, Carl Zeiss, Inc.). Transmission electron microscopy was conducted at 200 kV accelerating voltage (Tecnai G2 F20 X-TWIN, FEI Company). X-ray diffraction was conducted using the Cu Kα_1 X-ray line, \( \lambda = 0.15405 \) nm (X’Pert-MPD, PANalytical B.V.), unit cell parameters
were measured to be: $a = b = 2.4646 \text{ Å}$, $c = 6.7358 \text{ Å}$. Raman spectroscopy was conducted using a 100×, 0.9 N.A., objective and 488 nm laser excitation (Alpha 300, WITEC GmbH). The $G$ peak positions for all Raman spectra are $\sim 1580 \text{ cm}^{-1}$, corresponding to a negligible temperature rise on the illuminated GF strut wall which can be expected owing to our use of a low laser power of a few mW. The temperature rise does not affect our determination of high quality FLG/UG constituents within the macroscopic GF based on the $D$ peak intensity. Infrared spectroscopy of GF and background were conducted after purging with $N_2$ for $\sim 30$ min with a fixed aperture (Infinity Gold FTIR, Thermo Mattson).

**IV. Thermal conductance measurement and analysis.**

The few-layer graphene (FLG) and ultrathin graphite (UG) foam sample (GF) was fixed at each end to a copper heat sink using a high thermal conductivity, electrically insulating epoxy (STYCAST™ 2850 FT BLK, Emerson & Cuming, Inc.) and electrodes were attached in a four-point differential resistance configuration using an electrically conducting silver epoxy (EPO-TEK H20E, Epoxy Technology, Inc.), leaving a $\sim 9–15$ mm length suspended between the copper heat sinks. The experimental setup is shown in Figure S4. The sample was then placed into a vacuum cryostat (ST-100HT, Janis Research Co., Inc.) connected to a turbo/mechanical pumping system (Turbovac TW250S / Trivac D16B, Oerlikon Leybold Vacuum GmbH) that maintained a vacuum level better than $10^{-5}$ Torr. The local environment temperature surrounding the GF, denoted $T_0$, was actively controlled through a cryogenic temperature controller (Model 331, Lake Shore Cryotronics, Inc.). A high accuracy current source (Model 6221, Keithley Instruments, Inc.) was used to supply a DC current of up to 105 mA through the suspended GF, raising its temperature through Joule heating. The experiment was conducted and the data were processed as follows.
Figure S4. (a) Top- and (b) side-view photographs of the experimental setup for measuring the electrical and thermal properties of GF1. (c) Top- and (d) side-view photographs of GF6 (upper sample) and GF5 (lower sample). The electrical circuit is shown schematically in (a). Scale bars are 1 cm.

A direct current, $I_{DC}$, flows through the suspended GF and generates heating at the rate $\dot{Q} = I_{DC}^2 R_{GF}$, where $R_{GF}$ is the electrical resistance of the suspended GF. For each environment temperature $T_0$, the DC current applied was ramped from $I_{DC} = 0$ to $I_{DC} = -I_{DC,\text{max}}$ to $I_{DC} = +I_{DC,\text{max}}$ and back to $I_{DC} = 0$. The thermal time constant $\tau_{th}$ of the suspended GF was estimated to be on the order of 1 min at room temperature according to the expression $\tau_{th} = L^2 / (\pi^2 \alpha)$, where $L$ is the GF suspended length and $\alpha = \kappa_{GF} / (\rho_{m,GF} C_p)$ is the thermal diffusivity estimated from the measured GF thermal conductivity, $\kappa_{GF}$, and mass density, $\rho_{m,GF}$, and the specific heat of graphite, $C_p$. Based on this thermal time constant, the heating current was held constant for several minutes at each $I_{DC}$ before $\Delta V_{DC}$ was recorded to ensure a steady-state temperature rise.

The average temperature rise on the GF as a function of applied DC current is defined as $\bar{\theta}(I_{DC}) = \overline{T}(I_{DC}) - \overline{T}(I_{DC} = 0)$, where $\overline{T}(I_{DC} = 0)$ is the environment temperature. A change in temperature induces a change in electrical resistance which is interpreted by measuring the resistance at different environment temperatures. The quantitative average temperature rise can then be calculated.
from the measured electrical resistance as $\bar{\sigma}(I_{DC}) = [R_{GF}(I_{DC}) - R_{GF}(I_{DC} = 0)] / [dR_{GF} / dT]$. The measured $R_{GF}$ at the low electric bias limit is shown as a function of temperature in Figure S5. The resistance of the Joule-heated GF at different electrical heating rate was measured by either a DC or an AC method, as discussed below.

**Figure S5.** (a) Measured low-bias electrical resistance ($R_{GF}$) and (b) normalized low-bias resistance change with temperature $[(dR_{GF} / dT) / R_{GF}]$ versus temperature for GF1–6.

In the DC method, a low-noise voltage preamplifier (Model SR560, Stanford Research Systems, Inc.) was used to measure the voltage drop, $\Delta V_{DC}$, across the suspended GF. The measured four-point voltage drop, $\Delta V_{DC}(I_{DC})$, is shown in Figure S6a and can be expressed through a least-squares third-order polynomial curve fit as

$$\Delta V_{DC}(I_{DC}) = a_3 I_{DC}^3 + a_2 I_{DC}^2 + a_1 I_{DC} + a_0. \quad (S1)$$

The four-point electrical resistance of the GF can be determined from eq S1 as

$$R_{GF,fit}(I_{DC}) = \frac{\Delta V_{DC}(I_{DC}) - a_0}{I_{DC}} = a_3 I_{DC}^2 + a_2 I_{DC} + a_1. \quad (S2)$$

The electrical resistance of the GF can also be obtained directly from the experimental data without fitting as

$$R_{GF}(I_{DC}) = \frac{\Delta V_{DC} \Delta_{DC}}{\Delta_{DC}}. \quad (S3)$$
Figure S6. (a) DC voltage ($V_{DC}$), (b) electrical resistance ($R_{GF}$) by DC detection, and (c) average temperature rise ($\bar{\theta}$) plotted versus DC current ($I_{DC}$) for the electrically self heated GF1. Values for $R_{GF}$ shown in b calculated by the least-squares third-order polynomial fit of $V_{DC}(I_{DC})$ divided by $I_{DC}$ (open circles) and by $V_{DC}$ divided by $I_{DC}$ (filled diamonds) are in good agreement. (d) Joule heat generation rate in the GF ($\dot{Q}$) plotted versus average temperature rise ($\bar{\theta}$). Environment temperature for (a–d) is 201 K.

The results from the two methods are in good agreement with each other as shown in Figure S6b, however, the result from eq S3 is relatively noisy at the low current limit compared to that from eq S2.
Figure S7. Average temperature rise ($\overline{\theta}$) plotted versus DC current ($I_{DC}$) for the electrically self heated GF. The equivalence of the DC and DC + AC techniques are shown over the AC frequency range of $2 \leq f \leq 2 \times 10^4$ Hz. Due to the large thermal time constant of the suspended GF segment, the AC current causes negligible temperature modulation of the GF.

In the AC technique (Figure S7), a small sinusoidal current ($i_{ac,rms} = 1$ mA, $f = 500$ Hz) was sourced from a lock-in amplifier by placing a $5 \, k\Omega$ fixed resistor in series with the lock-in voltage output at $5 \, V_{rms}$ and coupled with the $I_{DC}$ sourced from a high accuracy DC current source. At this frequency, the thermal time constant of the GF, on the order of 1 min, is much larger than the inverse of the period of the AC current. Consequently, the AC current yields a trivial first harmonic oscillation ($\delta R_{GF,ac}$) in the resistance of the GF. The first harmonic component of the voltage drop, $v_{ac,rms}$, measured across the suspended GF contains mainly the $i_{ac,rms} R_{GF}$ drop, which is much larger than the $\delta R_{GF,ac} I_{DC}$ product.\textsuperscript{54} Hence, we have verified that it is accurate to obtain $R_{GF}(I_{DC}) = v_{ac,rms} / i_{ac,rms}$ for $f \geq 2$ Hz, as shown in Figure S7, where the measured resistance change has been converted into the average temperature rise in the GF. The AC method is more sensitive than the DC method for the GF samples with low electrical resistance.

The suspended GF is of uniform cross-sectional area $A = wt$, where $w$ and $t$ are the width and thickness of the sample, respectively. As its dimensions are much larger than the nominal pore size within the foam, 590 μm, we can assume that the volumetric heat generation due to Joule heating, $\dot{q} \equiv \dot{Q}/V$, is...
also uniform, where \( \nu = AL \) is the volume of the suspended GF. Radiation heat loss from the sample can lead to considerable errors in the thermal conductance measurement at high temperatures.\textsuperscript{55} In our measurement, two radiation shields were used to reduce the radiation loss, with the inner radiation shield thermally anchored to the sample stage. With the assumption that the inner radiation shield is at a temperature close to the sample stage temperature \( T_0 \), we account for heat transfer through both radiation and conduction with the following one-dimensional steady-state heat equation for the suspended GF sample

\[
\frac{d}{dx}\left( \kappa_{GF}(T) \frac{dT}{dx} \right) - \frac{h_r P(T - T_0)}{A} + \dot{q} = 0, \tag{S4}
\]

where \( \kappa_{GF}(T) \) and \( P = 2(w + t) \) are the thermal conductivity and the cross-sectional perimeter of the GF. An effective radiation heat transfer coefficient, \( h_r \), can be expressed as

\[
h_r = \varepsilon_{GF}(T)\sigma(T^2 + T_0^2)(T + T_0), \tag{S5}
\]

where \( \varepsilon_{GF}(T) \) is the emissivity and \( \sigma \) is the Stefan-Boltzmann constant. The porosity of the GF makes an analytical expression for the emissivity and surface area difficult, however we note that the emissivity of the surface defined by the effective perimeter \( P \) of the GF cannot be greater than 1. In order to increase the accuracy of our calculation, we have used Fourier transform infrared spectroscopy (FTIR, Infinity Gold, Thermo Mattson) to probe the optical properties of the GF in the spectrum of interest for thermal radiation heat transfer, and over the wavelength interval of \( 2.5 \leq \lambda \leq 25 \text{ \mu m} \) the spectral transmission normal to the \(~ 2 \text{ mm thick GF, } \tau_{GF,\lambda} \), ranges from 0.062 – 0.003 (Figure 3c, article). With the reflection neglected and the GF surface assumed to be diffuse,\textsuperscript{56} we obtain \( \varepsilon_{GF,\lambda} = 1 - \tau_{GF,\lambda} \). The temperature-dependent total hemispherical emissivity, \( \varepsilon_{GF}(T) \), can be obtained as

\[
\varepsilon_{GF}(T) = \int_{\lambda=0}^{\infty} \left( 1 - \frac{E_{\lambda,b}(\lambda,T)}{E_b(T)} \right) d\lambda, \tag{S6}
\]

where \( E_{\lambda,b} \) and \( E_b \) are the spectral and total black-body emissive power respectively,\textsuperscript{56} given by
\[ E_{\lambda,b}(\lambda, T) = \frac{2hc^2}{\lambda^5} \left( e^{\frac{hc}{\lambda k_B T}} - 1 \right)^{-1} \]  

(S7a)

and

\[ E_b(T) = \sigma T^4, \]  

(S7b)

where \( h \) is Planck’s constant, \( c \) is the speed of light in a vacuum and \( k_B \) is Boltzmann’s constant. The \( \varepsilon_{GF}(T) \) calculated from the experimental FTIR result is shown in Figure S8, and is close to the upper limit of unity given for a black surface. With the reflection accounted for, the actual emissivity could be somewhat lower than the value shown in Figure S8.

![Figure S8](image)

**Figure S8.** Total emissivity of the GF (\( \varepsilon_{GF} \)) plotted versus temperature.

We define the temperature rise along the length of the GF as \( \theta(x) = T(x) - T_0 \), where \( x = 0 \) is the mid-point and \( x = \pm L / 2 \) are the end-points so that \( \theta(x = 0) = \theta_{\text{mid-point}} \) and \( \theta(x = \pm L / 2) = 0 \). For small temperature rises, \( \theta(x) \) much smaller than \( T_0 \), the effective radiation heat transfer coefficient reduces to

\[ h_r = 4\varepsilon_{GF}(T_0)\sigma T_0^3. \]  

(S8)

Since the maximum temperature rise is only \( \theta_{\text{mid-point}}(I_{\text{DC,max}}) = (7.8 - 1.7) \, \text{K} \) at \( T_0 = (400.4 - 25.2) \, \text{K} \) for the DC measurement and \( \theta_{\text{mid-point}}(I_{\text{DC,max}}) = (5.1 - 1.0) \, \text{K} \) at \( T_0 = (399.7 - 11.0) \, \text{K} \) for the coupled DC and AC measurement, we assume constant \( \kappa_{GF} \) along the suspended GF and simplify the heat equation as
\[
\frac{d^2 \theta}{dx^2} - m^2 \theta + \frac{\dot{Q}}{\kappa_{GF} AL} = 0, \quad (S9)
\]

where
\[
m^2 \equiv \frac{h_r P}{\kappa_{GF} A}. \quad (S10)
\]

The general solution to the temperature profile is then
\[
\theta(x) = T(x) - T_0 = C_1 e^{mx} + C_2 e^{-mx} + \frac{\dot{Q}}{m^2 \kappa_{GF} AL}; \quad -L/2 \leq x \leq L/2. \quad (S11)
\]

Symmetry and the end-point temperature yield the boundary conditions, \( \frac{d\theta}{dx}|_{x=0} = 0 \) and \( \theta(x=L/2) = 0 \), respectively, where \( x \) is the distance from center of the suspended GF. Applying the temperature profile of eq S11 to the boundary conditions we then express the analytical temperature profile as
\[
\theta(x) = -\frac{\dot{Q}}{m^2 \kappa_{GF} AL} \left( \frac{e^{mx} + e^{-mx}}{e^{mL/2} + e^{-mL/2}} - 1 \right) = -\frac{\dot{Q}}{m^2 \kappa_{GF} AL} \left[ \frac{\cosh(mx)}{\cosh(mL/2)} - 1 \right]; \quad -L/2 \leq x \leq L/2. \quad (S12)
\]

We can define the thermal conductance of the GF as \( G_{GF} = \kappa_{GF} A / L \) and rewrite eq S12 as
\[
\theta(x) = -\frac{\dot{Q}}{m^2 L^2 G_{GF}} \left[ \frac{\cosh(mx)}{\cosh(mL/2)} - 1 \right]; \quad -L/2 \leq x \leq L/2. \quad (S13)
\]

The average temperature rise on the GF is obtained as
\[
\bar{\theta} = \frac{1}{L} \int_{x=-L/2}^{L/2} \theta(x) dx = -\frac{\dot{Q}}{m^2 L^2 G_{GF}} \left[ \frac{2}{mL} \tanh(mL/2) - 1 \right], \quad (S14)
\]

which allows us to express the thermal conductance and effective thermal conductivity of the GF as
\[
G_{GF} = -\frac{\dot{Q}}{m^2 L^2 \bar{\theta}} \left[ \frac{2}{mL} \tanh(mL/2) - 1 \right] \quad (S15a)
\]
and
\[
\kappa_{GF} = -\frac{\dot{Q}}{m^2 LA \bar{\theta}} \left[ \frac{2}{mL} \tanh(mL/2) - 1 \right], \quad (S15b)
\]
respectively. The value of $\frac{\dot{Q}}{\theta}$ is taken from a linear least-square curve fit of $\dot{Q}(\theta)$ as shown in Figure S6d. We additionally note that if we take the limits of eqs S14 and S15 as $m \to 0$, i.e. the case where radiation heat transfer becomes negligible, the analytical solutions take the simple forms

$$\lim_{m \to 0} \theta(x) = -\frac{\dot{Q}}{2G_{GF}} \left[ \left( \frac{x}{L} \right)^2 - \frac{1}{4} \right] \cdot -L/2 \leq x \leq L/2,$$  \hspace{1cm} (S16a)

$$\lim_{m \to 0} G_{GF} = \frac{\dot{Q}}{12\theta} ,$$ \hspace{1cm} (S16b)

and

$$\lim_{m \to 0} \kappa_{GF} = \frac{\dot{Q}L}{12\theta \Lambda} .$$ \hspace{1cm} (S16c)

The maximum temperature rise on the GF, $\theta_{\text{mid-point}}$, is on the order of $(1-8)$ K, so that the calculated $G_{GF}$ and $\kappa_{GF}$ are interpreted as the mean values over the temperature range $T_0$ to $T_0 + \theta_{\text{mid-point}}$. The obtained thermal conductance data of the GF samples shown in Figure S9 suggests that the radiation loss is not negligible for the low thermal conductance sample GF1 at temperatures above about 300 K, and only causes a small error for this sample at lower temperatures and for the other high conductance GF samples in the entire temperature range of measurements. Although the radiation correction is expected to yield a more accurate result than that obtained with the radiation loss ignored, the neglect of the reflectance and the assumption of a diffuse surface can overestimate the emissivity and radiation loss. Hence, the actual value is expected to lie between the two results with and without the radiation correction. Because these two results are close to each other except for the thermal conductance data for GF1 at above 300 K, we have used the radiation corrected thermal conductance to calculate the thermal conductivity data reported in Figure 4 in the article. The thermal conductivity data for GF1 at above 300 K are not included in Figure 4 because of the considerable difference between the two results obtained with and without the radiation correction.
V. Theoretical thermal conductivity model.

We have analyzed the experimental thermal conductivity values using a phenomenological model. The phonon dispersions for highly oriented pyrolytic graphites (HOPG), also referred to as Bernal\textsuperscript{87} or 3D graphite, differ from those of randomly oriented or turbostratic graphites and 2D graphene. First of all, the unit cell size along the $c$-axis is $2\delta$ for HOPG and $\delta$ for graphene, where $\delta$ is the interlayer spacing. Consequently, the primitive cell consists of two and four carbon atoms for HOPG and graphene, respectively. Therefore, there are three acoustic and nine optical phonon branches for HOPG (Figure S10a). In comparison, there are three acoustic and three optical phonon branches for graphene.
Figure S10. (a) Phonon dispersion for graphite of Al-Jishi, et al.\textsuperscript{58} used in the theoretical thermal conductivity model. (b) Thermal conductivity of the few-layer graphene and ultrathin graphite itself ($\kappa_G$) versus temperature for GF4 (purple up triangles). The total $\kappa$ calculated according to eqs S22–S26 using parameters listed in Table S1 (solid yellow and gray line) is shown along with the thermal conductivity contributions of individual phonon polarizations shown in (a). Line colors and styles of individual phonon polarizations in a correlate with their $\kappa$ contributions in (b).

The most notable difference is the appearance of the low-frequency out-of-plane and in-plane transverse optical modes, ZO' and TO', respectively, and the longitudinal optical mode, LO', for HOPG. While the TO' and in-plane transverse acoustic (TA) modes and the LO' and longitudinal acoustic (LA) modes are nearly degenerate, the ZO' and out-of-plane transverse acoustic, ZA, modes differ
significantly, with the ZO’ mode exhibiting much lower phonon velocity. The contribution of the remaining optical modes (i.e., out-of- and in-plane transverse optical, ZO1/ZO2 and TO1/TO2, respectively, and longitudinal optical modes, LO1/LO2) to the thermal conductivity is expected to be small due to low occupation probability in the temperature range considered here as well as strong scattering of these optical modes. Thus, weakly interacting graphitic layers had been modeled in the literature with dispersions calculated for 2D graphene, although we note that phonon scattering should differ between turbostratic graphite and graphene, and ordered graphites such as HOPG with dispersions calculated for 3D graphite. In fact, inelastic neutron scattering of ordered pyrolytic graphite and electron energy loss spectroscopy of monolayer graphite have shown the phonon dispersion of these materials is similar to those of 3D graphite and 2D graphene, respectively, with the observation of the ZO’, TO’, and LO’ modes only in the ordered pyrolytic graphite sample.

As we have verified ordered AB stacking in our GF, and that transport is mainly along the a–b plane in the FLG and UG, we use the full phonon dispersion for 3D graphite of Al-Jishi et al. (Figure S10a) with wave vectors, k, defined along the high symmetry Γ–M and Γ–K directions according to the carbon–carbon nearest neighbor distance for the GF determined by X-ray diffraction (XRD) as

\[ k_{\Gamma-M} = \frac{2\pi}{3a_{c-c}} \]  

(S17a)

and

\[ k_{\Gamma-K} = \frac{4\pi}{3\sqrt{3}a_{c-c}}. \]  

(S17b)

The unit cell parameters of the FLG and UG within the GF determined by X-ray diffraction (XRD) (Figure 3a, article) are \( a = b = 2.4646 \text{ Å} \) and \( c = 6.7358 \text{ Å} \), and the carbon–carbon nearest neighbor distance is \( a_{c-c} = 1.4229 \text{ Å} \). Interlayer spacings for \{0002\}, \{01\overline{1}0\}, and \{01\overline{1}1\} planes are 3.3679, 2.1316, and 2.0340 Å, respectively. Thermal transport in the basal plane is slightly anisotropic along the
and \(M\) and \(\Gamma\) high-symmetry directions, \(\kappa_{\Gamma-M}/\kappa_{\Gamma-M} \approx 1.25\) at 300 K, so we calculate \(\kappa\) in both transport directions and take the average value.

Based on the phonon dispersion of 3D graphite, the heat flux in the transport direction, \(J_{q,x}\), can be expressed as \(^{S15}\)

\[
J_{q,x} = \sum_{p=1}^{12} \frac{1}{2\delta} \int_{\omega_p=0}^{\omega_p,\text{max}} \nu_p \cos \theta \hbar \omega_p f_p(\omega_p) D_p(\omega_p) \frac{d\omega}{2\pi},
\]

where \(\delta = 0.3368\) nm is the interlayer spacing determined by X-ray diffraction for our GF sample (Figure 3a, article), \(\nu_p \equiv d\omega_p / dk\) is the polarization-specific phonon velocity, \(\omega_p\) is the polarization-specific phonon frequency, \(k\) is the wave vector, \(\hbar\) is the reduced Planck constant, \(f_p\) is the polarization-specific non-equilibrium phonon distribution function, \(D_p\) is the polarization-specific two-dimensional (2D) phonon density of states, and \(\theta\) is the angle of phonon propagation. The subscript \(p\) is used to denote each of the twelve individual phonon polarizations (Figure S10a).

The phonon Boltzmann Transport Equation (BTE) under the relaxation time approximation is \(^{S15}\)

\[
f_p = f_0 - \tau_p \nu_p \cos \theta \frac{df_0}{dT} \frac{dT}{dx},
\]

where \(\tau_p\) is the polarization-specific relaxation time and \(f_0\) is the equilibrium phonon distribution, i.e., the Bose-Einstein distribution

\[
f_0 = \frac{1}{e^{\hbar \omega_p/k_B T} - 1},
\]

where \(k_B\) is the Boltzmann constant. The 2D density of states \((D_p)\) can be obtained from

\[
D_p(k)dk = D_p(\omega_p)d\omega = \frac{kdk}{2\pi}.
\]

Substituting eqs S19–S21 into eq S18 and carrying out the integration over \(0 \leq \theta \leq 2\pi\), the term resulting from the first term in \(f_p\) becomes zero, which is to be expected since there should be no net energy transport for the equilibrium system. Noting that \(J_{q,x} = -\kappa \partial T / \partial x\) yields
\[
\kappa = \sum_{p=1}^{12} \kappa_p = \frac{1}{8\pi \delta k_B T^2} \sum_{p=1}^{12} \int_{k=0}^{k_{\text{max}}} v_p^2 \left( \frac{\hbar \omega_p}{e^{\beta \hbar \omega_p/k_B T} - 1} \right)^2 \tau_p e^{\beta \hbar \omega_p/k_B T} \frac{e^{\beta \hbar \omega_p/k_B T}}{e^{\beta \hbar \omega_p/k_B T} - 1}^2 k \, dk. \tag{S22}
\]

In order to approximate the total polarization-specific relaxation times, \(\tau_p\), we consider the contributions of phonon-boundary (\(\tau_{b,p}\)), phonon-impurity (\(\tau_{i,p}\)), and phonon-phonon (i.e. umklapp, \(\tau_{u,p}\)) scattering processes. These contributions can be combined using Matthiessen’s rule

\[
\tau_p^{-1} = \tau_{b,p}^{-1} + \tau_{i,p}^{-1} + \tau_{u,p}^{-1}. \tag{S23}
\]

Phonon-boundary scattering with a constant mean free path, \(l_b\), is the dominant phonon scattering process at low temperatures and can be expressed as

\[
\tau_{b,p}^{-1} = \frac{v_p}{l_b}. \tag{S24}
\]

Phonon-impurity scattering can be expressed according to Klemens & Pedraza\textsuperscript{S16} using the 2D phonon density of states of eq S21 as\textsuperscript{S11}

\[
\tau_{i,p}^{-1} = \sum_j c_j \left( \frac{M_j - \overline{M}}{\overline{M}} \right)^2 \frac{S_0}{4 v_p} \omega_p^2 k, \tag{S25}
\]

where \(c_j\) is the \(j\)th impurity concentration, \(M_j\) and \(\overline{M}\) are the \(j\)th impurity and average atomic masses, respectively, \(S_0 = \left( \frac{3 \sqrt{3}}{4} \right) a_{c-c}^2\) is the area per atom in the basal plane. We model \(\tau_{i,p}\) using a \(c_j\) of 1.1 % \(^{13}\text{C}\) in \(^{12}\text{C}\), as the carbon feedstock used to produce the GF was not isotopically enriched.

The umklapp phonon-phonon scattering rate is calculated according to the relaxation time approximation (RTA) of Klemens & Pedraza\textsuperscript{S16}

\[
\tau_{u,p}^{-1} = 2 \gamma_p^2 \frac{k_B T}{M_{\text{unit-cell}}} \frac{\omega_p^2}{M_{\text{unit-cell}} v_p^2 \omega_{\text{max},p}^2}, \tag{S26}
\]

where \(\gamma_p\) is the polarization-specific Grüneisen parameter, \(M_{\text{unit-cell}}\) is the mass of the graphite unit cell, and \(\omega_{\text{max},p}\) is the maximum frequency for each phonon polarization.\textsuperscript{S11} The Grüneisen parameters in eq S26 are modeled as

\[
\gamma_p = a_p T^{n_p}. \tag{S27}
\]
for the TA, LA, TO’, and LO’ polarizations, where \( a_p \) and \( n_p \) are polarization-specific adjustable parameters made in observance of the wavevector dependence reported by Mounet & Marzari.\(^{S17}\) The calculated Grüneisen parameters\(^{S17}\) for the ZA and ZO’ polarizations are much larger in magnitude than for the in-plane transverse and longitudinal modes. Consequently, eq S26 results in strong phonon-phonon scattering of these polarizations. We note that RTA does not satisfy the quantum mechanical selection rules, which can give rise to non-negligible thermal conductivity contribution from the quadratic ZA branch in suspended single-layer and few-layer graphene.\(^{S9, S12}\) However, interlayer coupling is expected to reduce the ZA contribution to be considerably smaller in AB stacked graphite than in single-layer and few-layer graphene. For example, the large ZA contribution is expected to result in \( \kappa \propto T^{1.5} \) behavior in single-layer\(^{S9, S18}\) and turbostratically-stacked bi-layer graphene\(^{S19}\) at low temperatures where boundary scattering is the dominant scattering mechanism. In comparison, \( \kappa \propto T^2 \) behavior has been reported for high quality NG\(^{S20}\) and HT-HOPG\(^{S21}\) at low temperatures, and can be attributed to the dominant contribution from the linear LA and TA branches. Besides a negligible ZA contribution based on the RTA analysis, we have used the same Grüneisen parameter for the TA and TO’ polarizations because of the considerable overlap between these two branches, \( \gamma_{TA} \). Similarly, we have used the same Grüneisen parameter \( \gamma_{LA} \) for the LA and LO’ polarizations. We choose \( \gamma_{TA} \) and \( \gamma_{LA} \) so that the relative contributions of the in-plane transverse and longitudinal polarizations to the thermal conductivity are similar to those reported by Lindsay \textit{et al.}\(^{S12}\) Despite these assumptions, especially the potential issue of an underestimated ZA contribution, this RTA approach initially developed for AB stacked graphite by Klemens & Pedraza\(^{S16}\) can still provide important insights in phonon transport in our GF consisting of ultrathin graphite and few-layer graphene of a thickness between 8 and 40 layers, as discussed below.

We employ the thermal conductivity model to analyze the reported values for natural graphite (NG)\(^{S20}\) and HOPG heat treated to 3200 °C (HT-HOPG)\(^{S21}\) in addition to the GF of this work. The calculated and experimental thermal conductivity of the FLG and UG within sample GF3 are shown along with
individual phonon polarization contributions in Figure S10b. The fitting parameters are given in Table S1. Based on the low-temperature experimental thermal conductivity data, the phonon-boundary scattering mean free path, $l_b$, was found to be $\sim 55 \, \mu m$ for NG and $\sim 9 \, \mu m$ for HT-HOPG indicative of the expected larger grain size in NG. For the thin-walled GF samples, $l_b$ was found to be 4.25 $\mu m$ for GF4 obtained from the gentle ammonium persulfate based Ni etching process, 1.5 $\mu m$ for GF2 and GF3 obtained from the gentle ferric nitrate based Ni etching process, and only 525 nm for GF1 obtained from the aggressive hydrochloric acid based Ni etching process. This large difference in $l_b$ is to be expected given the less continuous structure of GF1 when compared with other GF samples (Figure 1, article) and emphasizes the role processing conditions have on the electrical and thermal properties in GF. Although GF3 was synthesized using pre-annealed Ni foam of a larger grain size (Figure S1d–f), the electrical and thermal conductivities of the FLG and UG within GF3 is not enhanced outside the experimental error of those for GF2, which was synthesized using as-purchased Ni foam (Figure S1a–c). For the thick-walled GF samples, $l_b$ was found to be 1.5 $\mu m$ for both GF5 obtained from the aggressive hydrochloric acid based Ni etching process and GF6 obtained from the gentle ammonium persulfate based Ni etching process. In addition, the phonon-phonon scattering rates need to be higher for fitting the thermal conductivity data of the NG and the GF samples than for HT-HOPG.

**Table S1.** Theoretical thermal conductivity model parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$l_b$ ((\mu m))</th>
<th>$\gamma_{TA}(T)$</th>
<th>$\gamma_{LA}(T)$</th>
<th>$\gamma_{TA}(300K)$</th>
<th>$\gamma_{LA}(300K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT-HOPG</td>
<td>9.0</td>
<td>0.065 $T^{0.50}$</td>
<td>0.145 $T^{0.50}$</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>NG</td>
<td>55.0</td>
<td>0.096 $T^{0.60}$</td>
<td>0.206 $T^{0.60}$</td>
<td>2.612</td>
<td>2.513</td>
</tr>
<tr>
<td>GF1</td>
<td>0.525</td>
<td>0.200 $T^{0.50}$</td>
<td>0.443 $T^{0.50}$</td>
<td>3.077</td>
<td>3.055</td>
</tr>
<tr>
<td>GF2/GF3</td>
<td>1.5</td>
<td>0.055 $T^{0.65}$</td>
<td>0.122 $T^{0.65}$</td>
<td>1.991</td>
<td>1.980</td>
</tr>
<tr>
<td>GF4</td>
<td>4.25</td>
<td>0.051 $T^{0.55}$</td>
<td>0.113 $T^{0.55}$</td>
<td>1.044</td>
<td>1.036</td>
</tr>
<tr>
<td>GF5/GF6</td>
<td>1.5</td>
<td>0.073 $T^{0.60}$</td>
<td>0.162 $T^{0.60}$</td>
<td>1.987</td>
<td>1.976</td>
</tr>
</tbody>
</table>
VI. Comparison with graphitized carbon foams.

Table S2 summarizes the specific thermal conductivity, defined as the ratio between the effective thermal conductivity and the mass density expressed in specific gravity. Both Figure 5 in the article and Table S2 show that the specific thermal conductivity of the GFs synthesized by CVD at 1050 °C greatly exceeds those of the carbon foams graphitized at 1000 °C, and approaches the values for those graphitized at a much higher temperature of 2800 °C.\textsuperscript{S22}

Table S2. Comparison of GF thermal conductivity with that for graphitized carbon foams.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Gravity</th>
<th>Thermal Conductivity\textsuperscript{a} (Wm\textsuperscript{-1}K\textsuperscript{-1})</th>
<th>Specific Thermal Conductivity\textsuperscript{a,b} (Wm\textsuperscript{-1}K\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF1, 2800 °C\textsuperscript{S22}</td>
<td>5.9\times10^{-1}</td>
<td>151</td>
<td>261</td>
</tr>
<tr>
<td>CF2, 2800 °C\textsuperscript{S22}</td>
<td>5.9\times10^{-1}</td>
<td>134</td>
<td>227</td>
</tr>
<tr>
<td>CF1, 1000 °C\textsuperscript{S22}</td>
<td>5.8\times10^{-1}</td>
<td>1.20</td>
<td>2.57</td>
</tr>
<tr>
<td>CF2, 1000 °C\textsuperscript{S22}</td>
<td>5.3\times10^{-1}</td>
<td>1.20</td>
<td>1.95</td>
</tr>
<tr>
<td>GF1</td>
<td>(1.00\pm0.21)\times10^{-2}</td>
<td>0.26</td>
<td>25.9\pm5.5</td>
</tr>
<tr>
<td>GF2</td>
<td>(9.62\pm0.18)\times10^{-3}</td>
<td>0.71</td>
<td>73.6\pm14</td>
</tr>
<tr>
<td>GF3</td>
<td>(9.90\pm0.19)\times10^{-3}</td>
<td>0.71</td>
<td>71.6\pm14</td>
</tr>
<tr>
<td>GF4</td>
<td>(1.16\pm0.19)\times10^{-2}</td>
<td>1.70</td>
<td>146\pm23</td>
</tr>
<tr>
<td>GF5</td>
<td>(3.20\pm0.27)\times10^{-2}</td>
<td>2.28</td>
<td>71.3\pm6.0</td>
</tr>
<tr>
<td>GF6</td>
<td>(3.17\pm0.27)\times10^{-2}</td>
<td>2.12</td>
<td>66.8\pm5.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a}at near room temperature
\textsuperscript{b}defined as thermal conductivity divided by specific gravity

References.


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