

Tunable Anisotropic Heat Transport in Structurally and Chemically Modified 3D Graphene

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Abstract

Three-dimensional graphene (3DG) networks offer a route to translate the high intrinsic thermal conductivity of graphene into macroscopic, freestanding architectures. However, heat transport in 3DG is not governed by the intrinsic conductivity of graphene alone, but by a hierarchy of pores, sheet orientation, network connectivity, and graphene-graphene junctions. Here, room-temperature cross-plane and in-plane thermal transport in pristine, compressed, welded, and doped 3DG structures is reported. Cross-plane thermal conductivity is measured using a differential 3ω method with transferable polyimide-supported metal heater lines, while in-plane thermal conductivity is obtained using a suspended four-probe electrothermal method. Mechanical compression strongly modifies the directional thermal response: cross-plane thermal conductivity decreases with densification, while in-plane transport remains comparatively enhanced, indicating that compression redistributes the graphene network into a more anisotropic, aligned architecture. Welding introduces an additional discrete thermal resistance, with increasing weld-plane numbers. Chemical modification suppresses both directions without producing the strong anisotropy amplification caused by rolling, suggesting that cross-plane heat flow remains dominated by phonon-mediated networks and junction resistance rather than electronic heat conduction. These results establish structural compression and weld-plane insertion as practical routes for programming anisotropic heat flow in freestanding 3DG.

Keywords: Three-dimensional graphene, graphene foam, anisotropic thermal conductivity, interfacial thermal resistance, thermal management, 3ω method

1. Introduction

Graphene is often treated as a limiting case for carbon-based thermal transport because heat is carried efficiently along its covalently bonded sp^2 lattice, while transport normal to graphitic planes is limited by weak interlayer coupling. This bonding asymmetry gives graphene and graphitic materials a strongly anisotropic thermal foundation: in-plane thermal conductivity can reach the $10^3 \text{ W m}^{-1} \text{ K}^{-1}$ scale in high-quality graphene and graphitic crystals, whereas out-of-plane heat flow is limited by van der Waals coupling, interlayer phonon transmission, and boundary resistance.[1–3] This combination of high lateral heat conduction and weak cross-plane coupling has motivated graphene-based heat spreaders, thermal interface materials, polymer composites, graphitic films, foams, aerogels, and papers for thermal management.[4–6]

The difficulty is that the intrinsic conductivity of graphene is not automatically inherited by macroscopic graphene assemblies. In practical forms, heat must pass through finite flakes, wrinkles, defects, multilayer regions, inter-sheet contacts, pores, polymer or air gaps, and graphene–graphene junctions. These features introduce thermal resistance at length scales far larger than the phonon mean free path of ideal graphene and can reduce the effective conductivity by orders of magnitude.[3,7–9] As a result, the relevant question for three-dimensional graphene is not only how conductive graphene is, but how a connected, porous, junction-rich graphene network transmits heat across a macroscopic sample.

Three-dimensional graphene (3DG) networks are especially useful for examining this question because they are freestanding, lightweight, electrically conductive, mechanically compliant, and processable after synthesis. Unlike isolated graphene sheets, they can be handled and measured as bulk-like materials. Unlike polymer nanocomposites, the graphene network itself forms the continuous structural phase without polymeric fillers. Unlike dense graphite or pyrolytic graphite, the network retains large porosity and a high density of internal contacts. Prior studies on graphene foams and graphene papers illustrate this architectural dependence clearly. Pettes et al. measured thermal transport in few-layer graphene and ultrathin graphite foams and showed that porous 3D architectures conduct far below the intrinsic graphene limit.[7] O'Neill et al. reported room-temperature thermal conductivities up to $40 \text{ W m}^{-1} \text{ K}^{-1}$ in 3D graphene papers and linked the increase to density, flake size, and microstructure.[9] Guo et al. further showed that compressive strain can tune anisotropic thermal conductivity in graphene aerogels, reaching high in-plane conductivity $\sim 96 \text{ W m}^{-1} \text{ K}^{-1}$ while preserving a distinct through-thickness response to $\sim 3.3 \text{ W m}^{-1} \text{ K}^{-1}$. [10] Together, these studies show that macroscopic graphene networks are governed by architecture, not by graphene's intrinsic conductivity alone.

In many porous solids, increasing solid fractions would be expected to improve effective thermal conductivity by adding conducting material and increasing contact area. Compressed graphene networks can violate this expectation because deformation changes not only density but also pore shape, sheet orientation, contact topology, and cross-plane junction density. Xiong et al. showed that compressed flexible graphene foams can display an unconventional response in which in-plane thermal conductivity increases while cross-plane thermal conductivity decreases, a behavior not captured by conventional density-based effective-medium models.[11] This result reframes compression as a route for redistributing heat-flow pathways rather than simply increasing conductivity.

Internal interfaces provide a second, less explored control variable. Heat transfer across graphene junctions, multilayer overlaps, and layered graphene regions is limited by interlayer phonon coupling and thermal boundary resistance.[12] In a macroscopic 3DG stack, a mechanically joined internal plane should therefore not be treated as a passive geometric feature. It can act as an added cross-plane thermal resistance composed of many microscopic contacts, overlaps, voids, and misoriented graphene surfaces. Prior work on cold-rolled 3DG from this material family showed that rolling can densify the network, increase electrical conductivity and tensile strength, and join multiple 3DG pieces into larger structures.[13] Whether such joined planes also provide a controllable thermal-resistance element remains unresolved.

Chemical modification introduces a different type of perturbation. For thermal transport, however, the effect of doping is ambiguous. Added carriers can contribute to electronic thermal conductivity, but adsorbates, functional groups, disorder, and modified inter-sheet contacts can increase phonon and junction scattering. The Wiedemann–Franz relation provides a first estimate of whether electronic heat conduction is large enough to dominate the measured thermal response, but porous 3DG is expected to remain strongly influenced by phonon-mediated network and interface resistance. Comparing doped samples with mechanically rolled and welded samples can therefore separate chemical thermal suppression from structural anisotropy. Beyond heat spreading alone, 3DG is also relevant to coupled heat–charge transport because the same freestanding network can support electrical percolation, chemical doping, and thermoelectric response. Prior 3DG thermoelectric studies have shown that molecular and acid treatments can tune carrier type, Seebeck coefficient (S), electrical conductivity (σ), power factor, and flexible-device output, making directional thermal control an important missing part of the same materials platform.[14,15]

In this paper, we measure paired room-temperature in-plane and cross-plane thermal conductivity in pristine, cold-rolled, welded, and chemically modified 3DG. The study examines how post-synthesis processing transforms a freestanding graphene network into distinct directional thermal-transport states. Cross-plane conductivity is measured

using a differential 3ω method with transferable polyimide-supported heater lines, while in-plane conductivity is measured using a suspended four-probe electrothermal method. The paired dataset is analyzed based on thermal anisotropy, anisotropy amplification, directional suppression, and cross-plane area-normalized resistance. This framework allows rolling-induced network reorientation, weld-interface resistance, and dopant-driven thermal suppression to be distinguished within the same 3DG material platform.

2. Materials and Metrology

The experimental design was built around the graphene scaffold being the common material platform, while post-synthesis processing changes the dominant thermal bottleneck. The pristine 3DG was processed into three states: cold-rolled, welded, and chemically treated, using paired cross-plane and in-plane thermal measurements.

2.1 Synthesis and processing

Figure 1(a) illustrates the synthesis process of pristine 3DG. The pristine 3DG was prepared using a Ni-template chemical vapor deposition (CVD) route for freestanding porous graphene networks.[16,17] Nickel powder (99.9%, 3-7 μm , TSC, USA), polystyrene ($M_w \approx 210,000$, Scientific Polymer Products, USA), di (ethylene glycol) dibenzoate (TCI Chemicals, Japan), and toluene (HPLC grade, Fisher Scientific, USA) were used to prepare a Ni-polymer catalyst precursor. The precursor was heated to 1000 $^{\circ}\text{C}$ under argon (1000 sccm) and hydrogen (325 sccm), followed by graphene growth using methane (25 sccm) for 10 min. After growth, the catalyst was cooled under protective gas flow and removed from the reactor. The nickel template was removed by immersion in a 6 M hydrochloric acid solution prepared from concentrated 12 M hydrochloric acid (37 wt%, ACS reagent grade, Fisher Scientific) and deionized (DI) water at a 1:1 volume ratio. The etched samples were subsequently rinsed in DI water followed by ethanol ($\geq 99.5\%$, ACS reagent grade, Sigma-Aldrich, USA) and dried overnight to obtain pristine freestanding 3DG. This synthesis route produces a continuous 3D graphene architecture rather than a polymer-bound graphene composite, allowing post-synthesis structural and chemical modifications to be applied directly to the graphene network. Figure 1(b) shows the cross-sectional and top scanning electron microscopic (SEM) images of the pristine 3DG, Figure 1(e) shows optical image of 3DG. The 3DG differs from graphene aerogels, reduced-graphene-oxide foams, and graphene-polymer composites as the freestanding networks are produced without solution assembly, reduction of graphene oxide, or polymer binding. The resulting structure is porous and mechanically compliant like many graphene aerogels.[18–20]

Four material states were studied. The pristine sample represents the as-synthesized porous 3DG. Cold-rolled samples were produced by sequential rolling to final thicknesses of 109, 53, and 6 μm as illustrated in Figure 1(c)

Welded samples were formed by cold-rolling two or three stacked pristine 3DG sheets, producing structures with one or two internal weld planes, denoted as “one-weld” and “two-weld(s)” samples, respectively. Both welded samples were compressed to the same final thickness of $\sim 109\ \mu\text{m}$. Figure 1(d) illustrates the welding process of a “one-weld” sample made by compressing two stacked pristine 3DG sheets.

Chemical modification of pristine 3DG is illustrated in Figure 1(f). Samples were treated using the n-type dopants poly(vinylpyrrolidone) (PVP, average molecular weight $\approx 360,000\ \text{g mol}^{-1}$, Sigma-Aldrich, USA), thermally activated branched polyethyleneimine (PEI-A) (PEI, average molecular weight $\approx 25,000\ \text{gmol}^{-1}$, Sigma-Aldrich, USA), 4-(2,3-dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine (N-DMBI, 97%, Sigma-Aldrich, USA), and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Sigma-Aldrich, USA) at concentrations of 0.25, 0.50, 0.75, and 1.00 wt.%. P-type treatments were conducted using sulfuric acid (H_2SO_4 , 18 M, ACS reagent grade, 95-98%, Sigma-Aldrich, USA) and nitric acid (HNO_3 , 15.8 M, ACS reagent grade, 68-70%, Sigma-Aldrich, USA) for exposure times of 1, 2.5, 5, and 10 min. Detailed processing procedures are provided in Supplementary Information S1. The dopant set was selected from prior 3DG thermoelectric work to span weak polymeric, stronger molecular, and acid oxidative treatments within a concentration range that produced measurable electronic changes while preserving the freestanding network.[14] PEI-A, N-DMBI, and TBD were used as n-type dopants because they can donate electrons or promote charge transfer to graphene-derived systems; PVP was retained as a weaker n-type dopant for comparison; and $\text{H}_2\text{SO}_4/\text{HNO}_3$ were used as p-type oxidative treatments that introduce oxygen-containing surface groups. The 0.25-1.00 wt% range and 1-10 min acid exposure window were chosen to match the prior thermoelectric processing matrix and avoid excessive structural damage during thermal measurements.[14] The present work focuses on how those structural and chemical modifications change directional heat transport.

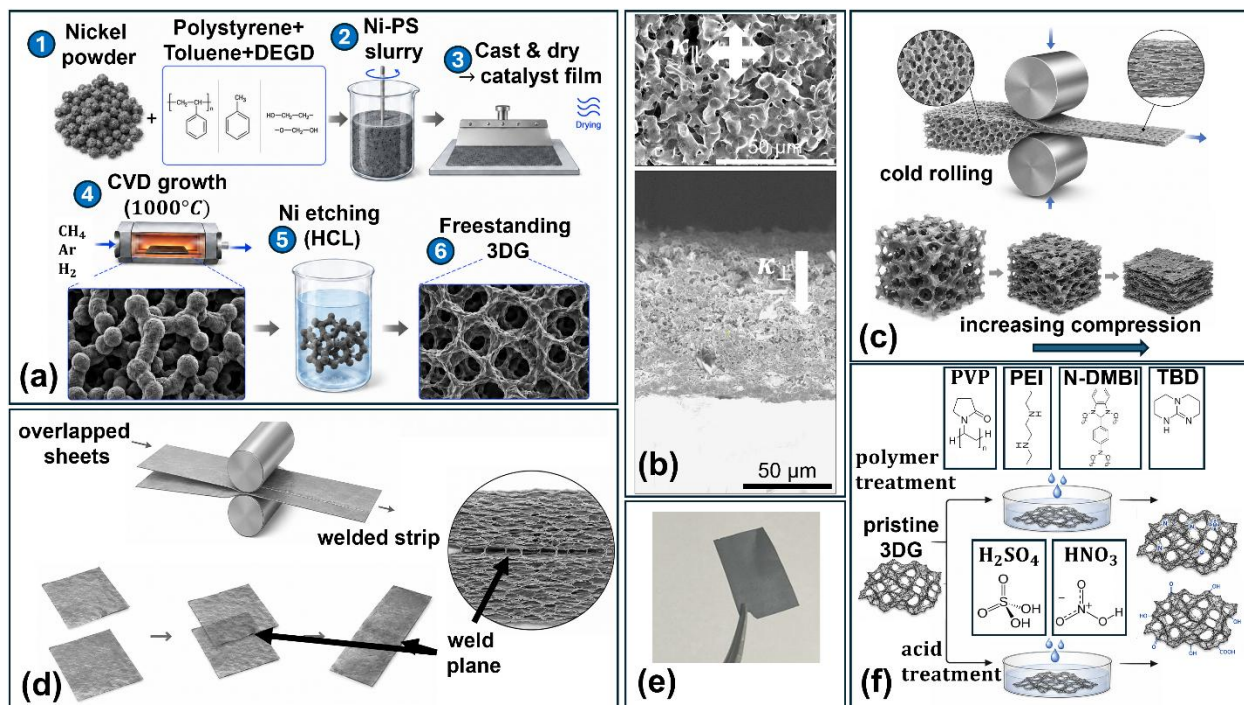


Figure 1: Synthesis and processing: (a) Schematic of the Ni–polymer-assisted CVD synthesis route (b) Top-view (top) and cross-sectional (bottom) SEM images of pristine 3DG (c) Cold-rolling process and schematic evolution of the 3DG network with increasing compression (d) Welding of overlapped 3DG sheets and schematic morphology of the resulting weld plane, (e) Optical image of a freestanding 3DG sheet, (f) Doping of pristine 3DG using PVP, PEI-A, N-DMBI and TBD molecular/polymeric treatments and H_2SO_4 and HNO_3 acid treatments.

2.2 Cross-plane Thermal Conductivity Measurement

Cross-plane thermal conductivity, $\kappa_{\perp}$, was measured using a differential 3ω method adapted for fragile, porous, electrically conductive 3DG.[21] The method follows the standard 3ω principle, as illustrated in Figure 2(a) and (b), in which a sinusoidal current at an angular frequency ω was driven through a metal heater line ($\sim 45\ \mu\text{m}$, $\sim 792\ \mu\text{m}$) producing Joule heating at 2ω , a temperature oscillation at 2ω , and a voltage response at 3ω through the heater temperature coefficient of resistance.[22,23] The heater line was patterned by photolithography directly on a thin polyimide film ($25.4\ \mu\text{m}$) and transferred onto the 3DG stack. This configuration avoids direct metal deposition on 3DG, where porosity, surface roughness, and electrical conductivity can produce nonuniform heater contact or electrical leakage.[24] The stacks were supported on $\sim 500\ \mu\text{m}$ silicon substrates. In the differential 3ω analysis, the temperature response of the heater-polyimide reference stack was subtracted from that of the heater-polyimide-3DG stack. The thermal contribution of the transferable polyimide platform was

characterized by using matched polyimide/Si configurations of two film thicknesses under the same assembly conditions used for the sample measurements. The complete procedure was validated using a 100 μm graphite reference, yielding a cross-plane thermal conductivity of $6.4 \pm 0.8 \text{ W m}^{-1} \text{ K}^{-1}$, consistent with established values. The same heater geometry, substrate, transfer procedure, assembly conditions, and data-reduction procedure were subsequently used for all 3DG measurements; residual assembly-to-assembly variation was included in the measurement uncertainty. Because the same heater platform and background stack were used for the series, the method is most robust for comparing processing-dependent trends, while absolute values include the stated interfacial/contact uncertainty.

For comparison across samples of different thickness, the cross-plane result was also expressed as an area-normalized thermal resistance, $R''_{\perp} = t/\kappa_{\perp}$ in the unit of $\text{m}^2 \text{ K W}^{-1}$, where ‘ t ’ is the measured sample thickness. Heater fabrication, background subtraction, validation, and uncertainty propagation are presented in the supplementary Information S2.

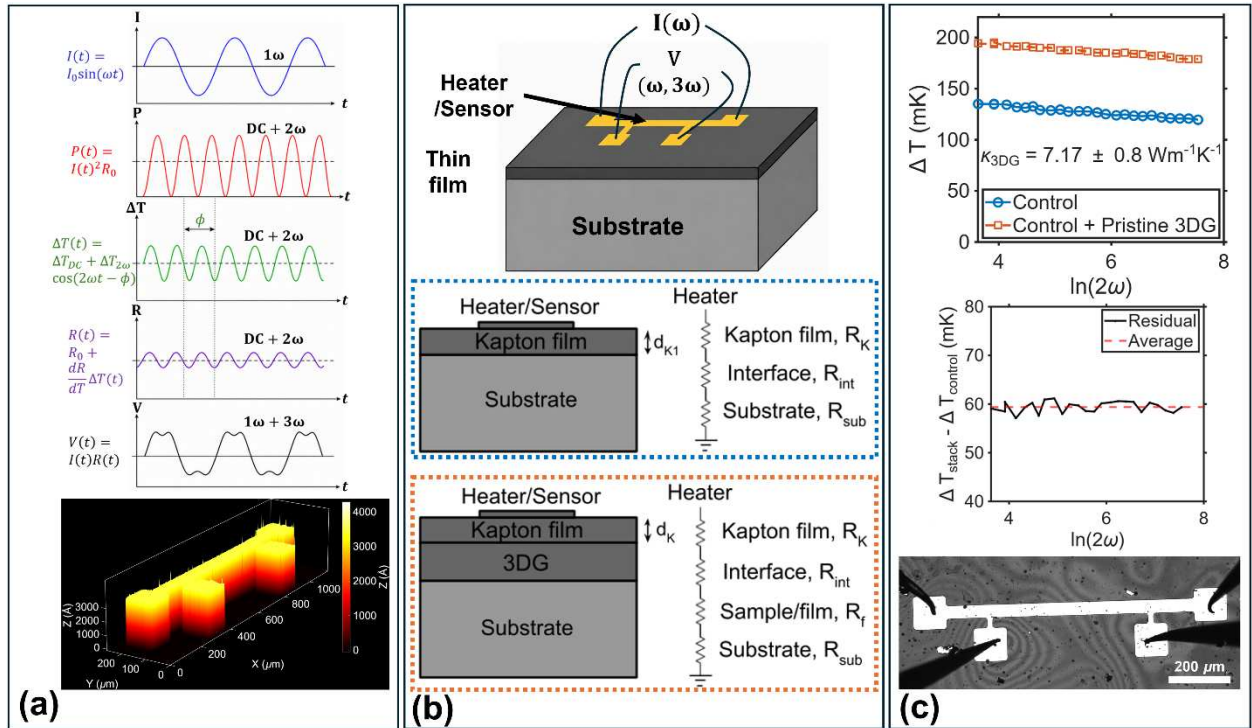


Figure 2: Differential 3 ω measurement of cross-plane thermal conductivity in 3DG (a)Harmonic detection in 3 ω method(top), microheater profilometry (bottom) (b)Schematic of the metal line operating simultaneously as heater and resistance thermometer on the electrically insulating thin-film support (top), differential measurement stacks comprising the heater/Kapton/substrate ‘control’ and the corresponding

heater/Kapton/3DG/substrate sample configuration (bottom) (c) In-phase temperature oscillation, ΔT , as a function of $\ln(2\omega)$ for the control and sample stack (top), resulting differential temperature response for pristine 3DG (middle), optical micrograph of the transferred heater (bottom).

2.3 In-plane Thermal Conductivity Measurement

In-plane thermal conductivity, $\kappa_{\parallel}$, was measured using a suspended four-probe electrothermal method. Electrothermal methods use Joule heating and resistance thermometry to extract thermal transport in suspended or supported low-dimensional samples, avoiding the need for separate optical thermometry or direct contact temperature probes.[25–27] In our geometry, the 3DG strip serves as both Joule heater and resistance thermometer (Figure 3(a)). This approach has also been used for graphene-derived films, including flexible reduced graphene oxide films where self-heating, resistance-temperature calibration, and heat-loss correction were used to extract thermal transport relevant to thermoelectric performance.[28]

Because the suspended electrothermal measurement is a steady self-heating experiment, heat loss to contacts, convection, and radiation can usually bias $\kappa_{\parallel}$. Measurements at multiple suspended lengths were used to separate axial heat conduction through the 3DG strip from distributed environmental heat losses and reduce sensitivity to end-contact effects as shown in Figure 3(a). For each material condition, specimens with suspended lengths (ℓ) of 7, 10, and 15mm and widths (w) of 2 mm were used. A resistance-temperature calibration was first obtained for each sample. Here R_0 is the resistance at reference temperature. During electrical self-heating, the resistance change was converted to average temperature rise using $\Delta T = \Delta R / (\beta R_0)$, where β is the temperature coefficient of resistance ($\beta = (1/R_0)(dR/dT)$). The applied electrical power was calculated as $P = I^2 R$ (Figure 3(b)). The resulting effective thermal resistance was obtained from the slope of the approximately linear relation $\overline{\Delta T} = R_{th} P + b$, where ‘ b ’ accounts for small residual baseline offsets (Figure 3(b)).

Heat loss from the suspended strip was accounted for using a one-dimensional distributed-loss model. The steady state temperature field was described by $\kappa_{\parallel} A \frac{d^2 \theta}{dx^2} - g\theta + \frac{P}{\ell} = 0$, where $\theta = T - T_{support}$, ℓ is the suspended length, and g is an effective heat-loss coefficient per unit length (Figure 3(c)). Because the specimens were nominally identical strips measured under the same ambient conditions, g was treated as a common distributed loss parameter, while the total parasitic heat loss remained length dependent through the suspended length and temperature profile. With the two supported ends treated as isothermal boundaries, the resistance-weighted average temperature rise was used to extract $\kappa_{\parallel}$. Self-heating traces, fitting procedure, and

uncertainty analysis are provided in the supplementary Information S3. The paired $\kappa_{\parallel}$ and $\kappa_{\perp}$ measurements were reduced to metrics that compare different processing routes without treating all conductivity changes as equivalent. The thermal anisotropy ratio was defined as $A_{\kappa} = \kappa_{\parallel}/\kappa_{\perp}$. This quantifies the contrast between lateral- and through- thickness heat transport.

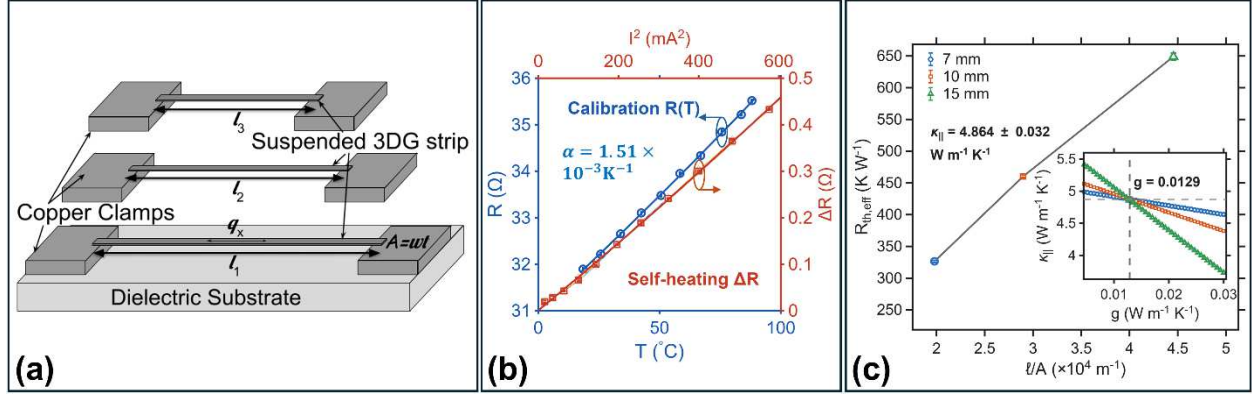


Figure 3: The suspended electrothermal method used for In-plane thermal conductivity measurement of 3DG samples. (a) Schematic of the four-probe electrothermal measurement configuration with varying length, (b) Resistance–temperature calibration of the 10 mm specimen (blue, bottom and left axes), the self-heating-induced resistance rise, ΔR , as a function of applied current squared (I^2) (red, top and right axes). Lines are linear fittings. (c) Effective thermal resistance, $R_{th,eff}$, as a function of l/A for the three suspended lengths, $\kappa_{\parallel}$ inferred as a function of the distributed heat-loss coefficient g .

3. Results and Discussion

3.1 Densification

Thermal transport in porous graphene networks is usually discussed through two competing ideas. In porous solids and networked thermal interface materials, increasing solid fraction and improving contact between conductive phases generally increases effective thermal conductivity by replacing low-conductivity voids with solid pathways and reducing contact resistance[29]. At the same time, compression can flatten pores, reorient graphene walls, and increase the number of cross-plane junctions that heat must traverse. Prior studies show that both effects can be important: compressed graphene papers and aerogels often show enhanced effective thermal conductivity in both directions at low strains with increasing density whereas compressed graphene foams can develop an unconventional anisotropic response in which $\kappa_{\parallel}$ increases while $\kappa_{\perp}$ decreases.[9–11] This makes cold-rolled 3DG a useful test case: the same

processing step increases density and contact area but also reshapes the network that carries heat. The pristine 3DG establishes the starting point for this comparison.

We found that our pristine 3DG exhibited $\kappa_{\parallel} = 4.86 \pm 0.03 \text{ W m}^{-1} \text{ K}^{-1}$ and $\kappa_{\perp} = 7.17 \pm 0.8 \text{ W m}^{-1} \text{ K}^{-1}$, giving a weak thermal anisotropy ratio, $A_{\kappa} \approx 0.7$. The as-synthesized network, therefore, does not behave as a conventional in-plane graphitic sheet. Rather its effective thermal response is governed by the 3D porous architecture, where heat can percolate through interconnected graphene boundaries, and junctions rather than only along aligned basal planes. This is consistent with earlier 3D graphene foam and paper studies, where effective conductivity was far below the intrinsic graphene limit and depended strongly on density, morphology, and inter-sheet connectivity.[7–9]

Cold rolling changed this baseline response in opposite directions. Figure 4(a)-(f) shows the cross-sectional and top-view SEM images of compressed 3DG samples and Figure 4(g) shows the thermal conductivity variation with thickness reduced by compression. As thickness was reduced from 170 μm to 109, 53, and 6 μm , $\kappa_{\parallel}$ increased to 12.9, 20.2, and 24.9 $\text{W m}^{-1} \text{ K}^{-1}$, respectively. Over the same compression sequence, on the other hand, $\kappa_{\perp}$ decreased to 2.2, 1.7, and 0.21 $\text{W m}^{-1} \text{ K}^{-1}$. Thus, the most compressed sample conducts heat about 5.1 times better than pristine 3DG in-plane, but about more than 34.6 times worse through thickness.

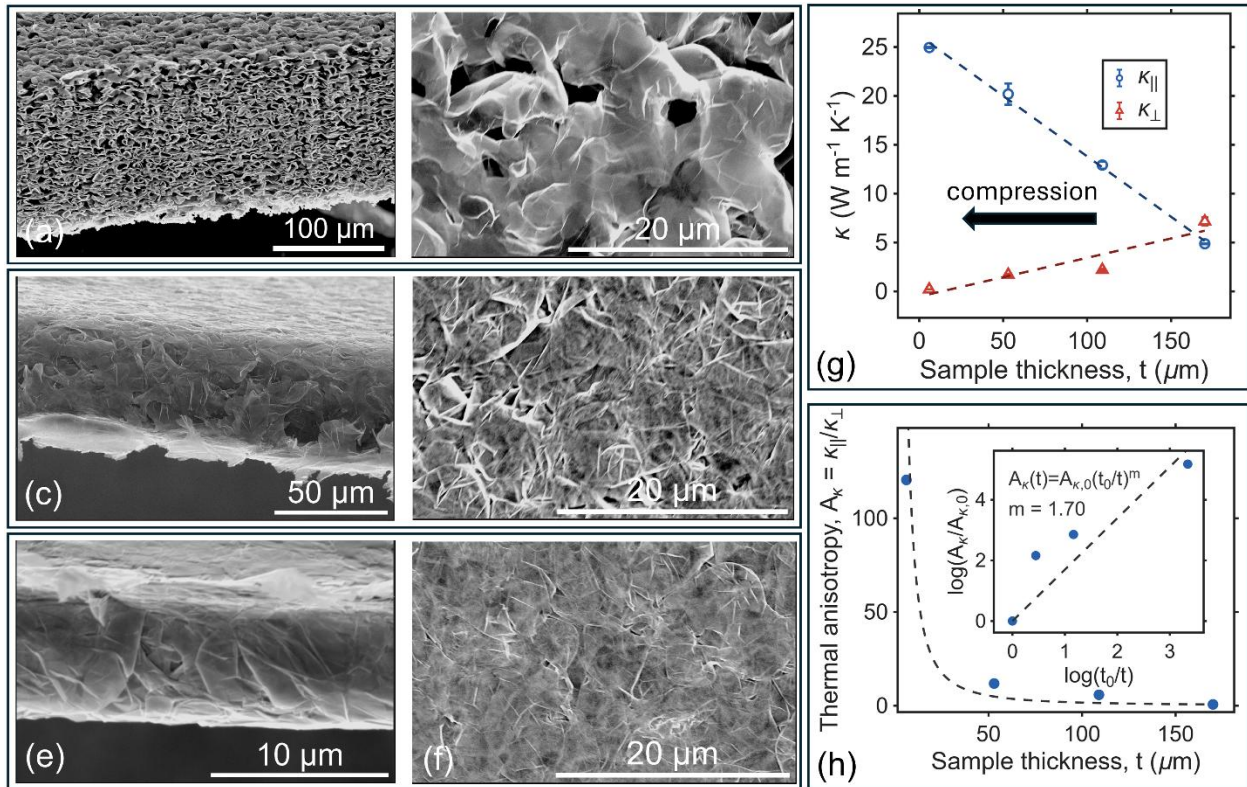


Figure 4: Cross-sectional (a, c, e) and corresponding top-view (b, d, f) SEM images of representative 3DG samples (109 μm , 53 μm , 6 μm), (g) $\kappa_{\parallel}$ and $\kappa_{\perp}$ as function of sample thickness. (h) Thermal anisotropy, A_{κ} as a function of sample thickness, $A_{\kappa,0}$ and t_0 correspond to pristine.

This directional split cannot be explained by solid fraction alone. If rolling acted only by densifying the network and graphene-graphene contact area, both conductivity components would be expected to improve or at least follow the same qualitative trend. Instead, rolling converts the initially three-dimensional network into a laterally conductive but vertically resistive architecture. The result agrees more closely with the mechanism proposed for compressed flexible graphene foams, where deformation redirected heat-flow pathways and produced a dynamically anisotropic response that conventional effective-medium models failed to capture.[11] The strength of the transition is clearer when the conductivities are expressed as an anisotropy ratio as shown in Figure 4(h). Compression increases A_{κ} from 0.7 in pristine 3DG to 5.9, 11.8, and 120.5 for the 109, 53, and 6 μm samples, respectively. Relative to the pristine state, the corresponding anisotropy amplification factors are 8.7, 17.4, and 177.7.

The physical picture of this change can be understood in terms of two directional contributions: the conductance of individual graphene segments and junctions, and the geometry and connectivity of the macroscopic network. A useful form is

$\kappa_{eff,i} \propto G_i \Gamma_i$, where G_i represents the average thermal conductance of the graphene segments and junctions participating in transport direction i , and Γ_i is a directional geometric factor describing the number of parallel heat-flow pathways, their orientation, their tortuosity, and the number of junctions connected in series. A related geometric-factor treatment has previously been used for transport in percolating nanotube networks, where conductivity depends on the density of parallel conduction paths relative to the number of junctions encountered along each path.[30] During rolling, pore collapse and wall rotation increase the in-plane geometric factor, $\Gamma_{\parallel}$, by aligning more graphene segments with the film plane, increasing lateral overlap, and creating additional parallel pathways. At the same time, the cross-plane geometric factor, $\Gamma_{\perp}$, decreases because through-thickness transport becomes more tortuous and increasingly requires heat to cross stacked, folded, and misoriented graphene regions connected through weak inter-sheet contacts. Rolling may therefore increase the total number of graphene-graphene contacts while still reducing effective cross-plane transport, because many of the newly created contacts contribute primarily to lateral continuity rather than to direct through thickness conduction.

Prior cold-rolling studies of the same 3DG family showed large improvements in density, electrical conductivity, and mechanical strength after rolling, confirming that compression consolidates the network.[13] The thermal measurements show the

directional consequence of that consolidation: lateral pathways are strengthened, while through-thickness pathways become increasingly junction-limited. The rolled 3DG series therefore resolves the first processing question of this study. In this architecture, it is a route to convert a weakly anisotropic 3D network into a highly in-plane-dominant thermal conductor. Over the measured thickness range, the growth in anisotropy can be described empirically by $A_{\kappa}(t) = A_{\kappa,0} \left(\frac{t_0}{t}\right)^m$, where 'm' measures how sensitively the directional response develops during compaction. In geometric-factor terms, $\Gamma_{\parallel}$ cannot increase indefinitely because the number of useful parallel pathways eventually approaches a packing and connectivity limited maximum. Similarly, $\Gamma_{\perp}$ cannot decrease indefinitely while preserving a continuous specimen, because further compression would eventually produce graphene contact saturation, fracture, delamination, or complete pore collapse. The anisotropy must therefore approach a finite structural limit rather than diverge as $t \rightarrow 0$. Even if the film were compressed to 1-2 μm , it would remain a folded, junction-rich graphene network rather than becoming equivalent to an ideal two-dimensional graphene crystal.

3.2 Weld interface

While rolling redistributes the internal graphene network continuously, welding introduces a more localized perturbation, creating an internal plane where two 3DG sheets are mechanically joined as illustrated in Figure 5(a)-(c). Such planes are important because cross-plane heat flow in graphene assemblies is often limited not by conduction along graphene itself, but by transmission across graphene-graphene contacts, overlaps, step junctions, and weakly coupled layered regions.[3,12] In porous graphene networks, this interfacial resistance is distributed across many internal contacts, while in a welded stack, it is concentrated into a defined macroscopic junction plane. Here, “welding” refers to mechanical joining of stacked 3DG sheets under rolling compression.[13] The term does not imply metallurgical fusion. The welded samples show the expected signature of an internal thermal resistance plane. The one-interface welded sample made by compressing two stacked pristine 3DG films exhibited $\kappa_{\parallel} = 14.2 \pm 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ and $\kappa_{\perp} = 1.01 \pm 0.06 \text{ W m}^{-1} \text{ K}^{-1}$. The two-interface welded sample made by compressing three pristine 3DG films exhibited $\kappa_{\parallel} = 16.8 \pm 0.7 \text{ W m}^{-1} \text{ K}^{-1}$ and $\kappa_{\perp} = 0.56 \pm 0.02 \text{ W m}^{-1} \text{ K}^{-1}$ as displayed in Figure 5(d). Thus, adding weld interfaces strongly reduces cross-plane thermal conductivity while retaining the increased in-plane thermal conductivity.

To distinguish the contribution of constituent-layer compression from the additional resistance associated with the weld zones, an ideal-contact baseline was constructed in Figure 5(d). Because the final thicknesses of the rolled and welded specimens were approximately equal, the constituent-layer thicknesses were estimated as $t_{\text{layer}} = t_{\text{tot}}/N$, where $N=1, 2$, and 3 for the zero-, one-, and two-weld specimens, respectively.

This corresponds to approximate layer configurations of $1 \times 109 \text{ } \mu\text{m}$, $2 \times 55.0 \text{ } \mu\text{m}$, and $3 \times 36.7 \text{ } \mu\text{m}$. The cross-plane conductivity assigned to each constituent layer was obtained from the independently measured thickness dependence of rolled 3DG, and the corresponding layer resistances were summed in series while assuming zero additional resistance at the joining planes. This provides a first-order compression-only baseline and assumes that the constituent sheets undergo approximately equal compression and follow the independently measured $\kappa_{\perp,roll}(t)$ dependence of rolled 3DG at the corresponding constituent thickness. The resulting ideal-contact resistance is therefore $R''_{\perp,ideal} = \sum_{i=1}^N \frac{t_i}{\kappa_{\perp,roll}(t_i)}$. The experimentally measured total resistance exceeded this ideal-contact baseline by approximately $4.5 \times 10^{-5} \text{ m}^2 \text{ K W}^{-1}$ for the one-weld specimen and $10.4 \times 10^{-5} \text{ m}^2 \text{ K W}^{-1}$ for the two-weld specimen. These differences are identified as weld-associated excess resistances, $\Delta R''_w = R''_{\perp,meas} - R''_{\perp,ideal}$. They represent the additional cross-plane resistance not explained by compression of the constituent layers alone. Microscopically, this excess may arise from incomplete contact, residual nanoscale voids, weak van der Waals coupling, flake misorientation, interlocked or folded graphene walls, and structural modification adjacent to the weld plane. Because these effects cannot be separated independently using the present macroscopic measurements, $\Delta R''_w$ is interpreted as an effective weld-zone resistance rather than an intrinsic thermal contact resistivity.

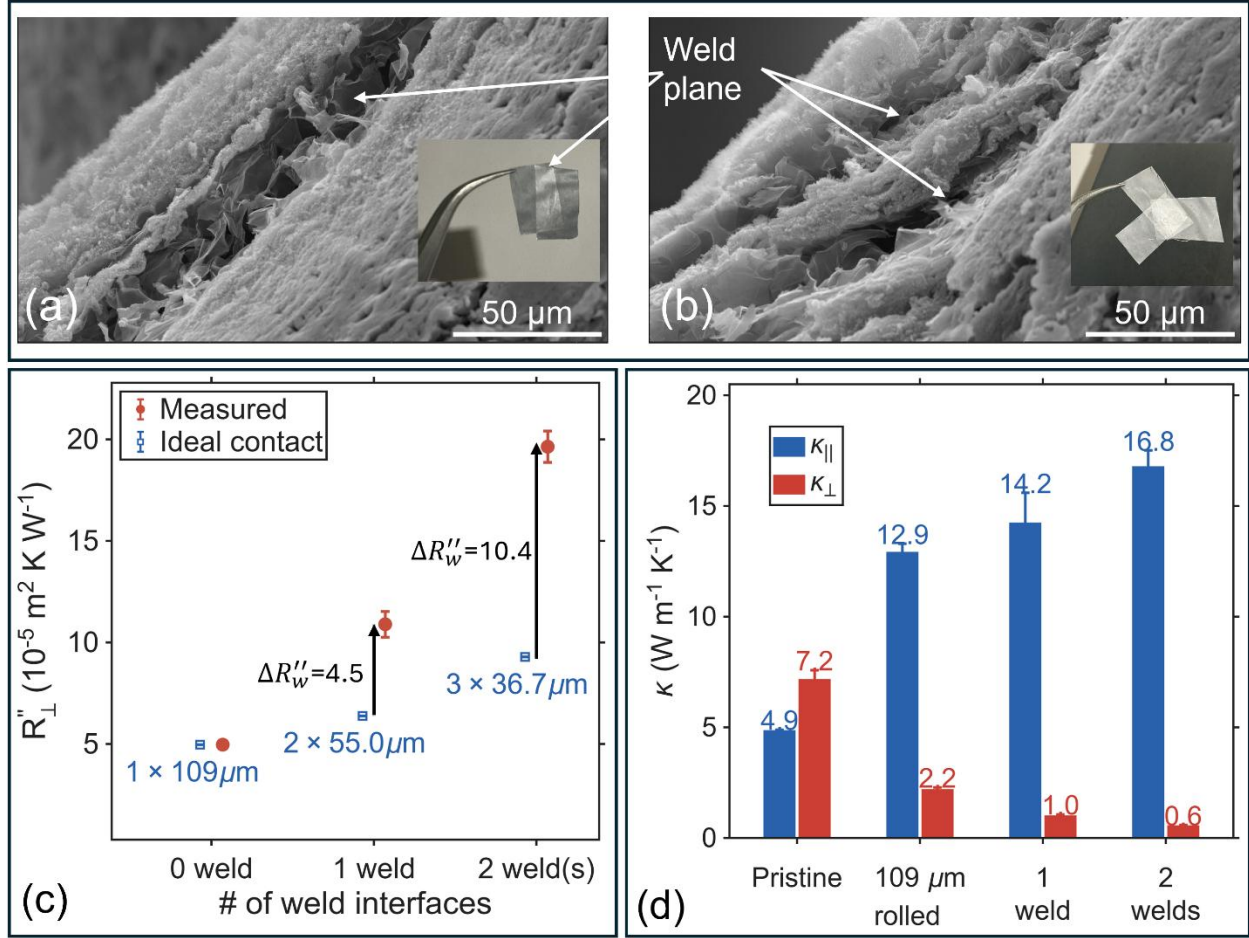


Figure 5: Effect of internal weld interfaces on directional thermal transport in 3DG. Representative illustrations of (a) one-weld 3DG, and (b) two-weld 3DG, (c) Measured area-normalized cross-plane resistance compared with an ideal-contact constituent-layer baseline; the gap, $\Delta R''_w$, denotes weld-associated excess resistance. (d) $\kappa_{||}$ and $\kappa_{\perp}$ of pristine, 109 μm rolled, one-interface welded, and two-interface welded 3DG.

3.3 Chemical modification

Chemical modification probes a different limit of the 3DG transport problem. Rolling and welding change the geometry of the thermal network; doping changes the local electronic structure, surface chemistry, and phonon-scattering landscape. In graphene-derived materials, molecular dopants, adsorbates, oxygen-containing groups, and point defects can modify carrier density and Seebeck response while also increasing phonon scattering and contact resistance.[3,31] The dopant set was selected from prior 3DG thermoelectric work. PEI-A, N-DMBI, and TBD were used as n-type molecular or polymeric dopants; PVP was retained as a weaker n-type dopant for comparison; and $\text{H}_2\text{SO}_4/\text{HNO}_3$ treatment were used as acid p-type treatments. The concentration range

of 0.25-1.00 wt.% and acid exposure range of 1-10 min follow the prior processing matrix, where these treatments produced measurable changes in carrier type, Seebeck coefficient, electrical conductivity, and power factor while preserving freestanding sample integrity.[14] In the present work, the same chemical space is used to test how electronic and surface-chemical modification affects $\kappa_{\parallel}$ and $\kappa_{\perp}$.

Figure 6 shows the thermal conductivity variation of 3DG with various doping methods and their treatment time or concentration. All chemical treatments gradually reduced thermal conductivity with increasing doping level, but the strength depended on dopant chemistry. PVP produced the weakest suppression, which agrees well with the fact that PVP has the lowest doping efficiency as observed in a previous work.[14] TBD produced the strongest suppression among the polymer/molecular series over the same loading range, reaching $\kappa_{\parallel} = 0.87 \text{ W m}^{-1} \text{ K}^{-1}$, and $\kappa_{\perp} = 1.2 \text{ W m}^{-1} \text{ K}^{-1}$ at 1 wt.% loading.

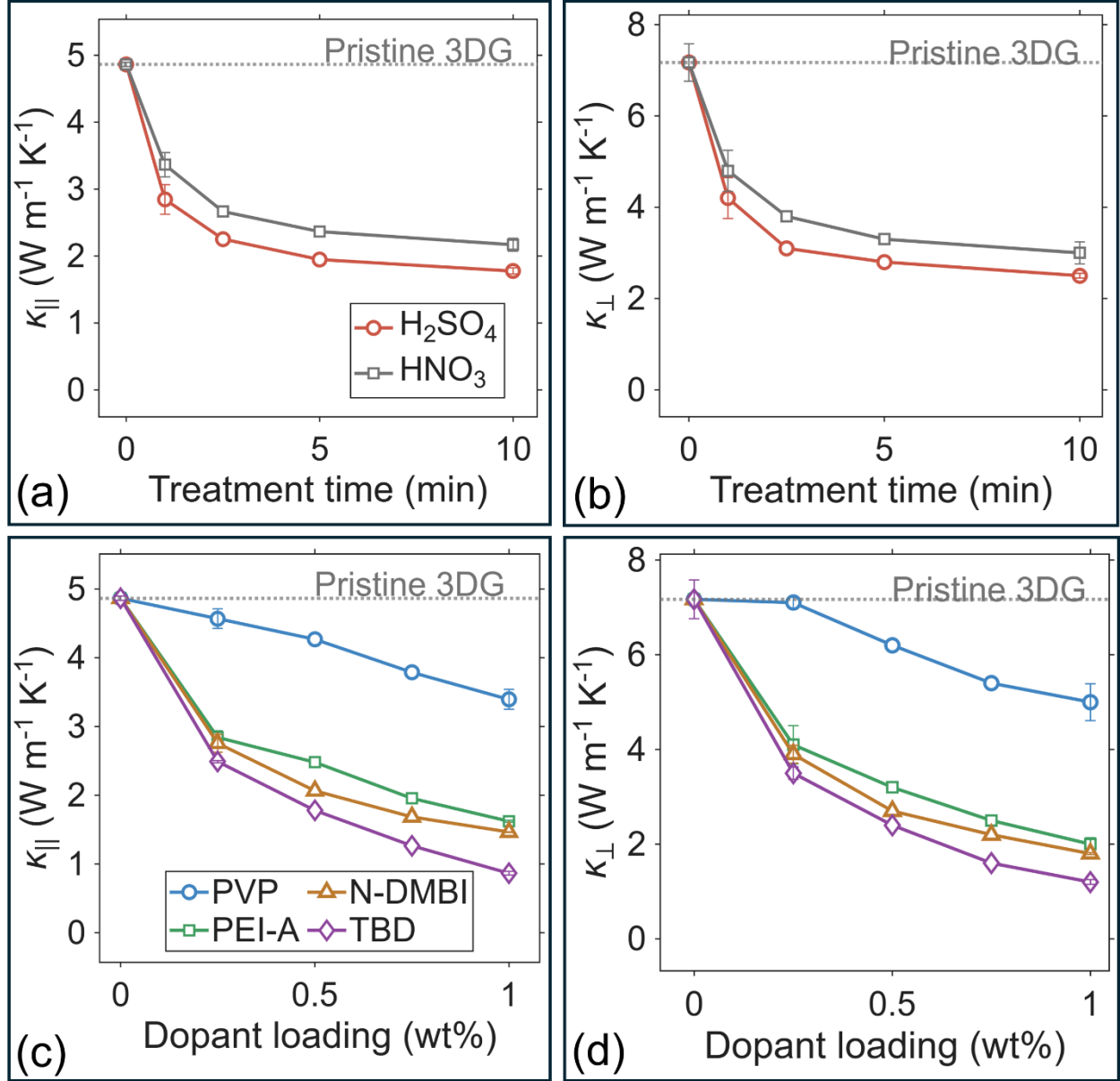


Figure 6: Directional thermal-conductivity response of three-dimensional graphene (3DG) to chemical modification, (a, b) $\kappa_{||}$ and $\kappa_{\perp}$, thermal conductivities of 3DG as functions of acid treatment time, (c, d) $\kappa_{||}$ and $\kappa_{\perp}$, respectively, as functions of PVP, PEI-A, N-DMBI, and TBD loading.

PEI-A and N-DMBI lie between these limits, closer to that of TBD. Across the measured polymer/molecular series, the suppression strength follows approximately $\text{PVP} < \text{PEI-A} \approx \text{N-DMBI} < \text{TBD}$.

Acid treatment produced the same qualitative trend with exposure time, saturating beyond 5 min exposure time to reach $\kappa_{||} = 1.78 \text{ W m}^{-1} \text{K}^{-1}$, and $\kappa_{\perp} = 2.5 \text{ W m}^{-1} \text{K}^{-1}$ by H₂SO₄ treatment, and $\kappa_{||} = 2.17 \text{ W m}^{-1} \text{K}^{-1}$ and $\kappa_{\perp} = 3.02 \text{ W m}^{-1} \text{K}^{-1}$ by HNO₃ treatment.

Under the conditions studied here, H_2SO_4 therefore produces stronger thermal attenuation than HNO_3 .

To evaluate whether carrier transport could account for the measured thermal response, the electronic contribution was estimated using the Wiedemann–Franz relation, $\kappa_e = L\sigma T$, where L is the Lorenz number ($=2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$), σ is the electrical conductivity, and T is the absolute temperature.[32] Using the highest electrical conductivity reported for the present dopant set, $\sigma \approx 57 \text{ Scm}^{-1}$ for PEI-A, the Wiedemann-Franz relation gives $\kappa_e \approx 0.042 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K. Even this upper-bound estimate is much smaller than the measured thermal conductivities, indicating that the observed thermal suppression cannot be explained primarily by changes in electronic heat conduction. The remaining suppression is therefore associated predominantly with the non-electronic thermal-transport channel and is consistent with dopant-induced phonon scattering, modification of graphene-graphene contacts, and changes in junction conductance. The chemical and thermoelectric responses should therefore be linked but not conflated. Prior doped-3DG work showed that these treatments can tune S , σ , and power factor.[14] The present data add the missing thermal dimension: the same dopants suppress heat transport, but they do not reproduce the anisotropic signature of mechanical rolling. Chemical modification acts primarily as a thermal attenuator while mechanical compression acts as a network reorientation process.

3.4 Directional thermal-transport landscape

Figure 7 places the measured 3DG states within a broader landscape of anisotropic thermal materials for which paired directional thermal conductivities have been reported. The comparison is expressed as the thermal anisotropy ratio, A_κ , as a function of cross-plane thermal conductivity, $\kappa_\perp$. Diagonal lines represent constant $\kappa_\parallel$. $A_\kappa < 1$ is possible for architectures engineered to conduct preferentially through the thickness. The comparison encompasses layered van der Waals solids, aligned carbon-nanotube (CNT) assemblies, graphene-based films and papers, porous graphene architectures, and anisotropic polymer composites.[10,26,33–52] Large thermal anisotropy can arise through markedly different structural mechanisms. Rotationally disordered molybdenum disulfide (r-MoS₂) exhibits extreme anisotropy because rotational disorder strongly suppresses interlayer transport while retaining comparatively high in-plane conductivity[26]. A similar separation of directional transport occurs in high-temperature-annealed reduced graphene oxide (rGO) films.[40] Other high-anisotropy carbon architectures include graphene/graphitized-polydopamine/carbon-nanotube (Gr/gPDA/CNT) films, graphene/cellulose-nanocrystal (Gr/CNC) films, structurally engineered graphene films, exfoliated graphite nanoplatelet (xGnP) papers, and horizontally or super-aligned CNT assemblies.[19,33,34,39,41,42] Bulk hexagonal boron nitride (h-BN) provides a crystalline layered benchmark in which strong basal-plane bonding and weak interlayer coupling similarly produce pronounced directional

transport.[43] In contrast, vertically aligned graphene/epoxy architectures can exhibit $A_k < 1$, because their engineered high-conductivity direction is through the composite thickness rather than along the film plane.[37,47–49,51,52] Thus, comparable values of A_k do not necessarily imply a common microscopic origin.

Against this literature landscape, the distinguishing feature of the present 3DG is the magnitude of the post-synthesis shift within a single freestanding material platform. The 6 μm rolled state reaches the same order of anisotropy as xGnP paper and exceeds the plotted h-BN and aligned-CNT states, although it remains below the most anisotropic r-MoS₂, annealed rGO, and engineered graphene films.[26,33,34,40,42,43,53]

Experimental studies reporting paired in-plane and cross-plane conductivities for the same freestanding porous graphene state remain comparatively limited, with many prior studies instead addressing dense films, layered crystals, or polymer-supported graphene architectures.[7,9,10,38,44] The paired measurements here directly show how post-synthesis network reorientation and weld-plane insertion redistribute heat flow without changing the underlying graphene scaffold.

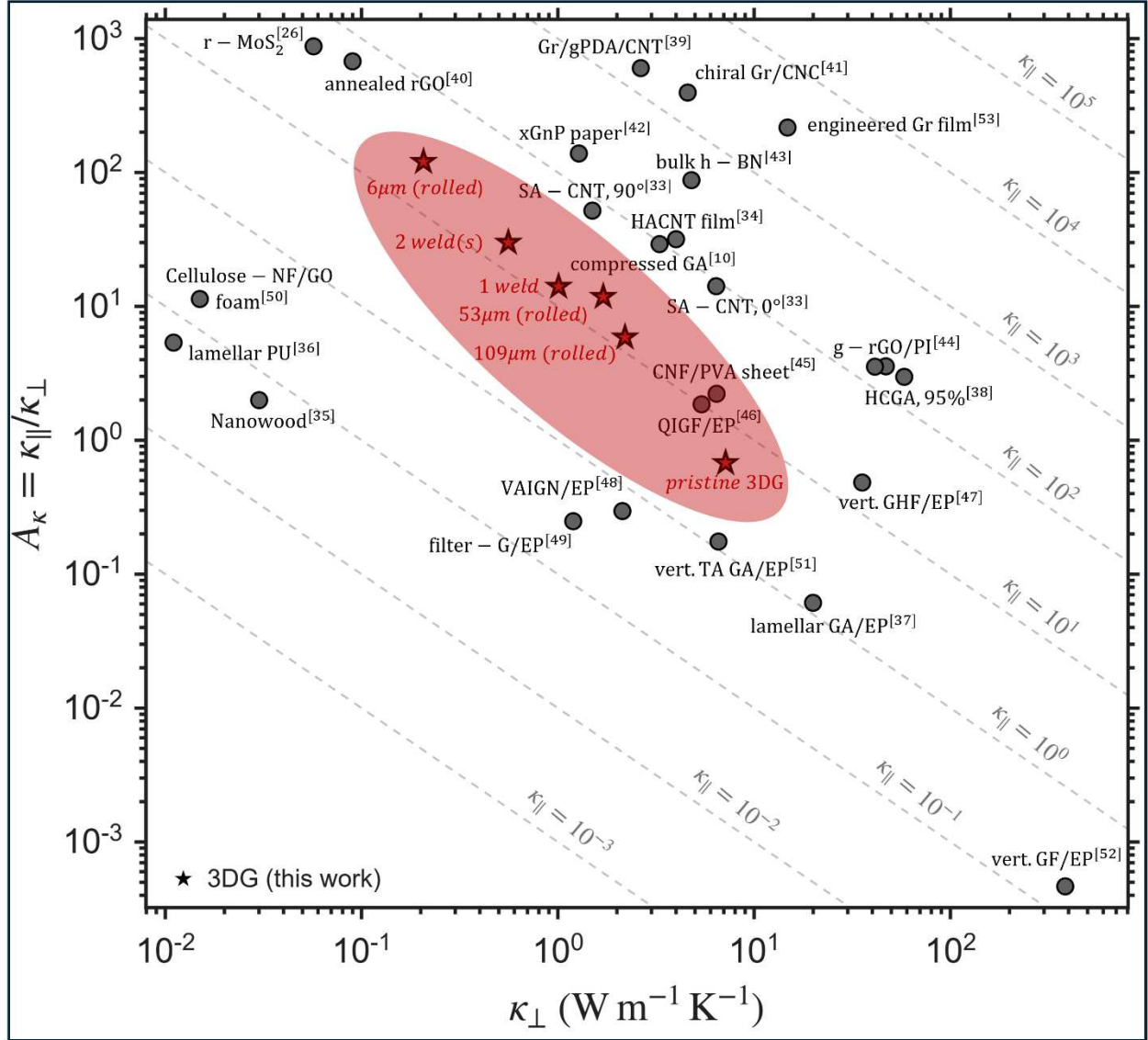


Figure 7. Comparison of thermal anisotropy, A_κ , as a function of cross-plane thermal conductivity.[10,26,33–53]

4. Conclusions

In this work, we systematically investigated how rolling, interfacial welding, and chemical modification alter in-plane and cross-plane thermal transport in freestanding 3DG films. We found that structural consolidation and welding progressively amplify thermal anisotropy by enhancing $\kappa_{\parallel}$ while suppressing $\kappa_{\perp}$, whereas chemical treatments primarily reduce the thermal-conductivity magnitude without requiring substantial geometric restructuring.

While compressed graphene papers and aerogels from previous works[9,10] can exceed the absolute thermal conductivities (Figure 7) obtained here, we demonstrated

that directional thermal response can be altered after synthesis while the graphene scaffold remains freestanding, electrically continuous, and mechanically processable. This positions 3DG uniquely between dense thermal conductors and architected porous networks. Copper, diamond, and graphitic sheets are generally selected for high absolute conductivity, whereas aligned carbon-nanotube assemblies, lamellar materials, and rotationally disordered van der Waals films use structural orientation or weak interlayer transport to separate fast and slow heat-flow directions.[26,33]

The present platform achieves comparable directional control through accessible post-synthesis operations. These controls make the material relevant to lateral heat spreading, through-thickness thermal isolation, and coupled heat-charge transport, where electrical conductivity, Seebeck response, and heat flow cannot be optimized independently.[14] Atomistic or mesoscale calculations could eventually connect these macroscopic trends to local junction conductance, but only after the relevant structures and interfaces are experimentally constrained. The principal contribution of this work is therefore a processing-resolved description of directional heat transport in freestanding 3DG films.

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