

Laser Photoreduction of Graphene Aerogel Microfibers: Dynamic Electrical and Thermal Behaviors

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This work reports the dynamic behaviors of graphene aerogel (GA) microfibers during and after continuous wave (CW) laser photoreduction. The reduction results in one-order of magnitude increase in the electrical conductivity. The experimental results reveal the exact mechanisms of photoreduction as it occurs: immediate photochemical removal of oxygen functional groups causing a sharp decrease in electrical resistance and subsequent laser heating that facilitates thermal rearrangement of GO sheets towards more graphene-like domains. X-ray and Raman spectroscopy analysis confirm that photoreduction removes virtually all oxygen and nitrogen containing functional groups. Interestingly, a dynamic period immediately following the end of laser exposure shows a slow, gradual increase in

electrical resistance, suggesting that a proportion of the electrical conductivity enhancement from photoreduction is not permanent. A two-part experiment monitoring the resistance changes in real-time before and after photoreduction is conducted to investigate this critical period. The thermal diffusivity evolution of the microfiber is tracked and shows an improvement of 277% after all photoreduction experiments. A strong linear coherency between thermal diffusivity and electrical conductivity is also uncovered. This is the first known work to explore both the dynamic electrical and thermal evolution of a GO-based aerogel during and after photoreduction.

Introduction

Graphene continues to demonstrate its seemingly limitless potential for engineers and scientists. The remarkable electrical, optical, and thermal properties make it perfectly suited for a wide range of applications in photovoltaics, energy storage, biosensing, and nanomedicine, to name a few.^[1–8] Recent research shows graphene synthesized into aerogels may be one of the best ways to exploit these favorable intrinsic properties.^[9] Graphene aerogels (GAs) are formed by assembling individual layers of graphene into a 3D porous network. The porous aerogel microstructure circumvents the agglomeration of individual graphene sheets caused by π - π stacking and Van der Waals interactions that reduce the specific surface area and inhibit the unique properties of graphene.

When synthesizing graphene-based materials such as aerogels, graphene oxide (GO) is the usual precursor material. The hydrophilic oxygen-containing functional groups of GO

(carbonyl, carboxyl, epoxy, and hydroxyl) facilitate dispersion in aqueous media which encourages uniform distribution in prepared composites.^[10,11] However, these same functional groups also hinder some of the properties of graphene that have made it so appealing to engineers, namely the superior electrical and thermal conductivity.^[12] Therefore, a large investment of research has been devoted to finding efficient, scalable methods to remove oxygen functional groups from GO to regain the desired graphene properties.

The various reduction strategies to produce reduced graphene oxide (rGO) can be divided into four principal methods: chemical, biological, thermal, and photo-mediated. Chemical reduction methods typically require highly toxic reducing agents such as hydrazine, dimethylhydrazine, and NaBH₄ that pose serious risks to human health and generate hazardous waste harmful to the environment.^[13] Alternatively, the natural world has provided an abundant amount of benign reductants for GO reduction sourced from extracts in plant material as diverse as green tea, pomegranate juice, and mung beans.^[14–16] Direct reduction of GO through thermal annealing has also proven to be effective at regaining the desired properties of graphene.^[17–19] Though the degree of reduction and structural composition of the resulting rGO show considerable sensitivity to annealing temperature.^[11,20,21]

In more recent years, advanced laser processing has opened a new avenue for the manufacturing of materials ranging from bioinspired micro/nanostructured surfaces to the texturing of battery materials.^[22,23] Consequently, photoreduction offers several advantages over the reduction methods just mentioned, especially in the field of micro- and nanoelectronics. Photon energy absorbed by GO materials removes oxygen functional groups while depositing heat into the material to facilitate rearrangement of the 3D network of graphene sheets. Laser

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irradiation allows for chemical-free reduction as well as precise patterning of conductive circuits through direct laser-writing.^[24] Consequently, direct laser-writing expands the potential for GO applications as electrodes in supercapacitors, sensors, and flexible electronics.^[25] The primary advantages of photoreduction techniques include low cost, efficiency, and scalability.^[26–28]

While ample evidence has demonstrated the utility of photoreduction, the depth of GO materials to which it has been applied remains limited and questions remain about the exact mechanisms by which reduction occurs. Currently, research has primarily focused on the reduction of GO materials with two-dimensional geometries as thin films.^[24,25,29–35] Spin-coating or drop-casting of aqueous GO suspensions on substrates are popular approaches that yield thin films through which photoreduction effects can easily be investigated. As of this writing, no published work has examined photoreduction in graphene-based three-dimensional architectures or aerogels. Furthermore, current research of photoreduced GO materials tends to neglect any robust analysis of thermal properties while focusing on the enhanced electrical conductivity instead.^[24,29,35] Lastly, no work has examined the photoreduction process in real-time. Many tools afford us an understanding of what happens to GO after laser irradiation, such as Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Less is known about the exact mechanisms involved in the evolution of GO to rGO as photoreduction is occurring.

This work investigates the dynamic electrical and thermal evolution of a graphene aerogel microfiber during photoreduction. Starting from a GO aqueous solution, a cylindrical-shaped hydrogel was synthesized and further processed into an aerogel by freeze-drying. The resulting aerogel microfiber was composed of a three-dimensional network of GO sheets. The ends of the microfiber were connected to electrodes so the electrical resistance across the sample could be measured during and after removal of oxygen functional groups by continuous wave (CW) laser irradiation. Besides the clear exponential decay in electrical resistance during photoreduction, Raman and energy-dispersive X-ray analysis confirm the reduced nature of the graphene aerogel microfiber. Additionally, the transient electrothermal technique (TET) was applied to the fiber to monitor the improved thermal diffusivity of the sample throughout the photoreduction process. Finally, a slowly evolving transient phase immediately following the end of laser exposure is observed. This newly uncovered phenomenon reveals the temporal nature associated with the structural rearrangement of graphene oxide sheets in an aerogel microstructure after photoreduction.

Sample Preparation and Structure Characterization

An aqueous solution of graphene oxide purchased from Graphene Supermarket was diluted with deionized water to form a GO suspension with 4 mg/mL concentration. The resulting 10 mL suspension was ultrasonicated for one hour to

exfoliate multilayered GO into few-layered and single-layered GO. Following the synthesis method developed by Deng et al., 40 μ L of ethylenediamine (EDA) was added as a nitrogen source.^[36] To prepare GA in the form of microfibers, the suspension was injected into 12 cm long glass pipes with an inner diameter of 1.0 mm. The two ends of the glass pipe were sealed using the flame of an alcohol lamp. Then, the glass pipes of GO underwent a hydrothermal reduction process at 120 °C for 12 hours. The hydrogel fibers were carefully removed from the pipes and placed in a 20 v% ethanol bath for 4 hours of dialysis. Finally, the GO hydrogels were freeze-dried to produce graphene aerogel microfibers with $\sim$ 600 μ m diameters. The entire synthesis procedure is summarized in Figure 1a.

SEM imaging reveals a microscale hierarchical porosity in the resulting GA fiber. Figure 1b and 1c show the surface-level pores with diameters in the tens of microns. These pores allow access to the high surface area regions within the fiber. A further magnified SEM image in Figure 1d shows pores in the sub- μ m range. Entire fibers were sliced into 4–5 mm segments to be prepared for suspension over a 2 mm gap.

Dynamic Thermal and Electrical Evolution of GA Fibers During Photoreduction

Observations of Significant Electrical Conductivity Enhancement in GA Microfibers

The real-time observation of photoreduction of a GA microfiber is facilitated by measuring the voltage difference between the two ends of the fiber. This requires special preparation by suspending a 2 mm long segment of the fiber in a vacuum environment to prevent combustion of the carbonaceous material during laser heating and to remove convection effects (for the subsequent measurement of heat conduction caused by joule heating). The two ends of the microfiber are connected to conductive copper tape electrodes on a glass wafer and secured by applying a small amount of silver paste. Because the size of particles in the silver paste are quite small relative to the aerogel sample, the electrical and thermal contact resistance is minimal and can be disregarded. The negligible impact of the contact resistance is confirmed by previous work.^[37] Additionally, another earlier work measured the electrical contact resistance between high purity graphene film and silver paste to be less than 0.2 Ω .^[38] Given that the intrinsic electrical resistance of our suspended GA microfiber initially measures 8 k Ω (before reduction), it is safe to assume that the contact resistance has an insignificant effect on our measurements.

Copper wires attached to the electrodes are fed through a feedthrough of the vacuum chamber which are then connected in parallel to a current source and multimeter. The current source supplies a small amount of current to induce a voltage change in the sample from which the resistance can be measured. This same current source will be also used for joule heating to cause a temperature rise in the sample from which the thermal diffusivity can be extracted based on the resultant

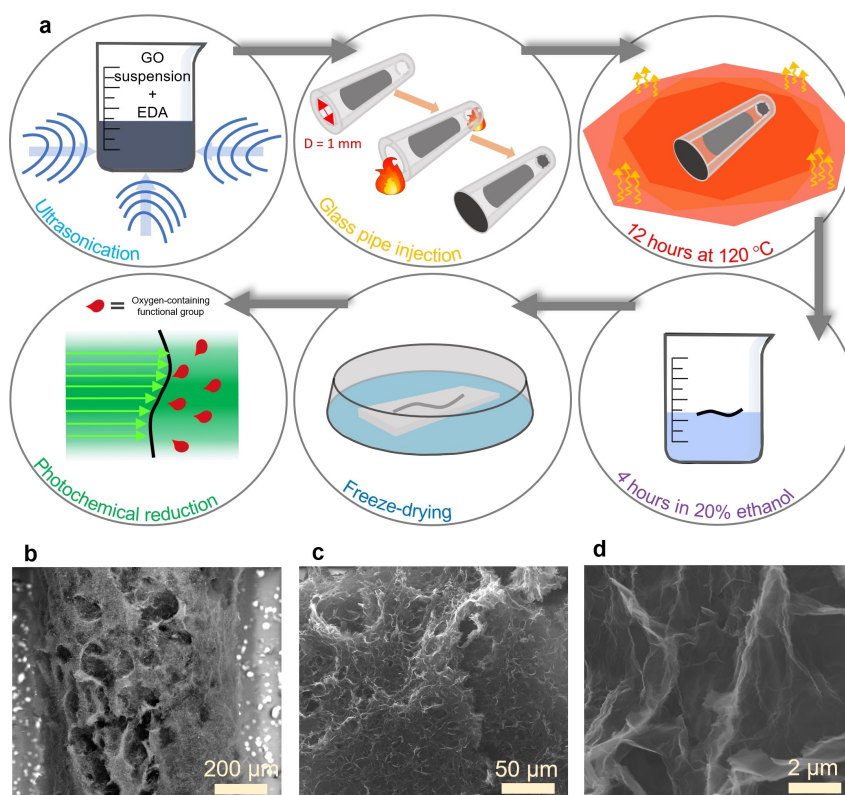


Figure 1. (a) The principal steps for GA microfiber synthesis: 1) ultrasonication of the GO + EDA suspension, 2) injection of suspension into glass pipes and subsequent sealing of open ends with flame, 3) hydrothermal treatment at 120 °C, 4) removal of hydrogel fiber from pipe and dialysis in 20% ethanol solution, 5) freeze-drying, 6) photoreduction. (b–d) SEM images at increasing magnifications illustrate a porous aerogel structure with a variety of pore sizes.

changing voltage signal (more details will be explained in section 3.2). Note that the current used to measure the voltage difference across the sample is small enough that it causes minimal sample heating. It is also important to note that the applied current happens after CW laser heating and does not cause structural property changes in the aerogel microstructure. The heat generated from the CW laser irradiation during photoreduction far outweighs the heating effect caused by the current and is solely responsible for the structural rearrangement of GO sheets. In the vacuum chamber ($P < 10$ mTorr), the suspended microfiber is placed in the path of a 532 nm CW laser with a 1 mm radius (maximum laser power of 2 W); the laser beam covers the entire length of the suspended sample. The experimental setup explained above is illustrated in Figure 2.

Arul et al. have proposed two steps in the process for converting GO to rGO via laser irradiation: 1) at the atomic level oxygen functional groups attached to the GO sheet surfaces are photochemically removed and 2) heat deposited by the laser facilitates highly localized thermal annealing which rearranges the newly reduced GO sheets into more graphene-like domains.^[25] With the oxygen groups removed and graphene features improved, electron flow through the aerogel microstructure will be less impeded. Thus, improved electrical conductivity registered by lower resistance measurements of

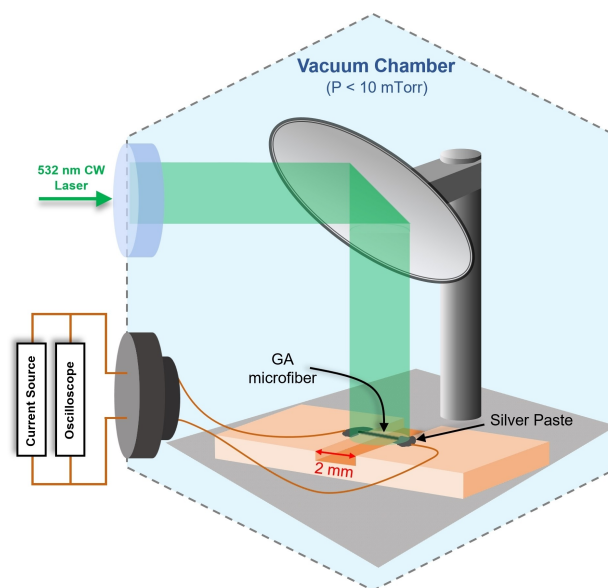


Figure 2. Physical setup for photoreduction experiments. The suspended GA microfiber is placed in a vacuum chamber with a window opening for CW laser irradiation. The copper wires connect to the microfiber with a small amount of silver paste and are fed through a feedthrough in the chamber. Once connected to the current source and oscilloscope, the photoreduction and subsequent thermal and electrical transport in the microfiber can be measured through the voltage-time data acquired.

the suspended sample will confirm the photoreduction of the sample.

The experimental procedure for monitoring in-situ photoreduction effects in the GA microfibers begins with laser irradiation at the lowest laser power, in this case 64 mW. Note that lower laser powers would also cause photoreduction. However, given that the upper limit at which sample breakdown begins was observed to be around ~ 700 mW, the lower limit was chosen such that a reasonably distributed set of laser power values could be tested. For the first three laser powers (64, 128, and 192 mW), laser exposure intervals were set at 10 s. In other words, the laser path was allowed to pass through the vacuum chamber window and onto the suspended sample for 10 s. At the end of the laser exposure interval, the laser path to the sample was blocked and the new electrical resistance was measured. At the higher laser powers (256 to 640 mW), the laser exposure interval was set at 4 s to maintain high resolution measurements of the changing electrical and thermal properties of the GA microstructure. Note that the 2 mm diameter laser beam covers the length of the entire suspended region of the sample, but ~ 0.1 mm on each end is left supported by the electrode and uncovered by silver paste.

The laser exposure process continues until the resistance of the suspended sample no longer decreases after laser irradiation. The experimental procedure repeats at the next higher laser power and continues until the final laser power of

640 mW. It should be noted that the resistance values recorded are collected during the TET characterization of the sample which measures thermal diffusivity from voltage-time (V - t) data acquired during joule heating. The recorded resistance values correspond to the initial V - t data point collected during TET measurements at the instant the current source induces a voltage change in the sample. After this moment, the sample immediately undergoes a small temperature rise (chosen to be < 10 K) before reaching a new steady-state thermal equilibrium. However, the electrical resistance values recorded in this work come from the initial V - t data point that measures the room temperature resistance, before the current source causes the subsequent temperature rise in the sample. TET measurement happens directly after laser exposure and will be further explained in the following section.

The collected resistance data clearly demonstrates the effectiveness of photoreduction for GA microfibers. For every laser power tested, the electrical resistance of the sample decreased. The electrical resistance against time plots for all laser powers are shown in Figure 3a–c. The largest decrease always occurs immediately following the first interval of laser exposure (i.e., either 4 s or 10 s) suggesting the rapid nature of CW laser photoreduction. It should be noted that this rapid, initial resistance drop originates in direct photochemical removal of functional groups. As laser exposure increases, the photochemical reduction effect decreases. The second stage of

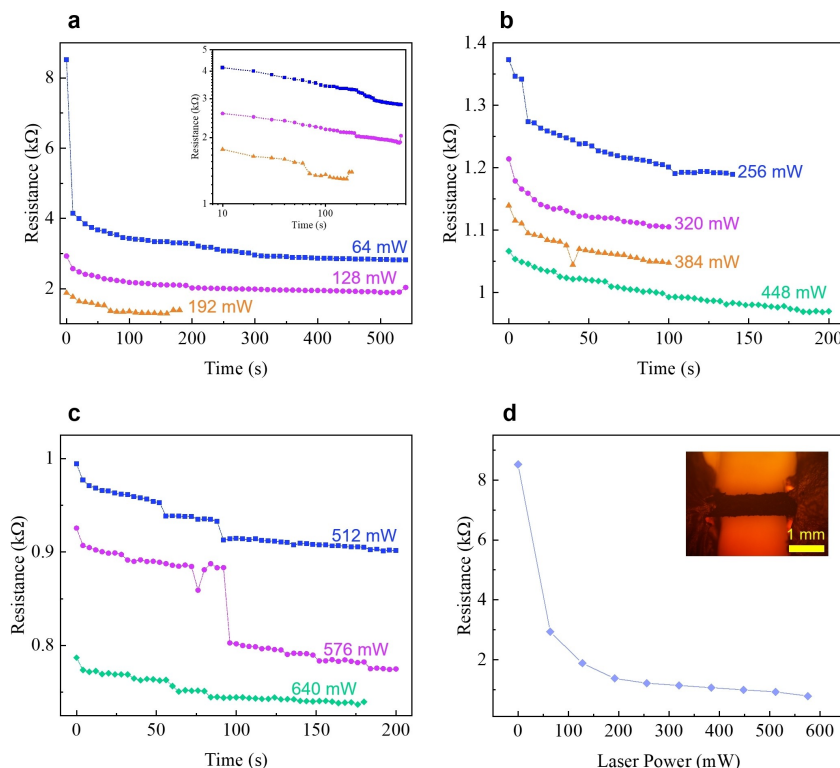


Figure 3. (a–c) Plots showing how photoreduction reduces the resistance in the GA microfiber with cumulative laser exposure over time. Each data point is collected after 10 s (64–192 mW data) or 4 s (256–640 mW) of photoreduction. The largest decrease by far happens upon initial laser exposure at 64 mW. (a) The three lowest laser power photoreduction results with the inset showing logarithmic time scaling. (b–c) Photoreduction results for the next six laser powers. (d) The evolution of the electrical resistance after each round of cumulative photoreduction for a given laser power. The inset shows the optical microscope image of the suspended sample.

resistance reduction from laser heating causes small structural rearrangement due to the short heating time interval. Though the laser heating will cause some minimal reduction of the GA microfiber due to the higher kinetic energy caused by laser energy absorption. The elevated temperature of the material and subsequent increased kinetic energy of impurity atoms and functional groups will be large enough to break some of the bonds attaching them to the graphene sheets.

Across all laser powers, the largest decreases occurred during the first two laser powers at 64 and 128 mW and there were diminishing returns of electrical conductivity enhancement as the laser power increased. Figure 3d plots the evolving electrical resistance of the GA microfiber at each laser power tested for photoreduction. The plotted data point corresponds to the final measured electrical resistance after cumulative laser exposure for a given laser power. By far, the biggest resistance change occurred during the very first 10 s of photoreduction at 64 mW, decreasing the resistance by over 50%. Overall, the series of photoreduction experiments resulted in more than one-order of magnitude electrical conductivity increase, bringing the initial, unreduced sample from 8.5 k Ω to 740 Ω .

Electrical resistance for lower laser powers shows decaying exponential-like trends with time. As the laser powers increase, the exponential nature of the curve flattens out and becomes more linear. However, a few aberrations to this general rule were seen at 512 mW and 576 mW laser power exposures (Figure 3c). For the 512 mW case, at $t=52$ s and $t=88$ s there are abrupt and sharp drops in resistance of 15 Ω and 20 Ω , respectively. Besides these aberrations, the resistance of the fiber demonstrated slow, incremental decreases of 1–2 Ω at each four second interval. Similarly, for the 576 mW case a significant and abrupt drop of 80 Ω is recorded at $t=92$ s. These rapid and drastic changes suggest significant structural rearrangements of graphene oxide sheets within the aerogel microstructure towards more graphene-like domains.

An important final note: the last measured resistance for any given laser power is most often less than the initial measured resistance recorded for the following round of measurements at the next higher laser power. As an example, the final resistance measurement at $t=540$ s during the 64 mW laser power experiments is 2818 Ω . Before photoreduction experiments begin at the subsequent 128 mW laser power, the initial resistance of the microfiber sample measures 2931 Ω . In other words, a small proportion of the enhanced electrical conductivity caused by photoreduction is not a permanent change in the material property of the GA microfiber. There is an unknown window of time immediately following the end of photoreduction in which the electrical resistance gradually increases due to heat dissipation effects. Following the immediate photochemical removal of impurities, the heat deposited by the absorbed laser energy creates a period of structural instability as the graphene sheets rearrange and form new bonds. The dynamic behavior of this electrical response during the post-photoreduction period will be further discussed in section 4.2.

TET Characterization of GA Microfibers

The transient electrothermal technique (TET) is a robust, proven method for thermal diffusivity measurements of conductive, semi-conducting, and dielectric microscale fibers. Extensive previous work has substantiated its accuracy and applicability for characterizing a wide range of material.^[37,39–42] The way in which the GA microfiber sample was prepared for photo-reduction experiments also suits TET measurements: namely, being suspended and in a vacuum environment. The low-pressure chamber (<10 mTorr) ensures that heat convection can be neglected.

The current source feeds a step current through the GA microfiber to induce joule heating. The heating changes the resistance of the microfiber which is registered in the voltage-time profile (V - t) collected by an oscilloscope. Before the microfiber reaches a steady-state temperature, a transient phase at the beginning of the step current occurs which is principally governed by the rate of heat conduction (i.e. thermal diffusivity). The transient voltage evolution parallels the transient temperature rise in the microfiber and can be fitted with a theoretical model to extract the thermal diffusivity.

The governing heat equation is written as:

$$\frac{1}{\alpha} \frac{\partial \theta(x,t)}{\partial t} = \frac{\partial^2 \theta(x,t)}{\partial x^2} + \frac{I^2 R}{kL A_c} + \frac{Q_{rad}}{kL A_c} \quad (1)$$

where α is the thermal diffusivity, I is the amplitude of the step current, R is the resistance of the sample, L is the suspended length, A_c is the cross-sectional area, k is the thermal conductivity of the sample, and Q_{rad} is the rate of thermal radiation from the sample surface. Note that θ represents the temperature rise $T-T_0$ where T_0 is the initial temperature. The solution to the partial differential equation involves integration of Green's function (see Ref. [32] for more details). Additionally, the spatial temperature distribution of the microfiber can be averaged by integration along the length of the microfiber as:

$$T(t) = \frac{1}{L} \int_{x=0}^{x=L} T(x,t) dx = T_0 + \frac{8q_0 L^2}{k\pi^4} \sum_{m=1}^{\infty} \frac{1 - \exp[-(2m-1)^2 \pi^2 \alpha t / L^2]}{(2m-1)^4} \quad (2)$$

where q_0 is the joule heating rate per unit volume. Thus, the normalized temperature rise of the sample, defined as $T^*(t) = [T(t) - T] / [T(t \rightarrow \infty) - T_0]$, can then be expressed as:

$$T^* = \frac{96}{\pi^4} \sum_{m=1}^{\infty} \frac{1 - \exp[-(2m-1)^2 \pi^2 \alpha t / L^2]}{(2m-1)^4} \quad (3)$$

The small current used to induce joule heating (50–400 μ A) will cause a minor temperature rise such that the temperature coefficient of resistance can be assumed to be constant.

Therefore, the normalized temperature rise will be equivalent to the normalized voltage-time profile. A MATLAB code applies the least squares fitting method (LSF) on the experimental V - t curves based on the normalized temperature rise equation and determines the best theoretical fit for the TET data.

To account for thermal radiation heat loss from the microfiber sample surface during TET measurements, corrections must be applied to this fitted diffusivity value. The effective (measured) thermal diffusivity can be written as $\alpha = \alpha_{\text{real}} + \alpha_{\text{rad}}$ where α_{real} is the true thermal diffusivity of the GA sample and α_{rad} is the TET measured diffusivity component attributed to thermal radiation. In the general form, α_{rad} can be expressed as $4Pe\sigma T_0^3 L^2 / (\rho c_p A \pi^2)$ where ε is emissivity, σ is the Stefan-Boltzmann constant, ρ is density, c_p is specific heat, P the sample's circumference, and A its cross sectional area. For a cylindrical-shaped sample of diameter D , α_{rad} is expressed as $16\varepsilon\sigma T_0^3 L^2 / \rho c_p D \pi^2$. Xie et al. have already carefully studied the thermal radiation effect during TET measurements for a rectangular shaped graphene aerogel^[43] synthesized using the same method of this work. Given the paralleled GA synthesis method, we use reference values from the previously published work to calculate α_{rad} for our GA microfiber. Note that in the previously mentioned work, the rectangular GA samples were cut from a bulk GA sample which did not exhibit any volume shrinkage during hydrothermal treatment or lyophilization. In our case, the microfiber's diameter shrunk by 36% (with negligible length shrinkage) resulting in an estimated density of 10 mg cm^{-3} . Using the reference value of $850 \text{ J kg}^{-1} \text{ K}^{-1}$ for c_p at

room temperature (also from the previous work), the α_{rad} for the GA microfiber samples during TET measurements is calculated as $0.977 \text{ mm}^2 \text{ s}^{-1}$.

Four representative TET signals are plotted in sequential order (at $t = 0, 100, 300, 540 \text{ s}$) along with their best theoretical fitting to highlight the increasing thermal diffusivity trend during the 64 mW photoreduction experiments (Figure 4c). Note that TET measurements were conducted immediately after each 4 s (or 10 s) laser photoreduction interval. The initial voltage data point in these plotted curves was used to calculate the room temperature electrical resistance of the sample given the current amplitude used for TET joule heating.

TET results for the GA microfiber reveal that photoreduction improves the thermal diffusivity of the aerogel microstructure as well as the electrical conductivity. As shown in Figure 4a, the very first instance of photoreduction using a laser power of 64 mW shows a $\sim 100\%$ increase in α . Successive intervals of photoreduction continue to enhance the aerogel's capability of heat conduction. Increasing the laser power to 128 mW (see Figure 4b), the thermal diffusivity enhancement continues, but the increasing trend is less obvious. Overall, the first two laser powers tested caused the most significant improvement in thermal diffusivity out of all laser powers tested for photoreduction. Higher laser powers showed minimal additional benefit for the development of thermal diffusivity. Figure 4d tracks the evolving diffusivity of the GA microfiber by plotting the resulting α_{real} value after photoreduction at a given laser power. As the laser power increases over time, α_{real} begins to

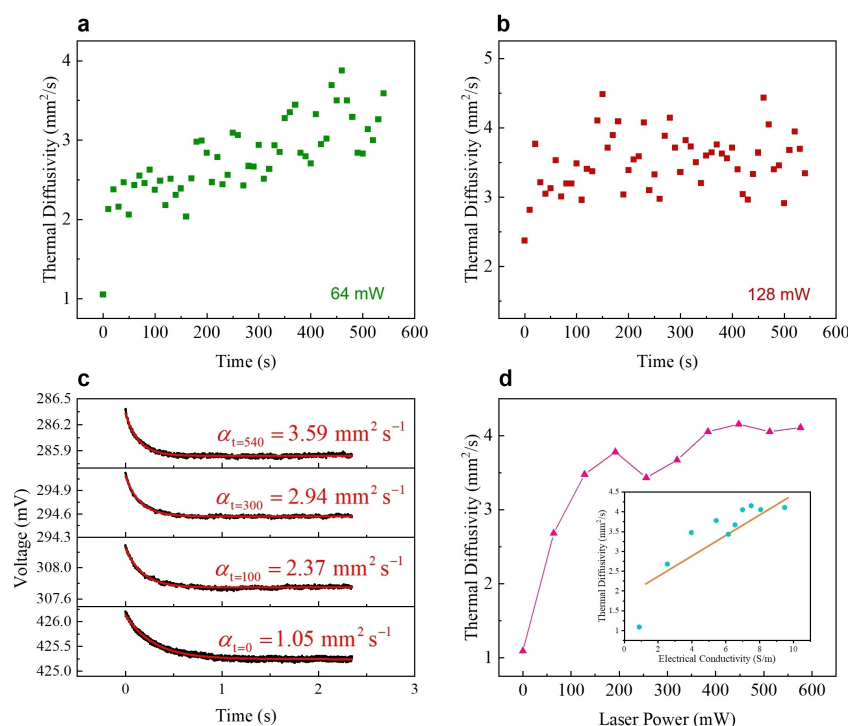


Figure 4. Thermal diffusivity of the sample during photoreduction at (a) 64 mW and (b) 128 mW. The 64 and 128 mW laser powers show the most obvious increase in thermal diffusivity. (c) The TET signals collected throughout photoreduction at 64 mW with the theoretical curve fitting used to extract thermal diffusivity. (d) As the laser power increases, the thermal diffusivity reaches a steady state value. The inset shows the linear coherency between improved electrical conductivity and thermal diffusivity caused by the improving ordered structure of GO sheets composing the aerogel.

level out around $4 \text{ mm}^2 \text{ s}^{-1}$. Overall, the cumulative effect of multiple rounds of photoreduction increased the microfiber's thermal diffusivity by $\sim 275\%$ (1.09 to $4.11 \text{ mm}^2 \text{ s}^{-1}$).

The inset of Figure 4d demonstrates the notable linear coherency between the electrical conductivity (σ) and thermal diffusivity improvement in the GA microfiber. This coherency has been thoroughly investigated and explained for multiple carbon-based nanomaterials in a previous work.^[44] The physics reasoning behind this linear correlation stems from the structural arrangement of GO sheets that run parallel to the principal direction of both electron and phonon transport along the length of the microfiber. After photoreduction removes functional groups from individual GO sheets, the laser-facilitated thermal annealing yields a more ordered GO network with enhanced electrical connections between adjacent GO layers (i.e. photoreduction transforms the layered GO from internal disordered structure to ordered structure). These improved connections also facilitate thermal transport. As shown in the inset, a noticeable linear trend governed by the physical mechanisms explained above shows α_{red} increasing alongside σ . Note that the line drawn in the inset is meant to guide the eye.

Structure Evolution

Raman and EDS Analysis of Reduced GA Microfibers

Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDS) are used to analyze the GA fiber material structure and chemical composition before and after photoreduction. These spectroscopic tools confirm the removal of oxygen-groups and the graphenization of the aerogel material. The Raman D-band corresponding to the A_{1g} phonon mode at $\sim 1350 \text{ cm}^{-1}$ indicates the sp^2 ring-breathing mode characteristic of graphene-like structures. The Raman G-band corresponds to the E_{2g} in-plane vibrational mode at $\sim 1580 \text{ cm}^{-1}$. The peak intensity ratio $I(\text{D})/I(\text{G})$ is often used as a normalized parameter to describe the defect density: as D-band peak intensity increases, so does the defect density.^[45]

The 2D Raman contours shown in Figure 5a highlight the characteristic D and G peaks observed across the length of the reduced microfiber sample. A weaker 2D peak near 2690 cm^{-1} is also present along most of the microfiber indicating the graphene structure has been maintained post-reduction. These 2D contours emphasize the consistent graphene features across the length of the suspended sample. Additionally, a comparison of Raman spectra before and after photoreduction in Figure 5b reveals the graphene characteristics are maintained in the aerogel following CW laser irradiation. The absolute intensities are lower in the unreduced sample and can mostly be attributed to minimal differences in the focusing area of the Raman excitation laser and the corresponding differences in volume of material generating Raman scattered light. Notably, the D and G peak intensity ratio is consistent between reduced and unreduced samples suggesting the photoreduction technique does not increase defects. The Raman spectra also reveals a

slight redshift in the G peak after photoreduction. The unreduced control sample shows the G mode at $\sim 1592 \text{ cm}^{-1}$. This is a higher wavenumber than the range of G peak locations covered over the length of the photoreduced sample: 1578 – 1588 cm^{-1} (shown in the top panel of Figure 5c). This G-band redshift has also been recorded by Yung et al. after laser direct patterning on a graphene oxide thin film.^[35] The redshift effect has been attributed to the transition of GO to graphene after reduction and an enhancement of the interlayer coupling in rGO.^[46,47]

Further Raman analysis of the D and G peak features at different points along the length of the photoreduced GA microfiber reveal other structural properties of the sample. Figure 5c also plots the varying linewidth and $I(\text{D})/I(\text{G})$ intensity ratio starting near the center point of the suspended sample (Position = $0 \mu\text{m}$) to the edge of the sample (Position = $1300 \mu\text{m}$). The ratio hovers consistently around 1.18 across most of the sample suggesting a uniform distribution of defects after photoreduction. The linewidths for both the D and G peaks show more variation across the length of the reduced microfiber. The D-band ranges from 119 to 162 cm^{-1} and the G band ranges from 69 to 89 cm^{-1} . The Raman linewidth contains information related to phonon lifetimes. Longer phonon lifetimes correspond to more narrow peaks while shorter lifetimes mean broader peaks. Since phonon lifetime is related to grain boundary structure, the Raman linewidth also reveals information on the crystalline nanostructure of the aerogel microfiber: more narrow linewidths indicate a smaller crystallite size distribution.^[48] Additionally, as detailed by Ribeiro-Soares et al., there is a clear correlation between the G-band linewidth and crystallite size for polycrystalline graphene systems; larger crystallite sizes correspond to more narrow linewidths.^[49] Therefore, the range of linewidths measured along the length of the sample for both D and G Raman modes suggest inhomogeneous grain sizes for the graphene sheets composing the GA material. This would be consistent with the hierarchical porous structure evident in SEM imaging.

The EDS data for the photoreduced GA microfiber and a control, unreduced fiber validates the successful reduction of the aerogel sample via CW laser irradiation. Measurements of the elemental composition revealed by EDS show significant decrease in oxygen content in the reduced GA microfiber. A control sample before reduction showed oxygen content as $\sim 11\%$. The photoreduced sample showed oxygen content as $< 2\%$. Correspondingly, the proportion of carbon went from 81 – 85% to greater than 97% after reduction. A summary of the EDS data for three different locations on each sample, photoreduced and control, are shown in Figure 5d. Note the small amount of nitrogen (5 – 7%) originates from the EDA added during GA synthesis. As shown in the figure, photoreduction removes virtually all nitrogen. Note the trace amount of silicon ($< 1\%$) most likely represents residual contaminant from breaking the glass pipes to remove the hydrogel microfiber after hydrothermal treatment.

As applied to our $\sim 600 \mu\text{m}$ diameter sample, it should be noted that EDS effectively serves as a surface level elemental analysis of the photoreduced GA microfiber due to the typical

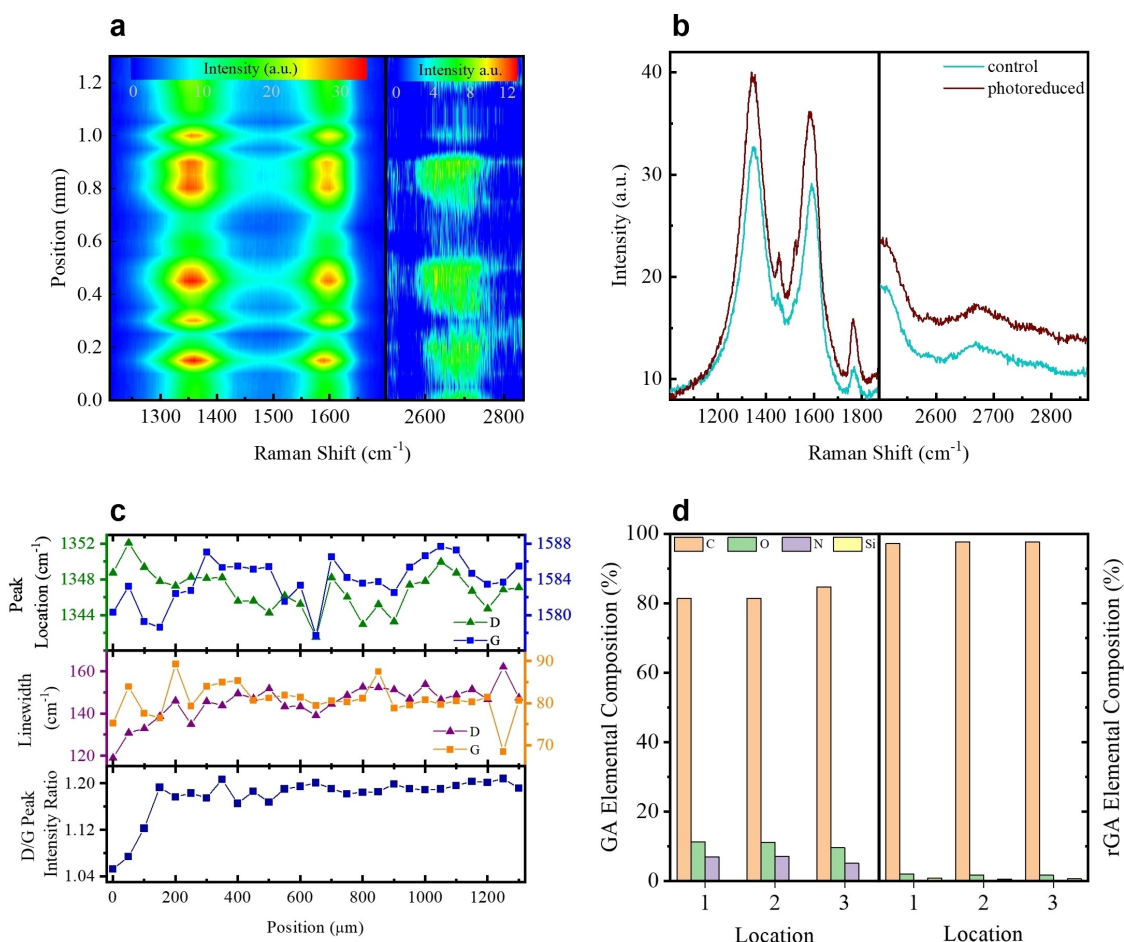


Figure 5. (a) The 2D Raman contour plotted along the length of the sample showing the Raman spectral region focused on the D ($\sim 1350\text{ cm}^{-1}$) and G ($\sim 1580\text{ cm}^{-1}$) modes characteristic to graphene. The 2D peak spectral region ($\sim 2690\text{ cm}^{-1}$) also confirms the graphene structure along the length of the sample. (b) Raman spectra of a photoreduced microfiber and a control sample. (c) Plots showing different Raman peak spectral features with x-axis representing distance along the length of the sample with $0\text{ }\mu\text{m}$ being near the center of the suspended sample and $1300\text{ }\mu\text{m}$ being the very edge. The y-axis represents the peak location, linewidth, and the intensity ratio for the D and G modes determined from Gaussian peak fitting of the raw Raman intensity data. (d) EDS data showing elemental composition for carbon, oxygen, nitrogen, and silicon for the unreduced sample on the left (GA) and the photoreduced sample on the right (rGA).

electron penetration depth ($<5\text{ }\mu\text{m}$) for X-ray spectroscopy. Similarly, the photoreduction from the CW laser source is limited to the surface of the microfiber sample. The absorption depth for the synthesized GA material can be estimated using the density of the sample ($\rho_{\text{GA}}=10\text{ mg/cm}^3$), the density of graphite ($\rho_{\text{gr}}=2210\text{ g/cm}^3$),^[50] the interlayer spacing between graphene layers in graphite ($L=0.335\text{ nm}$), and the light absorption of a single layer of graphene (2.3%).^[51] Due to the reduced density, the effective interlayer spacing between graphene layers in the GA microfiber is estimated as $L_e=74\text{ nm}$ [where $L_e=(\rho_{\text{gr}}/\rho_{\text{GA}})\cdot L$]. Using the effective interlayer spacing and the absorption of single layer graphene, the absorption depth for the sample can be calculated as $\tau=3.2\text{ }\mu\text{m}$. This implies that all the laser energy is absorbed within the first $20\text{ }\mu\text{m}$ of the GA microfiber. Despite being a surface level treatment of the suspended sample where only a small fraction of the total volume is reduced, the photoreduction still resulted in significant, observable improvements to the electrical and thermal conductivity of the sample. This implies the photo-

reduction technique will have substantial impacts on the energy and charge transport characteristics of GA microstructures with even smaller dimensions. In terms of applications, photoreduction will allow for high precision control of direct pattern writing on few- μm thick GO films.

Dynamic Electrical Response During and After Reduction

As mentioned in section 3.1, some amount of electrical conductivity enhancement of the GA microfiber caused by the removal of oxygen functional groups via laser photoreduction is not entirely permanent. As briefly discussed before, following laser photoreduction, a proportion of the GA sample's electrical resistance is recovered over time. This is true for 8 out of the 10 laser power values tested for photoreduction. Besides the large electrical resistance regained following the end of laser irradiation at 64 mW ($+113\text{ }\Omega$), the range of resistance values

regained in the GA microfiber after laser exposure is characterized by 12–34 Ω increases.

The observed recovery of electrical resistance was explored in a two-part experiment to understand the exact nature of this process: 1) real-time monitoring of the electrical resistance evolution during continuous laser irradiation and 2) real-time monitoring of the electrical resistance recovery immediately after laser exposure. A new, unreduced GA microfiber was prepared following the same steps as described earlier and a mid-range laser power of 192 mW was used for the photo-reduction. The connected current source provided a 50 μ A current to induce a voltage difference across the suspended sample that was measured by the oscilloscope. Note the minimal amplitude current was selected to cause negligible heating in the sample. For the first part of the experiment, the laser irradiation continued until the voltage evolution reached quasi-steady state. As shown in Figure 6a, this resulted in 15 minutes of total photoreduction time. The logarithmic time scaling shows a more detailed look of the exponential decay nature of the voltage evolution during CW laser-mediated reduction as oxygen-containing functional groups are removed from the GO sheets in the microfiber and the sample undergoes laser heating.

The initial resistance before reduction measured 6054 Ω . Right before the end of laser exposure, the measured final resistance was 2198 Ω (the final data point displayed in Figure 6a). Within 90 s after blocking the sample from further laser irradiation, the microfiber resistance increased to 2996 Ω . Clearly, a significant proportion of the resistance reduction during photoreduction can be attributed to laser heating; as the temperature of the fiber increases by absorbing the incident laser energy, the electrical resistance decreases. But it should be noted that the initial, sharp resistance drop displayed in Figure 6a also originates in the photochemical removal of impurities and oxygen functional groups that impede the flow of electrons. It is the phase immediately following laser exposure that reveals the extent and nature of how energy provided by CW laser irradiation removes oxygen groups and rearranges the network of GO sheets into more graphene-like structures. Closer observation of this transient period is

necessary to understand the exact dynamics of this photo-reduction technique.

To observe the full dynamic electrical response of the transient phase post-laser exposure, a second round of photo-reduction is conducted on the same suspended sample. The laser power is increased to 320 mW to ensure further reduction of the GA microfiber. In this case, the photoreduction process is limited to only 4 s of laser exposure. After ending the laser irradiation on the sample, the voltage-time data is collected over the course of ~16 minutes to capture the immediate heat dissipation and resistance recovery stage. Upon ending the period of photoreduction, the resistance jumps from 1923 to 2624 Ω within 0.5 s. This is shown as a sharp increase in Figure 6b at $t=4$ and represents the thermal relaxation time for the GA microfiber as the laser energy quickly dissipates as heat along the length of the sample towards the two contact ends. After this rapid resistance increase defined by the negative temperature coefficient of electrical resistance for GA, this figure shows a separate and distinct increase in resistance that occurs at a significantly slower rate. Over the course of the next 15 minutes, the resistance slowly increases to a quasi-steady state value of 2.7 k Ω .

Curiously, the final measured resistance for this GA sample after the 4 s of 320 mW laser irradiation is approximately 100 Ω higher than before the short photoreduction period. This seemingly contradicts the previously observed behavior of decreasing electrical resistance of the microfibers following laser exposure. It is proposed that this 3.8% increase in electrical resistance is attributed to the already fully reduced nature of the second GA sample after the first photoreduction at 192 mW for 15 minutes.

By observing the photoreduction trend for the first sample, it is shown in Figure 3d that the microfiber undergoes an electrical resistance decrease of 7.15 k Ω after the 64, 128, and 192 mW laser irradiation tests. This represents >90% of the total resistance reduction after all laser powers were tested on the first microfiber sample. Therefore, in the case of second microfiber, it is possible that the first 15 minutes of 192 mW laser removed most of the functional groups and impurities that impeded electron transport. Thus, further laser irradiation at 320 mW for 4 s would only result in depositing laser energy

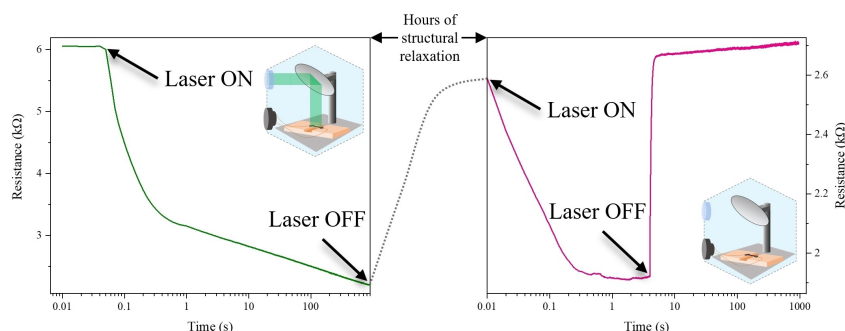


Figure 6. Real-time measurements of electrical resistance changes in the GA microfiber sample for ~15 minutes during and after photoreduction. (a) The dynamic electrical response during 192 mW photoreduction. (b) Following 4 s of 320 mW photoreduction, the electrical resistance evolution is recorded after ending laser irradiation of the sample.

into the GA sample which would facilitate thermal rearrangement of the graphene network microstructure. It is also possible that the higher laser power caused structural damage to the GA microfiber. Further experiments are required to properly calibrate the relationship between laser power, amount of photoreduction, and exposure time.

It is worth emphasizing that the immediate rise in resistance right after photoreduction can be attributed to the negative resistance temperature coefficient as the GA microfiber cools after laser heating. The following stage of slow resistance growth can be attributed to the structural changes within the porous microstructure of newly reduced GO sheets. Also, the dynamic tracking of the resistance change in Figure 6b after laser off shows that the heating by 320 mW laser induces about 36% resistance change. In Figure 6a, immediately after the laser on, the resistance change is about 87.5% under 192 mW laser heating. This suggests a large portion of this resistance change is induced by structural change rather than temperature-induced resistance change.

The interesting, dynamic electrical response of the GA microfiber captured in this transient phase reveals the impermanent nature of some of electrical conductivity enhancement induced by CW laser photoreduction. We propose that this unstable period is characterized by a quick heat dissipation stage and slow-process thermal rearrangement of the carbon lattices making up the GA microfiber. As soon as the heat dissipates from the aerogel microstructure following laser irradiation, the new rGO sheets making up the GA microfiber must find new, stable arrangements to account for the now missing oxygen groups. The dynamic behavior observed in the electrical resistance during this period shows that the rearrangement is a relatively slow and gradual process. More experimental work is needed to understand this transient phase more comprehensively. Yet, the information provided by this reported work is critical for researchers looking to expand the scope of photoreduction techniques for GO-based materials.

Conclusions

This work has reported the successful photoreduction of graphene aerogel microfibers synthesized from a GO solution. The electrical resistance and thermal diffusivity of suspended 2 mm GA samples were measured after 532 nm CW laser irradiation. This is the first known instance the electrical response of a GO-based aerogel microstructure has been recorded in real-time. The near instantaneous photochemical removal of oxygen functional groups and other impurities from the self-assembled GO sheets is quantified through tracking the electrical resistance changes during and immediately after laser exposure. Additionally, a dynamic period of instability is observed following the end of photoreduction as a non-negligible proportion of electrical resistance is recovered over time. To understand this process, a two-part experiment is designed to evaluate the in-situ electrical property changes in the GA sample during and after photoreduction. This period is marked by obvious, rapid heat dissipation effects and followed

by a proposed gradual structural rearrangement of GO sheets as they transition to more stable bonding states to account for the removed functional groups. Overall, photoreduction experiments removed most oxygen and virtually all nitrogen-containing functional groups. This resulted in decreasing the electrical resistance from 8.5 k Ω to 787 Ω . The TET method was used to track the changing thermal diffusivity which improved from 1.09 to 4.11 mm²s⁻¹. The electrical conductivity and thermal diffusivity exhibit a coherent, linear relationship characteristic of other graphene-based nanostructures. This work provides important insight into the exact mechanisms underlying photo-mediated reduction of GO-based aerogel materials.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: graphene aerogel • photoreduction • micro-fiber • thermal diffusivity • electrical resistivity

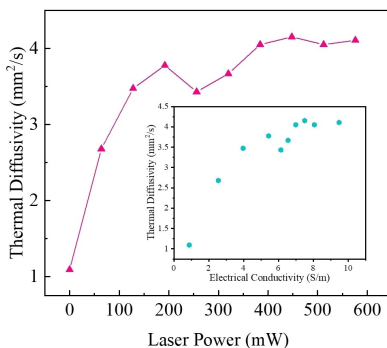
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RESEARCH ARTICLE

Real-time monitoring of the electrical and thermal behaviors of graphene aerogel microfiber during and after photoreduction reveals the dynamics of structural rearrangement of graphene oxide sheets after removal of oxygen functional groups. Photoreduction of graphene aerogel microfiber improves electrical conductivity by one order of magnitude and thermal diffusivity by more than 250 %.



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Laser Photoreduction of Graphene Aerogel Microfibers: Dynamic Electrical and Thermal Behaviors