High-Efficiency Thermoelectrics with Functionalized Graphene

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Supporting Information

ABSTRACT: Graphene superlattices made with chemical functionalization offer the possibility of tuning both the thermal and electronic properties via nanopatterning of the graphene surface. Using classical and quantum mechanical calculations, we predict that suitable chemical functionalization of graphene can introduce peaks in the density of states at the band edge that result in a large enhancement in the Seebeck coefficient, leading to an increase in the room-temperature power factor of a factor of 2 compared to pristine graphene, despite the degraded electrical conductivity. Furthermore, the presence of patterns on graphene reduces the thermal conductivity, which when taken together leads to an increase in the figure of merit for functionalized graphene by up to 2 orders of magnitude over that of pristine graphene, reaching its maximum $ZT \sim 3$ at room temperature according to our calculations. These results suggest that appropriate chemical functionalization could lead to efficient graphene-based thermoelectric materials.

KEYWORDS: graphene, chemical functionalization, transport, thermoelectrics

Recent progress in enhancing the figure of merit for thermoelectric materials has relied on a range of innovative strategies, including reduction of the dimensionality,\textsuperscript{1–3} use of complex bulk materials,\textsuperscript{4,5} or introduction of impurity states in the bulk phase.\textsuperscript{6,7} These advances, based on modifications to three-dimensional (3D) crystalline materials, have been enabled by a deep understanding of the key thermoelectric (TE) properties such as thermal and electronic transport, and the impact of structural and chemical changes on these properties, in turn providing new design strategies for high-efficiency TE materials. In contrast to the case of 3D materials, two-dimensional (2D) materials such as graphene, single-layer boron nitride, or molybdenum disulfide have received little attention regarding their potential for thermoelectric applications. Given the fact that 2D materials are “all-surface,” any modification to their environment or chemical functionalization will be expected to have enormous impact on properties, an appealing attribute when faced with such constrained optimization problems as in the case of thermoelectrics. Chemical functionalization, in particular, plays a key role for both thermal and electronic transport in 2D materials because either all or nearly all atoms in the system can be functionalized, leading to large modifications of charge carriers and phonon modes,\textsuperscript{8} this is in contrast to the 3D case, where surface chemical functionalization has a much smaller impact on transport. Although such potentially controllable transport in 2D is appealing for thermoelectric applications, a unified understanding of the key TE properties in 2D materials is needed in order to assess the potential of 2D TE and to provide design strategies for increasing the efficiency of this new class of TE materials.

Recent work has shown that the most familiar 2D carbon material, namely graphene, exhibits remarkable electronic transport properties, with a record carrier mobility of $\sim 200,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported for a suspended single layer,\textsuperscript{10} as well as a moderate Seebeck coefficient ($S$) of $\sim 80 \mu V K^{-1}$.\textsuperscript{11,12} Graphene is well known to possess an ambipolar nature, such that the sign of $S$ can be controlled by changing the gate bias instead of doping.\textsuperscript{13} Experimentally measured values of the thermoelectric figure of merit ($ZT$) for pristine graphene at room temperature are in the range of $0.1−0.01$,\textsuperscript{11,12,14,15} roughly 2 orders of magnitude lower than the most efficient 3D thermoelectric materials such as Bi$_2$Te$_3$ alloys.\textsuperscript{16} Such low $ZT$ values for graphene are to be expected due to its extremely high thermal conductivity ($\kappa$), on the order of $2000−5000 \text{ W m}^{-1} \text{ K}^{-1}$.\textsuperscript{15,17,18} As mentioned above, graphene can be modified controllably with chemical functionalization, which in turn modulates its electronic and thermal transport properties; a range of methods have been employed to fabricate graphene heterostructures, for example, hydrogen functionalization,\textsuperscript{19} introduction of in-sheet regions of hexagonal boron nitride (h-BN),\textsuperscript{20} or the attachment of polymers using patterning processes such as lithography.\textsuperscript{21} These controllable patterning techniques facilitate routes to the formation of a range of confined graphene patterns, including dots, lines, and more complex structures, within a single sheet of graphene.

Received: November 5, 2014
Revised: March 23, 2015

DOI: 10.1021/nl504257q
Nano Lett. XXXX, XXX, XXX−XXX
In this work, we consider the prospect of patterned graphene nanoroads as an efficient thermoelectric material. The patterning introduces quantum confinement in pure (unfunctionalized) graphene by reducing its dimensionality from 2D to quasi-1D, with the periodic functionalization lines forming arrays of parallel graphene regions. Confinement in the material leads to an improvement in the power factor by increasing the density of states at the Fermi level, as demonstrated in recent studies for low-dimensional thermoelectric materials. Here, ab initio electronic structure calculations and the Boltzmann transport approach are used to determine the role of such functionalization on the electrical transport properties, including the electrical conductivity ($\sigma$) and Seebeck coefficient ($S$), which combined with our computed thermal conductivities enables us to predict the full ZT in these materials. Our results show that ZT can reach values as high as 3 at room temperature, and demonstrate the potential for controllably tuning the properties of 2D materials for thermoelectric applications.

**Methodology.** Room-temperature transport calculations of patterned graphene nanoroads are carried out using electronic structure calculations and the Boltzmann transport approach. First-principles calculations are performed within the framework of density functional theory (DFT) as implemented in the plane-wave basis VASP code. The projected augmented wave pseudopotentials with the PW91 generalized gradient approximation of Perdew and Wang is used for treatment of transport properties, including the electrical conductivity ($\sigma$) and Seebeck coefficient ($S$), which combined with our computed thermal conductivities enables us to predict the full ZT in these materials. Our results show that ZT can reach values as high as 3 at room temperature, and demonstrate the potential for controllably tuning the properties of 2D materials for thermoelectric applications.

In general, the relaxation time ($\tau$) is taken to be energy-independent, and obtained by fitting experimental values for pristine bulk materials even in the cases with structural and chemical modifications. However, in principle $\tau$ is a complex function of the electron energy, temperature, and atomic structure. In this respect, using a $\tau$ value obtained from pristine graphene is not a reasonable approximation for use in patterned graphene nanoroads, where chemical modification in those samples plays an important role in opening the energy gap, which indirectly relates to the relaxation time. Because the goal of our work is to determine the quantitative effect of functionalization on charge transport, we calculate the relaxation time of functionalized graphene samples with Boltzmann transport theory for a reliable quantitative approximation. Here, we consider only the acoustic phonon scattering, and the relaxation time can be expressed as:

$$\frac{1}{\tau(\varepsilon_k)} = \frac{2\pi k_B T D_k^2}{\hbar A \rho_m v_{ph}^2} \sum_k \delta(\varepsilon_k - \varepsilon_k)$$

where $\varepsilon$ is the electronic charge, $\tau_n$ the energy-dependent relaxation time, $v_k = (1/\hbar)\nabla\varepsilon_k$ the group velocity in the nth band at $k$, $\varepsilon_k$ the energy eigenvalues obtained from DFT, $\mu$ the chemical potential, and $f(\varepsilon_k)$ the Fermi–Dirac function at a given temperature $T$. Here, we are interested in transport along the pattern direction ($y$), which is obtained from $\sigma = L_y^{(0)}$ and $S = -(1/eT)(L_y^{(0)})^{-1}L_y^{(1)}$. The converged values of $\sigma$ and $S$ are obtained using a dense k-point mesh of 121 points along the $y$ direction. All simulations are carried out at 300 K and a carrier concentration range of $10^{11}$–$10^{13}$ cm$^{-2}$.

For calculations of the thermal transport, we employ equilibrium molecular dynamics (MD) simulations as discussed in ref 9, which shows a large $\kappa$ reduction in functionalized graphene with the use of 2D periodic patterns. The MD
simulations describe well the scattering effects of functionalization on thermal transport in graphene, especially for short-wavelength phonons. However, given the current limits of system size and time scales, our simulations do not capture the contributions of long-wavelength phonons, which are important for thermal transport in graphene, resulting in lower $\kappa$ values in our simulations by an order of magnitude than measured values. In order to predict ZT, we modify our computed $\kappa$ values by adding the long-wavelength phonon contributions from the Klemens model, allowing one to obtain approximate $\kappa$ values for larger graphene samples (see Supporting Information).9

Atomic Structure. Figure 1a shows a schematic of a 2D thermoelectric device based on graphene nanoroads with armchair-type interfaces formed via partial functionalization. This type of superlattice is modeled with a repeated structure of pristine graphene (sp$^2$ network) and graphene with functionalization (sp$^3$ + sp$^3$ network) within the same sheet, where the former exhibits semimetallic behavior, and the latter shows insulating or semiconducting behavior depending on the functional groups. The electronic structure of functionalized graphene is strongly influenced by the functionalized configurations on the graphene sheet, determined by the shape and chemistry of the functional groups. For example, H-functionalization generates full functionalization (perfect sp$^3$ network) showing insulating behavior, whereas hydrocarbon chains generate partial functionalization of the graphene sheet due to the steric repulsion between the chains, exhibiting a graphene-like electronic structure with a distorted cone-shaped band. In this work, we consider two different functional groups (H and pentane C$_5$H$_{12}$, referred to as C$_5$) to investigate how chemical functionalization influences the thermoelectric properties of a patterned graphene superlattice.

H-Functionalized Graphene. We first compute the electronic structure of partially H-functionalized graphene (HG). The width (W) of the pattern in our simulations ranges from 6–23 Å and can be represented by the number of pure carbon dimers ($N_C$) along the pattern direction in the unit cell as shown in Figure 2a. Although graphene is a zero-gap semiconductor with a 2D cone-shape linear energy dispersion, all HG samples show semiconducting behavior with a finite energy gap due to confinement effects of the graphene parts of the structure. As in the case of armchair graphene-based nanoribbons, the gap can be categorized into three different families depending on $N_C$: $E_g (N_C = 3p + 2) < E_g (N_C = 3p) < E_g (N_C = 3p + 1)$, where $p$ is an integer. This hierarchy is in good agreement with previous work on the energy gaps of hydrogenated graphene superlattices and it is also found that $E_g$ decreases with $N_C$ values within each family due to decreasing confinement effects. All HG samples show a flattened energy dispersion across the pattern direction, whereas energy bands along the pattern direction ($\Gamma \rightarrow \text{Y}$) retain the dispersive nature of pristine graphene, implying quasi-1D transport in such graphene superlattices. The reduction of the charge transport dimension in all HG samples introduces a peak in the DOS near the band edge, which would be expected to enhance S according to Mahan–Sofo theory.31

The relaxation time of HG samples is calculated using eq 2 with density of states from first-principle calculations. Here, the $D_{ac}$ value of pristine graphene (16 eV)$^{32}$ is used for the HG cases, which is a reasonable approximation since charge carriers are confined within the 1D pristine graphene regions as shown in Figure 1b. Figure 2b shows our calculated $\tau$ for pristine graphene and a HG sample ($N_C = 6$) as a function of the carrier energy. For pristine graphene $\tau$ decreases with carrier energy, in good agreement with experiments that showed the room-temperature intrinsic resistivity of graphene $\sim 30 \, \Omega$ is limited only by intrinsic LA phonon scattering. Scattering becomes more severe in HG samples compared with graphene, particularly near the band edge. We also find that calculated $\tau$ values in HG samples are proportional to the width of the pattern, resulting in stronger scattering for narrower patterns, similar to the ribbon width dependence in GNR.$^{34}$

The electrical conductivity and Seebeck coefficient, are calculated as a function of carrier concentration ($n_i$), where $\sigma$ increases with $n_i$ and $S$ decreases, resulting in a maximum power factor ($S^2\sigma$) at carrier concentrations ($n_{\text{peak}}$) between $10^{12} - 10^{13}$ cm$^{-2}$, corresponding to the band edge. Our calculated $\sigma$ and $S$ values at $n_{\text{peak}}$ as a function of band gap are presented in Figures 2c and d for the range of HG samples considered. Here, we are only interested in thermoelectric properties along the pattern direction because values in the

\[ E_g = \frac{\hbar \cdot \pi}{2L} \quad \text{for} \quad L = \frac{W}{N} \]

\[ \tau = \frac{\hbar}{(2\pi)^2 m^* E_g} \]

\[ S = \frac{\hbar}{2 e m^* v_F} \]

\[ \sigma = \frac{2 e^2 n_i}{h^2} \]

\[ n_{\text{peak}} = \left(\frac{v_F}{2\pi m^*}\right)^{1/2} \]

\[ ZT = \frac{\sigma S^2}{\kappa} \]

\[ \kappa = \frac{1}{L^2} \int_0^L \frac{\partial n(x)}{\partial x} \left(\frac{\partial E}{\partial n(x)}\right) dx \]

\[ V = \frac{e}{m^*} \left(\frac{dE}{dn} \right) \]

\[ I = \frac{e}{m^*} \left(\frac{dE}{dn} \right) \]

\[ n_{\text{peak}} = \left(\frac{v_F}{2\pi m^*}\right)^{1/2} \]

\[ \text{DOS} = \frac{2 e^2 n_i}{h^2} \]

\[ S = \frac{\hbar}{2 e m^* v_F} \]

\[ \sigma = \frac{2 e^2 n_i}{h^2} \]

\[ n_{\text{peak}} = \left(\frac{v_F}{2\pi m^*}\right)^{1/2} \]

\[ ZT = \frac{\sigma S^2}{\kappa} \]

\[ \kappa = \frac{1}{L^2} \int_0^L \frac{\partial n(x)}{\partial x} \left(\frac{\partial E}{\partial n(x)}\right) dx \]

\[ V = \frac{e}{m^*} \left(\frac{dE}{dn} \right) \]

\[ I = \frac{e}{m^*} \left(\frac{dE}{dn} \right) \]

\[ n_{\text{peak}} = \left(\frac{v_F}{2\pi m^*}\right)^{1/2} \]
direction perpendicular to the pattern are negligible due to the band flattening.

As can be seen in Figure 2c, \( \sigma \) decreases with \( E_g \), implying that wider H-patterns exhibit higher \( \sigma \) because \( \tau \) increases. Clearly, the presence of the H-pattern reduces \( \sigma \) compared to pristine graphene, especially for the \( 3p \) and \( 3p + 1 \) families, due to both the reduced \( \tau \) as well as reduced group velocities. Among the three different families, samples in the \( 3p + 1 \) family show the lowest \( \sigma \), which can be explained by the lowest slope in the band dispersion as shown in the inset of Figure 2c. It is interesting to observe that \( 3p + 2 \) family samples with \( E_g < 0.1 \) eV show higher \( \sigma \) than graphene because the maximum power factor arises at a higher carrier concentration, where more carriers contribute to the transport. In contrast to \( \sigma \), most of the HG samples show larger \( S \) than pristine graphene. This can be explained by a peak in the DOS near the band edge, induced from the reduction of the charge transport dimension as shown in the inset of Figure 2d. This sharp increase in the DOS enhances \( S \) by a factor of 2 for the \( 3p \) and \( 3p + 1 \) family samples. Because \( S \) is proportional to the magnitude of the DOS peak, \( S \) is expected to increase as the pattern width decreases in going from the bulk to the nanostructured case. This is indeed what we observe for the \( 3p + 2 \) cases. However, for the \( 3p \) and \( 3p + 1 \) family, the maximum power factor occurs at higher carrier concentration for narrower pattern samples, and the decrease of \( S \) due to higher carrier concentration is large enough to compensate the increase of \( S \) due to stronger confinement effects as the pattern width decreases, resulting in nearly constant \( S \) values among samples.

These two conflicting thermoelectric properties produce a strong dependence between the power factor and band gap (Figure 2e), with a maximum value of \( S'\sigma \) at \( E_g \sim 0.15 \) eV for the HG sample with the \( N_C = 8 \) pattern (\( W = 10 \) Å). For \( E_g > 0.15 \) eV, \( S'\sigma \) decreases as \( E_g \) increases, due to the fact that the wider H-pattern generates superior charge transport in these graphene superlattices. The reduction in \( S'\sigma \) in this regime is mainly due to more severe scattering for narrower H-patterns. On the other hand, \( S'\sigma \) decreases as \( E_g \) decreases for \( E_g < 0.15 \) eV, and this behavior can be explained by the \( S^2 \) term in the power factor, which is significantly reduced with H-pattern width, due to weaker confinement effects. Thus, the HG sample with the \( N_C = 8 \) pattern exhibits the best performance for TE applications with \( S^2\sigma \sim 0.93 \) W m\(^{-1}\) K\(^{-2}\), which is about 1.6 times larger than pristine graphene. We note that this large enhancement in power factor arises from considerably enhanced \( S \) as well as a comparatively small reduction in \( \sigma \) in spite of strong scattering due to the H-pattern.

**C5-Functionalized Graphene.** We next consider the case of functionalizing graphene with pentane chains (CS), which was shown previously to further reduce \( \kappa \) in graphene superlattices beyond simple hydrogen functionalization due to a clamping effect imposed by the steric hindrance between chains (see Supporting Information). In contrast to the one-dimensional dispersion of HG cases, C5-functionalized graphene (CSG) exhibits a 2D distorted cone-shape band, resulting in an anisotropic \( \sigma \) (Figure 3a). This difference is caused by the fact that C5 patterns cannot generate confinement effects in graphene due to their inability to pack closely enough to functionalize every carbon atom (Figure 3b). As a result, the DOS of a CSG sample is similar to that of pristine graphene (Figure 1c), showing no peak at the band edge, and our computed \( S \) values are similar in all directions to

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**Figure 3.** (a) Power factor of fully functionalized CSG as a function of spatial direction. The black dashed line indicates the average value of the power factor. The background represents the energy band contour of constant energy, showing a distorted cone-shape dispersion. (b) Configuration of C5-functionalized graphene (CSG) with the structure of C5 (pentane: C\(_5\)H\(_{12}\)). C5 chains are arranged in a two-dimensional hexagonal close-packed lattice on the graphene sheet. (c) Deformation potential constant (\( D_{\alpha} \)) and corresponding power factor of CSG samples, where \( \alpha \) represents calculated values for CSG samples. CSG_all represents a CSG sample with full coverage. Power factor calculated with the Dac value of pristine graphene (16 eV) are shown for comparison. (d) Relaxation time for CSG as a function of the carrier energy.
that of pristine graphene. Among the CSG samples we considered with different pattern widths, the case of fully C5-functionalized graphene (i.e., width = 0, so no "nano-roads") exhibits the largest $S\sigma$, with an average value close to the value of pristine graphene ($0.486 \text{ W m}^{-1} \text{ K}^{-2}$). The peak in $S\sigma$ is $0.88 \text{ W m}^{-1} \text{ K}^{-2}$, which is inversely proportional to the square of temperature, even without periodic patterning on the graphene sheet, suggesting that chemical functionalization by itself offers further opportunities for graphene to become an appealing TE material without complex nanopatterning. The results suggest that chemical functionalization could be an important route to designing high-efficiency graphene-based TE materials, by allowing for independent control of charge transport and thermal transport.

In this work, we investigated the thermoelectric properties of patterned graphene nanoroads functionalized with H and C5 chains using both classical and quantum mechanical calculations. Periodically patterned sp$^3$-hybridized carbon regions on graphene were shown to introduce DOS peaks at the band edge, which lead to substantially enhanced $S$ and $S\sigma$ compared to that of pristine graphene at carrier concentrations corresponding to the band edge. These results also demonstrate that the thermal transport in such materials can be tuned by functional groups separately from the power factor, which simply depends on the pattern width. We note that unlike the case of standard, 3-dimensional TE materials, for the 2D cases considered here it is not difficult to achieve reduced $\kappa$ and enhanced $S\sigma$ simultaneously, resulting in broad tunability of thermoelectric properties for this class of materials. Finally, although fabrication of functionalized graphene with 100% H coverage or regular C5 chain ordering may be challenging, we note that incomplete H-functionalization in the patterned region has a negligible influence on ZT values of HG and (C5 + H) – G samples since charge transport in these samples is mainly determined by the condition of the pristine graphene region. Furthermore, our calculations of a fully functionalized CSG sample with random (as opposed to regular) C5 chain ordering still shows high ZT values at room temperature, as the decrease in thermal conductivity roughly tracks the decrease in the power factor, indicating that perfectly controlled ordering is not crucial for the potential use of functionalized graphene in TE applications.

**ASSOCIATED CONTENT**

1) Supporting Information

Additional simulation details on thermal conductivity calculations (molecular dynamics simulations and Klemens model), relaxation time calculations, and thermoelectric coefficient as a function of carrier concentration for pristine graphene, HG, and C5G samples. This material is available free of charge via the Internet at http://pubs.acs.org.
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**Notes**
The authors declare no competing financial interest.

**REFERENCES**


