High figure of merit in an ac driven graphene nanoribbon

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Abstract. Generally, pristine graphene nanoribbons show poor thermoelectric (TE) performance. Several proposals are available to enhance the TE performance, which however requires some highly structural modifications of the system. In the present work, we explore a new prescription where a favorable TE response can be achieved by irradiating the ribbon. The electronic conductance, thermopower and thermal conductance due to electron are found to be highly sensitive to the irradiation. We obtain significantly enhanced thermopower along with highly suppressed thermal conductance for typical sets of irradiation parameters. As a result of this higher \textit{figure of merit} is found. Therefore, we can suggest that a graphene nanoribbon can be used as an efficient energy conversion device in the presence of irradiation and hope that it will bear a significant impact in the energy market soon.

1. Introduction
Providing a sustainable supply of energy to the world’s continually increasing population has been a major challenge as fossil fuel supplies decrease and world demand increases day by day. Thermoelectric (TE) phenomena, which involve the conversion between thermal and electrical energies are expected to play a crucial role in meeting the energy crisis of the future. According to the Energy Statistics (24\(^{th}\) Issue, 2017) published by Central Statistics Office, Ministry of Statistics and Programme Implementation, Government of India, it has been reported that about two-thirds of energy was wasted as heat in India during 2015-16. Undoubtedly, it would lead to huge economic benefits to the society if highly efficient TE materials can be created and convert that waste heat into electrical energy. Therefore, in order to achieve real energy savings, we need to fabricate thermoelectric devices with very high efficiency. In addition to that, the “green” nature of conversion process (i.e., harvesting power from waste heat) and simpler maintenance of the devices due to the absence of moving mechanical parts \cite{1}, TE energy conversion has attracted wide attention to the research community both theoretically as well as experimentally.

The efficiency of a TE material can be measured by a dimensionless quantity, \textit{figure of merit} (FOM), \(ZT = GS^2 T/k\), where \(G\) is the electronic conductance, \(S\) is the Seebeck coefficient (thermopower), \(T\) is the temperature and \(k(= k_e + k_{ph})\) is the thermal conductance which includes
the electronic contribution \((k_e)\) and the phononic contribution \((k_{ph})\). Generally, materials with \(ZT > 1\) are considered as good for TE devices, but that is not enough to employ the device for large-scale energy conversion systems. \(ZT \sim 2 - 3\), is preferable [2] and experimentally that scenario is still not achieved.

In general, due to very low thermopower (few \(\mu V/K\)) metals are regarded as poor TE materials. Hence, semiconductors [3-7] were mostly explored in the early TE works. Bismuth and its alloys [6] have been studied extensively among the various semiconducting materials, and in most cases \(ZT \sim 1\) at room temperature. The highest \(ZT\) obtained so far is about 2.6 at 923K in SnSe crystals [8], while the maximum \(ZT\) at room temperature is even lower than that. Moreover, most of the compounds are toxic in nature, expensive and have limited availability. In addition to that, it is hard to obtain higher \(ZT\) in bulk materials due to the limitation of Wiedemann-Franz law [9], which states that the electrical conductance \(G\) and the thermal conductance \(K\) cannot be controlled independently. Thus, increasing \(ZT\) is still an active research field and we need to incorporate new developing strategies.

Hicks and Dresselhaus in their seminal works [10,11] have shown that the electronic and thermal conductances can be optimized independently in low-dimensional systems, where the Wiedemann-Franz law is no longer valid [12] and thus providing an opportunity to enhance \(ZT\). Consequently, the TE properties have been explored in various low-dimensional systems [13], such as, molecular junctions [14–23], quantum dots [24,25], nanowires [26,27], etc. In those explorations, higher \(ZT\) was found from experimental findings and theoretical predictions than that were reported in bulk materials. Recently, Carbon-based materials, specifically, graphene [28] has attracted much attention to the research community as a TE material due to its unique features like high flexibility, fracture toughness, high strength, and high-temperature stability. Although, the presence of zero bandgap and high thermal conductivity [29,30] makes graphene a poor TE material [31], finite width graphene sheets, the so-called graphene nanoribbons (GNRs) show band gap openings [32]. Generally, GNRs can be of two types, depending on their edge structures, namely zigzag graphene nanoribbon (ZGNR) and armchair graphene nanoribbon (AGNR). AGNRs can be either metallic or semiconducting in nature according to the width of the ribbon [33], whereas, ZGNRs are always metallic. Various strategies with more sophisticated structures have been proposed to enhance the FOM further in GNRs, where the thermal conductance can be suppressed significantly, both in the electronic and phononic parts. Such proposals are, for instances, edge disorder [34], various kinked structures [35], superlattice structures [36], introduction of edge-defects and vacancies [37], presence of adatoms [38], use of carbon isotopes [39], presence of surface roughness [40], drilling nanopores with different shapes and sizes [41-43], etc. Most of the above mentioned sophisticated GNR structures show higher \(ZT\) greater than unity.

In view of the promising aspects of GNR as a TE material, in this work, we propose a completely new method to achieve better TE performances. We irradiate the GNR with a suitable polarized light and study different TE properties. Our proposed method does not involve any sophisticated structural modification of the system, which certainly makes the present work more interesting to study and easier to implement in a suitable laboratory setup compared to the methods as stated above to get a high \(ZT\).

The work is arranged as follows. With the above brief introduction (Sec. 1), in Sec. 2 we present the quantum system and give a theoretical description for the calculation of all the thermoelectric quantities in presence of light irradiation. All the essential results are thoroughly discussed in Sec. 3, and finally, in Sec. 4 we conclude our findings.

2. Quantum System and Theoretical Formulation

Let us now describe our quantum system as shown in figure 1, which we consider here as a pristine ZGNR. The ZGNR is attached with two semi-infinite pristine graphene leads having zigzag edges. The left lead (denoted with red color) is maintained at a higher temperature than the right lead (denoted with blue color). The temperature difference between the two leads is assumed to be
infinitesimally small. The ZGNR is illuminated with an arbitrarily polarized light as shown by the red sinusoidal wave, while the leads are free of any kind of irradiation and other interactions.

We describe the quantum system under the tight-binding (TB) framework based on nearest-neighbor hopping (NNH) approximation, which is a standard prescription to study the electronic properties of a system at the nano-scale level. When a quantum system is irradiated with light, the NNH integrals become time-dependent. Following the minimal coupling scheme approach, the effect of light irradiation is included through a vector potential \( A(\tau) \). This vector potential is introduced according to Peierls substitution by a phase factor \( \frac{e}{\hbar} \int \mathbf{A} \cdot d\mathbf{l} \). For a homogeneous electric field, the vector potential can be assumed to take the form as \( A(\tau) = (A_x \sin(\omega \tau), A_y \sin(\omega \tau + \phi)) \), which denotes an arbitrarily polarized light in the \( x-y \) plane. Here \( A_x \) and \( A_y \) are the amplitudes, \( \phi \) is the phase, and \( \omega \) is the frequency of the incident light.

In presence of light irradiation, the effective hopping integral takes the form \([44-47]\),

\[
\tilde{t}_{n,m} = \frac{1}{\Omega} \int e^{i\omega(n-m)}e^{i\mathbf{A} \cdot \mathbf{d}_{nm}} t_{nm} d\tau
\]  

(1)

Where \( \mathbf{d}_{nm} \) is the vector joining the nearest-neighbor sites \( n \) and \( m \) and \( \Omega \) is the time period. The term \( t_{nm} \) represents the NNH strength in the absence of irradiation and is assumed to be uniform, that is, \( t_{nm} = t \). Then, with this modified hopping integral, the TB Hamiltonian becomes,

\[
H = \epsilon_n \sum_n c_n^\dagger c_n + \sum_{\langle nm \rangle} \tilde{t}_{n,m} c_n^\dagger c_m + h.c.
\]  

(2)

Here \( \epsilon_n \) is the on-site potential of an electron at site \( n \), and \( c_n^\dagger (c_n) \) is the creation (annihilation) operator of electron at site \( n \).
Now, we evaluate the thermoelectric quantities $G$, $S$, and $k_e$ using Landauer prescription as \[ G = \frac{2e^2}{h} L_0 \] \[ S = -\frac{1}{eT L_0} \] \[ k_e = \frac{2}{\hbar T} \left( L_2 - \frac{L_1^2}{L_0} \right) \]

(3a) \hspace{1cm} (3b) \hspace{1cm} (3c)

Where the Landauer integrals $L_n$ are defined as,

\[ L_n = -\int dE T(E)(E - E_F) \frac{\partial f}{\partial E} \]

(4)

Here $E_F$ is the equilibrium Fermi energy and $f(E)$ represents the Fermi-Dirac distribution function. The important factor in the above equation is the two-terminal transmission probability, $T(E)$, which we compute using KWANT [50].

Once the thermoelectric quantities are determined following the above equations, the figure of merit ($ZT$) is obtained from the relation

\[ ZT = \frac{GS^2T}{k_e} = \frac{1}{L_0L_2 - \frac{L_1^2}{L_0}} \]

(5)

Here the phononic contribution to the thermal conductance is ignored due to the small size of the system. However, for the precise measurement of $ZT$, one should consider the phonon thermal conductance $k_{ph}$.

3. Numerical Results and Discussions

Before we start, let us first describe the different parameters used in the present work. Throughout the calculations, we set the isotropic hopping term in the absence of light as $t = 2.7$ eV. All the energies are measured in the unit of $t$. We fix the system dimension with length $L \sim 9.8$ nm and width $W \sim 8.4$ nm. The widths of the right and left leads are chosen as same as that of the central scattering region, which is 8.4 nm. Throughout the analysis, we restrict ourselves in the high-frequency limit where $\hbar \omega \gg 6t$. This is a very good approximation, since as all the essential physics are captured in this limiting condition. Unless stated otherwise, all the TE quantities are calculated at room temperature, $T = 300$ K. We refer the irradiation free ZGNR as pristine ZGNR in the present work.

Figure 2: (Color online). Characteristic features of the TE quantities both in the absence and presence of light irradiation. (a) Electronic conductance $G$, (b) thermopower $S$, and (c) thermal conductance due to electrons $k_e$ as a function of the Fermi energy. The results for the pristine ZGNR are denoted with black color and those in the presence of light are denoted with red color.
Figure 2 shows the behaviour of different TE quantities as a function of Fermi energy at room temperature. The results corresponding to the presence of light are shown by the red color, while that corresponding to the pristine ZGNR are also included for comparison and denoted with black color. The light parameters are considered here as \( A_x = A_y = 2.5 \) and \( \phi = \pi/8 \), which represents an elliptically polarized light. The electronic conductance decreases significantly in the presence of light than that corresponding to the irradiation free case (figure 2(a)). The conductance \( G \) approaches close to zero near \( E_F = 0 \). However, a close inspection reveals that the electronic conductance does not vanish near zero of the Fermi energy, but attains a very low value, which is almost one order of magnitude less than that corresponding to the irradiation free case (see inset of figure 2(a)). This significant suppression of the electronic conductance is solely due to the modified hopping term in the presence of light. However, such low values of \( G \) is not a favorable response for an efficient TE device. On the other hand, the maximum thermopower increases almost by a factor of 3 in the presence of light than the irradiation free case (figure 2(b)). This increased \( S \) can further enhance the FOM at least one order in magnitude since \( \Delta T \propto S^2 \). Moreover, the Seebeck coefficient is antisymmetric about \( E_F = 0 \) due to the electron-hole symmetry of the system. The behavior of the thermal conductance due to electrons \( k_e \) as a function of the Fermi energy is shown in figure 2(c), where we observe that \( k_e \) is significantly reduced near the zero of the Fermi energy in the presence of light than the irradiation free case. In the inset of figure 2(c), we observe that \( k_e \) decreases to almost about \( \sim 20 \) pW/K, which is much lower than that corresponding to the irradiation free case \( (\sim 1 \) nW/K). This higher value of \( k_e \) in pristine GNR qualitatively agrees well with the existing results as discussed by Zheng et al. [51]. Since the irradiation effect reduces the thermal conductance due to electrons significantly, it is expected that the phononic part will also get suppressed accordingly. This decreased nature of \( k_e \) is certainly a favorable response for an efficient TE device, since \( \Delta T \propto 1/k_e \). Similar to the behaviour of the electronic conductance, \( k_e \) is also symmetric about \( E_F = 0 \) due to the electron-hole symmetry of the system.

![Figure 3](color online). \((\partial I/\partial E)(E-E_p)T(E)\) as a function of energy \( E \) at the Fermi energy (a) \( E_F = 0.1 \) and (b) \( E_F = 1.5 \). The red dotted line denotes the position of the Fermi energy.

Now, the significant reduction of \( G \) and \( k_e \) in presence of light is due to the modified hopping integral as given in equation (1). This suppression of \( G \) on the other hand enhances the thermopower since the thermal integral \( L_0 \) (associated in the expression of \( G \)) comes into the denominator of the expression of \( S \) as given in equation (3b). However, this fact is not the only reason for the enhancement of \( S \). There is another reason for that and is explained as follows. As given in equation (3b) and the corresponding expression for the thermal integral \( L_1 \) (equation (4)), the transmission spectrum is weighted by two terms, namely, \( \frac{\partial f}{\partial E} \) and \( (E-E_p) \). The derivative term \( \frac{\partial f}{\partial E} \) gives the broadening effect and is antisymmetric about \( E_F \). Thus, if \( T(E) \) is symmetric about \( E_F \), then \( S \) will definitely be zero, irrespective of the value of \( G \). To achieve higher thermopower, \( T(E) \) should be asymmetric, which makes the thermal integral \( L_1 \) non-zero. This whole mathematical argument can also be understood from the graphical representation as given in figure 3. Here we show the variation...
of the integrand $\mathcal{T}(E)(E - E_F)\frac{\partial f}{\partial E}$ (as given in equation (4)) as a function of energy $E$, at two different chemical potential, one at $E = 0.1$ (the maximum $ZT$ occurs near this energy) and the other at $E = 1.5$ (at this energy, $ZT$ is vanishingly small, not shown here). In figure 3(a), the integrand is highly asymmetric around $E_F$ and the area under the curve is much more than that at the other chemical potential. The larger area means higher thermopower and thus higher $ZT$. On the other hand, the curve is smooth and almost antisymmetric at $E_F = 1.5$. As a result of this, the area under the curve is almost zero. Consequently, we get vanishingly small $S$ and thus $ZT$.

Finally, in figure 5(a) we show the behavior of the FOM as a function of Fermi energy in the presence of light as denoted with the red color. The irradiation free case is also included for comparison which is denoted with black color. For the pristine ZGNR, the maximum $ZT$ is about $\sim 0.24$. However, this low value of $ZT$ is relatively large compared to the reported values ($\leq 0.1$) [52], since only the electronic contribution to the thermal conductance is considered. In the presence of light, the FOM is significantly enhanced which is mainly due to the combined effect of $S$, $G$, and $k_e$ as discussed in figure 2. The maximum FOM is about $ZT \sim 3.3$, observed near the zero of the Fermi energy. We also study the temperature variation of FOM in figure 5(b), where the maximum FOM, namely $ZT_{\text{max}}$ (maximum of $ZT$ is taken by scanning over the full energy window) is plotted as a function of temperature $T$ in the presence of light. An interesting feature is observed in figure 5(b). $ZT$ decreases uniformly and monotonically with temperature, whereas, in pristine GNR this behavior is completely opposite, that is $ZT$ increases with temperature (not shown here) [20,43]. Generally, it is expected that $ZT$ will increase with temperature, since $T$ comes in the numerator of the expression of $ZT$ (equation (5)). However, a rigorous inspection reveals that $S$ decreases and $k_e$ increases significantly with temperature in the presence of light. Consequently, $ZT$ shows a decreasing behavior with temperature. Such an anomalous feature is also reported in several other materials, such as Al-doped Bi$_{0.4}$Sb$_{1.4}$Te$_3$ [53], $p$-type Bi$_{0.4}$Sb$_{1.4}$Te$_3$ [54], $n$-type Bismuth Telluride [55], etc. Though $ZT$ decreases with temperature, the overall $ZT$ is still much greater than unity even up to $T \sim 400$ K and hence we can emphasize that our proposed device can be used as an efficient TE material over a wide range of temperatures.

![Figure 4](image_url)  
Figure 4: (Color online). (a) $ZT$ as a function of $E_F$ both in the absence (black curve) and presence of light irradiation (red curve). (b) $ZT_{\text{max}}$ as a function of temperature $T$ in the presence of light.

So far, the phonon thermal conductance was not included in the calculation of the FOM which is however required for precise measurement. The reported results suggest a wide variation of $K_{ph}$, within the range of 5-50 pW/K [56-59]. As our system size is reasonably small, we can safely assume the phonon thermal conductance as 20 pW/K. With this assumed value of $K_{ph}$, the maximum FOM for our system in the presence of light comes out to be $ZT \sim 1.5$. This value is still large and greater than unity. Therefore, we strongly believe that the present analysis can be utilized for an efficient energy conversion device at nano-scale level.

4. Conclusions
To conclude, in the present work, we have given a new prescription to enhance the TE performance considering ZGNR by irradiating it. To the best of our knowledge, this method is completely new and has not been discussed anywhere in the literature. The quantum system is described within a tight-binding framework, and the irradiation effect has been incorporated following the standard Floquet-Bloch ansatz in the minimal coupling scheme. We have also included the TE results for the pristine ZGNR for comparison. The essential findings of the present analysis are pointed out as follows.

- The thermopower gets enhanced significantly in the presence of light irradiation, which is about one order of magnitude larger than that of pristine ZGNR.
- The electronic thermal conductance is reduced about two orders of magnitude near the zero of the Fermi energy in the presence of light, while it is about ~ 1 nW/K for the pristine ZGNR.
- The maximum FOM is about $ZT \sim 3.3$ for the irradiated ZGNR, which is much higher than unity and thus shows a favorable response as an efficient TE device.
- Instead of having the decaying behaviour of FOM with temperature, favorable TE response persists over a wide range of temperatures.
- Even though we include the phononic contribution to the thermal conductance, the FOM is still large and greater than unity.

Finally, since incorporating the irradiation effect does not require any additional sophisticated structural modification, we believe that our proposed method can be examined in a suitable laboratory setup.

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