Tuning the thermoelectric efficiency of a polyaniline sheet using strain engineering

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Abstract
Two-dimensional polyaniline monolayers (C₃N) have been recently synthesized as indirect semiconductors with high electron mobility. We investigate the electrical and thermal properties of a C₃N sheet using a combination of density functional theory and the Green function formalism. Tensile strain along a zigzag direction can drive the transition from an indirect to a direct semiconductor, whereas the sheet transitions from a semiconductor to a metal under compressive strain. The thermoelectric efficiency of an unstrained C₃N sheet is higher in p-doping, and its maximum value is obtained when the transport is along the zigzag direction. A reduction in the figure of merit is found upon applying strain, independent of its direction. To overcome this reduction, we show that when the electrical transport and strain are perpendicular to each other, the thermoelectric efficiency of the C₃N sheet can be significantly increased, depending on the type of strain (tensile or compression). The results support the potential application of C₃N sheets in the thermoelectrics and optoelectronics industries through using strain engineering.

Supplementary material for this article is available online

Keywords: polyaniline sheet, density functional theory, thermopower, figure of merit

1. Introduction
The discovery of graphene in 2004 [1] opened new doors for research in solid state physics and materials science. The unique properties of graphene, such as its high electrical and thermal conductivity [1, 2], ballistic transport [3], and high electron mobility [4], place it among the most fascinating advanced materials. The integer and half-integer quantum Hall effects [5, 6], and the topological insulator properties observed in graphene revealed its great potential. One of the most important challenges in using graphene in electronics is the absence of the band gap, making graphene unsuitable for field effect transistors. Silicene and germanene as counterparts to graphene were theoretically predicted and experimentally synthesized [7, 8]. More types of single element monolayers have been synthesized in recent years, possessing individual properties. Borophene, a monolayer of boron atoms, is a metal with different allotropes [9]. Antimonene is an indirect semiconductor, the band gap of which can be tuned with strain engineering [10]. The story of two-dimensional (2D) materials entered a new era after the discovery of transition metal dichalcogenide monolayers (TMDs). Unlike graphene, they cover a wide spectrum of band gaps and can be used in light emitting diodes and the optoelectronics industry.

In 2016, Mahmood and co-workers prepared a 2D polyaniline sheet via the direct pyrolysis of hexaaminobenzene trihydrochloride single crystals in the solid state [11]. The synthesized structure has an empirical formula of C₃N and a hexagonal lattice composed of six carbon and two nitrogen atoms. Unlike other graphical carbon nitrides, the prepared...
sheet is hole-free. Yang et al [12] showed that the C\textsubscript{3}N sheet is an indirect semiconductor with a band gap of 0.39 eV and can be changed to a magnetic semiconductor by partial absorption of hydrogen atoms. The mechanical and electrical properties of C\textsubscript{3}N sheets has been studied theoretically [13–17]. In addition, the suitability of the sheet for application in lithium-ion batteries has attracted some attention [18, 19]. We demonstrated that C\textsubscript{3}N nanoribbons show a transition from semiconductor to half-metal under an external electric field and a transition from magnetic metal to semiconductor through passivation of the edge atoms [20]. Furthermore, it is shown that a fully hydrogenated C\textsubscript{3}N sheet is an insulator with a band gap of 5 eV [21]. Due to its similarity to graphene and having a band gap, the C\textsubscript{3}N sheet is a suitable candidate for next-generation electronic devices.

Reducing thermal energy loss in devices is an important challenge in science and industry. Good thermoelectric materials can economize energy usage and increase efficiency. The thermoelectric efficiency of a material is measured by a dimensionless quantity, the figure of merit, ZT, given by:

$$ZT = \frac{S^2GT}{\kappa_e + \kappa_{ph}},$$

where $S$ is the thermopower, $G$ is the electrical conductance, and $T$ denotes the operating temperature. $\kappa_{ph}(\kappa_e)$ is the lattice (electron) thermal conductance. A lot of research has been performed on the thermoelectric properties of 2D materials [22–27]. The thermal conductivity of monolayer band bilayer C\textsubscript{3}N sheets has attracted a lot of attention in recent years [28–33]. Mortazavi investigated the thermal conductivity of a C\textsubscript{3}N sheet with a combination of the density functional theory (DFT) method and molecular dynamics simulations [28]. He and co-workers showed how one can tune the thermal conductivity of the sheet by adding or removing carbon atoms [29]. Hong et al computed the thermal conductivity of monolayer and bilayer C\textsubscript{3}N sheets using classical molecular dynamics [30]. Kumar et al showed that the thermal conductivity of the C\textsubscript{3}N sheet is ultralow in comparison to the case of graphene [31].

In this study, we investigate the thermoelectric properties of a C\textsubscript{3}N sheet in a linear response regime using a combination of DFT and the Green function formalism. It is shown that the thermal conductivity of the C\textsubscript{3}N sheet is one order lower than for graphene, so it is suitable for application in thermoelectric devices. The thermopower, electrical conductance, lattice thermal conductance, and figure of merit are analyzed as a function of strain. Strain can be used as an important tool to tune the band gap of the sheet. We show how the thermoelectric efficiency of the sheet can be affected by tensile and compressive strains. In addition, the results reveal that the thermoelectric efficiency is strongly dependent on the transport and strain directions, such that there is a noticeable increase in ZT when the strain and transport directions are perpendicular to each other. Our analysis demonstrates that the strain direction, type of strain (tensile or compressive), and transport direction (along the zigzag (ZZ) or armchair (AC) direction) can significantly modulate the thermoelectric performance of a C\textsubscript{3}N sheet. The article is organized as follows: the simulation details and theoretical background are presented in the next section; section 3 is devoted to the electrical and thermoelectric properties of the C\textsubscript{3}N sheet under strain; and a brief summary is provided at the end of the article.

2. Computational method

Electronic calculations are performed using DFT implemented in the SIESTA package [34]. The norm-conserving Troullier–Martins pseudopotential [35] is used to describe the core electrons and the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) [36] is employed as the exchange-correlation functional. The cut-off energy is 100 H and 50 × 50 × 1 k-point sampling is used to mesh the Brillouin zone of a C\textsubscript{3}N sheet. A double-zeta single polarized basis set is used to describe the valance electrons. With respect to the fact that the GGA approximation underestimates the band gap of semiconductors, the Heyd–Scuseria–Ernzerhof (HSE) hybrid exchange-correlation functional [37] is also used to measure the band gap of samples. All considered structures are optimized so that the net force on each atom is less than.

To investigate the mechanical properties of the C\textsubscript{3}N sheet, a rectangular supercell composed of 16 atoms is considered. For each strain, the lattice constant perpendicular to the strain direction and the position of atoms is optimized so that the net force on each atom and the stress of the lattice are less than 0.001 eV\textpercm and 0.001 GPa, respectively. The Brillouin zone of the supercell is meshed by a 40 × 60 × 1 k-point sampling. The energy dependent electronic transmission of the sheet for each strain is obtained by counting the electronic bands crossing each energy. This method corresponds to obtaining the transmission coefficient from the nonequilibrium Green function formalism when the structure is perfect and the electrodes and scattering region are the same as in this study.

To compute the phonon band structure and phonon transmission coefficient, the empirical Tersoff potential [38] parametrized by Matsunga et al [39] is employed. A comparison between the phonon band structure obtained from the DFT method and the classical approach (figure S1) shows that the Tersoff potential can produce a phonon band structure with suitable quality. To compute the phonon transmission coefficient, we use the nonequilibrium Green function formalism and define a central region with a length of 4 nm coupled to two electrodes. The dynamical matrix is obtained from the empirical Tersoff potential and the retarded Green function is given as:

$$G_{ph}(\omega) = [\omega^2 I - K_e - \Sigma_{ph,L}(\omega) - \Sigma_{ph,R}(\omega)]^{-1},$$

where $K_e$ is the mass-weighted force constant of the central region. $\Sigma_{ph,L(R)}(\omega)$ denotes the self-energy due to coupling between the central region and left (right) electrode.

The thermoelectric properties of the sheet are investigated in the linear response regime and using the Landau formula. Electrical and thermal currents are given as follows:

$$I_E = \frac{2e}{h} \int dE T(E) [f_L(E) - f_R(E)],$$

where\dots
where $T_e(E)$ is the electron transmission coefficient and $f_{L(R)}(E)$ is the Fermi distribution function of the left (right) electrode. By expanding the Fermi distribution function in terms of potential and temperature up to first order, one can obtain thermoelectric coefficients in the linear response regime. Electrical conductance, thermopower, and electrical thermal conductance are given as:

$$G = e^2L_0,$$

(5)

$$S = \frac{\Delta V}{\Delta T}|_{T=0} = \frac{L_1}{eTL_0},$$

(6)

$$\kappa_e = \frac{1}{T} \left( L_2 - \frac{L_1^2}{L_0} \right),$$

(7)

where

$$L_n = \frac{2}{\hbar} \int dE(E-E_f)^n T_e(E) \left( \frac{\partial f}{\partial E} \right).$$

(8)

the Landau formula for phonons is:

$$I_{ph} = \int_0^\infty d\omega \frac{\hbar \omega}{2\pi} T_{ph}(\omega) |n(\omega,T_L) - n_B(\omega,T_R)|,$$

(9)

and the phonon thermal conductance in the linear response regime is given as:

$$\kappa_{ph} = \int_0^\infty d\omega \frac{(\hbar \omega)^2}{2\pi \hbar T} T_{ph}(\omega) \frac{\exp\left(\frac{\hbar \omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1\right)^2}. $$

(10)

Finally, the thermoelectric efficiency of the structure is computed as:

$$ZT = \frac{S^2GT}{\kappa_{ph} + \kappa_e}. $$

(11)

3. Results

3.1. Electronic properties

Figure 1(a) shows the band structure of a C$_3$N monolayer based on both the GGA and HSE functionals. The C$_3$N sheet is a semiconductor, and the valance band maximum (VBM) is located at the $M$ high symmetry point and the conduction band minimum (CBM) is located at the $\Gamma$ point. The energy band gap, $E_g$, is equal to 0.39 eV based on GGA calculation. It is well-known that the GGA underestimates the band gap. The HSE-based band structure predicts a higher band gap of 1.06 eV. Our results are consistent with previous experimental and theoretical reports [12, 13]. The VBM is located near the Fermi level while the CBM is far from it, so the C$_3$N sheet can be considered as a p-type indirect semiconductor. There is a Dirac point at the energy of ~2.3 eV in the $K$ high symmetry point of the Brillouin zone. The position of the Dirac cone is the same as the graphene sheet, but it is located in the negative energy due to the existence of nitrogen atoms with five valance electrons in the structure. The existence of the Dirac cone was confirmed by the experiment of Mahmood et al [11]. Unlike the electronic band gap, the position and slope of the Dirac cone are independent of pseudopotentials. The velocity of Dirac fermions is nearly isotropic and equal to 7.6 × 10$^5$ m s$^{-1}$, comparable to that in the graphene sheet. The electron effective mass is equal to 0.76$m_e$ in the $\Gamma$→$K$ direction and 0.56$m_e$ in the $\Gamma$→$M$ direction. For the hole effective mass, it is 0.33$m_e$ in the $M$→$K$ direction and 0.96$m_e$ in the $M$→$\Gamma$ direction. Thus, the hole mobility is an anisotropic quantity and is dependent on direction, leading to interesting behavior in the charge transport. Analyzing the electron density of states (DOS) reveals that the valance and conduction band edges are composed of the hybridization of p-orbitals of carbon and nitrogen atoms. There is an anisotropy in the contribution of atoms in the VBM and CBM, suchthat the VBM is composed of an equal contribution of nitrogen and carbon p-orbitals. In contrast, the CBM belongs to the p-orbitals of carbon atoms, and there is no contribution from nitrogen atoms. The Dirac point also appears due to hybridization of the p-orbitals of carbon and nitrogen atoms, but with different weights. The Bloch states plotted in figures 1(c) and (d) show that the VBM is arising from the $\pi$-hybridization of carbon and nitrogen orbitals, whereas the electronic wave function is distributed on just the carbon atoms in the CBM, as was predicted by the DOS.
The dynamical stability of the structures is evaluated using phonon band dispersion. Figure S1 (available online at stacks.iop.org/JPhysD/53/255302/mmedia) shows the phonon band structure of the C$_3$N monolayer. The sheet is dynamically stable because there is no imaginary phonon mode in the band structure. The results prepared using the classical approach based on Tersoff parameters is also plotted for comparison with DFT-based results. There is a flexural mode with quadratic dispersion around the $\Gamma$ point and two acoustic modes with linear dispersion at that point. Some active Raman modes are observed at energies higher than 45 meV. The phonon modes cross each other at the $K$ point, which is a property of the hexagonal lattice. The results obtained from the two different methods are the same for energies less than 100 meV and some deviation is observed at higher energies. However, the qualitative behavior is the same and, as a consequence, we have used the classical method to compute the phonon transmission spectrum in the following.

2D materials are grown on a substrate. The difference between the lattice parameter of the sheet and the substrate can induce some compressive or tensile strain in the sheet, which results in changing electronic properties of the structure. Here, we investigate the electronic and thermal properties of the C$_3$N sheet under compressive and tensile uniaxial strain in the range of $-10\% < \epsilon < +10\%$. Previous reports showed that the sheet is stable in the considered strain range [13, 28].

Our analysis reveals that there is no imaginary phonon mode in the phonon dispersion for tensile strain as large as 10%, as shown in figure S9. Uniaxial strain is applied along the $x$-direction, ZZ, and the $y$-direction, AC, as shown in figure 2(a). For this purpose, we consider a supercell composed of 16 atoms with orthorhombic shape. The variation of the band gap versus strain is plotted in figure 2(b). The electronic response of the C$_3$N sheet to applied strain is very interesting and strange. First, we analyze its response to strain along the ZZ direction. The results obtained from both the GGA and HSE functionals show that the band gap variation is significantly dependent on the kind of strain and is more drastic for compressive strain. We observe a phase transition from semiconductor to metal for compressive strain higher than $\geq 8\%$.

We fitted the data with a linear function with a standard error smaller than 3% and found that the slope of variation is three times higher in the compressive strain. The band structure of the sheet under $\epsilon = -10\%$ and $+10\%$ is plotted in figure 3. A phase transition from an indirect semiconductor to a direct one is observed upon applying tensile strain, showing the potential of C$_3$N for optoelectronic applications and LED devices using strain engineering. Also, the range of $E_g$ obtained from HSE calculations shows that the C$_3$N sheet can be used in solar cell devices due to the closeness of the obtained $E_g$ to the silicane one. The HSE-based data demonstrate that the band gap decreases by 44% for $\epsilon = -10\%$, while the reduction is about 18% when $\epsilon = +10\%$. The anisotropy can be attributed to the change of the lattice constant perpendicular to the strain direction. For $\epsilon = +10\%$, the lattice constant is reduced by 0.1, whereas an increase of 0.2 is observed when $\epsilon = -10\%$. Variations of the lattice constant and bond length are more pronounced under compressive strain, leading to more reduction of the band gap in that strain. The change of bond length with and without applying strain is presented in table. S1.

Strain along the AC direction produces different electronic properties to those along the ZZ direction due to the different...
arrangement of atoms in two directions. We find that the compressive strain induces a transition from an indirect semiconductor to a direct one. In addition, a transition from semiconductor to metal is observed for compressive strain higher than 4%. To examine the validity of the phase transition, we calculate the band structure using the HSE functional. The results obtained from the HSE calculations do not support the transition from semiconductor to metal, but a change of band gap from indirect to direct is supported. Also, variation of band gap versus compressive strain is more noticeable for the AC direction. On the other hand, variation of the band gap for tensile strain along the AC direction is smoother than in the ZZ direction. Unlike the ZZ direction, no transition from an indirect to direct semiconductor is observed for tensile strain. The HSE calculations support the observation. The band structure of the C$_3$N sheet under uniaxial strain along the AC direction is plotted in figure 3.

3.2. Thermal properties

The thermopower of the pristine C$_3$N sheet is plotted in figure 4(a). Thermopower is completely isotropic, such that its behavior is independent of the electron transport direction. A slight difference in its maximum value on two sides of the charge neutral point is observed, such that $S_{\text{max}}$ is slightly higher in p-doping ($\mu < 0$) than n-doping ($\mu > 0$). The maximum of the thermopower is about 0.5 mV K$^{-1}$. Unlike the thermopower, the power factor (PF, $S^2G$) is an anisotropic function and is dependent on the electron transport direction. It is clear from figure 4(b) that its value is higher in the ZZ direction. The peaks of PF correspond to the band edges where the thermopower has a high magnitude. A higher value of PF in the ZZ direction is directly related to the higher value of the electrodevice are about transmission coefficient in that direction. $T_{el}$ in the ZZ direction is twice that in the AC direction, as shown in figure 4(c). One reason could be related to the higher width of the unit cell used in the ZZ direction. However, the main reason for the difference comes from the different arrangement of atoms along the transport direction. The phonon transmission spectrum is also direction dependent so, in most ranges of energy, its value is higher in the ZZ direction than the AC direction. The maximum value of $T_{ph}$ calculated in this research is three times greater than the value reported for phosphorene, arsenene, and SnS monolayers [26], showing stronger atomic bonds in the C$_3$N sheet. Thus, it is concluded that C$_3$N is a very good thermal conductor, like its counterpart graphene.

The comparison of the thermopower and PF of the C$_3$N sheet and those of other 2D materials is important and illustrative. The maximum of thermopower for the synthesized graphene sheet is about 100 $\mu$V K$^{-1}$ [40], which is one order lower than for the C$_3$N sheet. The thermopower of the supported graphene is strongly dependent on the technique used to prepare the sheet. The thermopower of the monolayer graphene grown using the chemical vapor deposition (CVD) technique on a Si/SiO$_2$ substrate is about 10 $\mu$V K$^{-1}$ due to the presence of defects on the sheet [41]. On the other hand, exfoliated graphene on a SiO$_2$/Si substrate shows a thermopower of 100 $\mu$V K$^{-1}$ due to the purity of the structure [42]. The thermopower of a suspended pristine graphene sheet was investigated theoretically in [43] using a combination of DFT and the Boltzmann transport equation. The reported value is about 30 $\mu$V K$^{-1}$, which is 20 times lower than thermopower of the C$_3$N sheet. Yan et al. investigated the thermopower of a silicene sheet using a four-band second-nearest-neighbor Hamiltonian and reported the maximum value of thermopower as 80 $\mu$V K$^{-1}$ [44], which is six times lower than that of the C$_3$N sheet.

Very recently, Zare studied the thermopower of a borophene sheet using an exact solution of the Boltzmann transport equation within the linear-response theory, and the maximum value of the thermopower was about 250 $\mu$V K$^{-1}$ [45]. The thermopower of C$_3$N is slightly lower than the values reported for arsenene and antimonene [26, 27] and higher than for MoS$_2$ [46]. The maximum value of PF obtained for C$_3$N is equal to the values reported for phosphorene ($6 \times 10^{-13}$ W K$^{-2}$) and lower than for arsenene [26]. Another difference between the PF of C$_3$N and other 2D materials is the existence of the maximum of PF being close to the Fermi level attributed to the low band gap of the sheet.

TMD monolayers are new 2D materials which have attracted a lot of attention in recent years because of their structural diversity. They are promising candidates for thermoelectric materials due to their large band gap and low thermal conductivity. Pu et al. measured the thermoelectric power of WSe$_2$ grown using the CVD technique by means of an electrolyte gating method [47]. The maximum of thermopower and PF of the prepared device are about 400 $\mu$V K$^{-1}$ and 3.65 $\times$ 10$^{-13}$ W K$^{-2}$, respectively. To convert PF from W mK$^{-2}$ to W K$^{-2}$, the length, thickness, and width of the device are considered as 400 $\mu$m, 7.3, and 668 $\mu$m, respectively [48]. Although the obtained thermopower is nearly equal to that of the C$_3$N sheet, the PF of the latter is much higher than for WSe$_2$ owing to the higher electrical conductivity of the C$_3$N sheet.

Figure 5 shows the phonon and electron thermal conductance and figure of merit as a function of chemical potential corresponding to n- or p-type doping. At low temperatures, $T < 200$ K, phonon thermal conductance is isotropic and an increase of temperature induces some anisotropy. The phonon transmission depicted in figure 4(d) is...
Figure 5. (a), (b) Phonon and electron thermal conductance as a function of temperature. $\kappa_e$ is computed at 200 K (400 K) and shown by the thick (thin) line. (c), (d) Color show color maps of the figure of merit as a function of temperature and chemical potential for transport along the ZZ and AC directions, respectively.

Figure 6. PF of the sheet versus chemical potential for (a) tensile and (b) compressive strain along the ZZ direction.

...a direction-independent quantity at low energies, while it becomes direction-dependent at high energies. $\kappa_{ph}$ is greater in the ZZ direction at high temperatures. The same results were reported in [28, 30], obtained from molecular dynamic simulations. $T_{ph}$ is independent of direction for $E > 0.05$ eV, see figure 4(d), and after that, $T_{ph}$ of the ZZ direction is slightly higher than for the AC direction, so $\kappa_{ph}$ for ZZ is greater than for AC at high temperatures. The linear increase of $\kappa_{ph}$ at high temperatures is attributed to high energy phonon modes and is a common phenomenon for ballistic phonon transport. Indeed, at high temperatures optical phonon modes contribute to thermal transport. Because the Debye temperature of C$_3$N is much higher than for arsenene or antimonene, saturation of $\kappa_{ph}$ is not observed in the C$_3$N monolayer, unlike for arsenene or antimonene [26, 50].

The scaled thermal conductance is introduced as $\kappa_{ph}/S$, where $S = W \times D$ is the cross-sectional area, and $W$ and $D$ are width and thickness, respectively. It is worth noting that the thickness of the sheet is chosen as 3.3 [30]. The scaled thermal conductance of the C$_3$N sheet is about 1.90 $\text{W m}^{-1}\text{K}^{-1}$ at room temperature which is slightly higher than that of MoS$_2$, 1.2 $\text{W m}^{-1}\text{K}^{-1}$ [51], and phosphorene, 1.08 $\text{W m}^{-1}\text{K}^{-1}$ along the ZZ direction and 0.76 $\text{W m}^{-1}\text{K}^{-1}$ along the AC direction [52]. However, the obtained value is significantly lower than that of graphene nanoribbons, 4.1 $\text{W m}^{-1}\text{K}^{-1}$ [53]. In addition, it is lower than the value reported for hydrogen boride, 4.0 $\text{W m}^{-1}\text{K}^{-1}$ [54], obtained using the same formalism. We computed the thermal conductance of the suspended sheet. The substrate reduces the thermal conductivity of the sheet significantly due to the scattering of phonons or substrate-induced defects. For example, the suspended graphene sheet shows a thermal conductivity of 4000 W m K$^{-1}$ [55, 56], while it is reduced to 600 W m K$^{-1}$ on the SiO$_2$ substrate [57].

Electron thermal conductance exhibits a greater direction-dependent property than phonon thermal conductance because of the existence of more anisotropy in the electron transmission coefficient. Like $\kappa_{ph}$, $\kappa_e$ calculated in the ZZ direction is higher than in the direction. An increase of temperature increases $\kappa_e$, which was predictable. $\kappa_e$ in the AC direction at 400 K is equal to that for the ZZ direction at 200 K. The figure of merit shows two main peaks, one in p-type and the other in n-type doping. The VBM and CBM have a nearly equal distance from the Fermi level in the GGA calculation so the position of the $ZT$ peaks is symmetric relative to the Fermi level. An increase of temperature widens the $ZT$ peaks. It is observed that p-type doping can produce higher thermoelectric efficiency than n-type doping. In addition, $ZT$ is higher in the ZZ direction so that $ZT_{max}(ZZ) = 1.49$. Thermopower and electrical conductance increase more in the ZZ direction than the AC direction and also the rate of increase is higher than the increase of thermal conductance, giving rise to the increase of $ZT$. The maximum of $ZT$ obtained for a pristine C$_3$N monolayer is lower than for phosphorene, arsenene, or antimonene because of its higher thermal conductance. However, it is higher than the value reported for graphene based on molecular dynamic simulations ($ZT = 0.08$) [58] or graphyne with $ZT = 0.15$ based on first-principles calculations [58].

In the following, we analyze the thermoelectric response of the C$_3$N sheet to uniaxial strain in different directions. Figure 6 shows the PF of the sheet versus strain along the ZZ direction. An increase of strain gives rise to a reduction of the PF. The reduction is more intensive in n-doping. Another point is the appearance of side peaks by applying tensile strain in p-doping. Reduction of the band gap by strain reduces the gap in conductance and increases the oscillation of the thermopower and these effects induce some extra peaks in the PF spectrum. The main reasons for the reduction of the PF under tensile strain are as follows. The band gap decreases with an increase of strain and, according to Goldsmid–Sharp relation [59], $S_{max} \propto L_z$, the maximum of thermopower reduces through band gap reduction. Thermopower has a dominant role in the PF, so the PF is significantly decreased by an increase of strain. The other reason is the vanishing of band convergence through strain. An unstrained sheet is an indirect semiconductor, so the VBM is located at the $M$ point. In addition, there is a valley at the $\Gamma$ in the valance band which is 0.12 eV below the VBM. The degeneracy leads to the increase of DOS at the valance band and, as a result, an increase of thermopower. A transition from indirect to direct band gap is observed upon applying tensile strain, see figures S4–S8. The transition destroys band degeneracy, so that the energy...
The dependence of lattice thermal conductance and maximum of thermoelectric efficiency on the strain is plotted in figure 7. We observe a uniform increase of phonon thermal conductance with increase of tensile strain. The increase is more obvious in the ZZ direction than the AC direction. In contrast, $\kappa_{\text{ph}}$ shows oscillatory behavior versus compressive strain along the ZZ direction. For AC strain less than $-6\%$, $\kappa_{\text{ph}}$ is almost constant and after that a linear increase is observed. The results show that the lattice thermal conductance is always higher in the ZZ direction. Applying strain results in a decrease of the maximum of $ZT$, and this result is independent of strain direction. The reduction is attributed to the band gap reduction and band degeneracy. For tensile strain less than $4\%$, $ZT_{\text{max}}$ for the ZZ direction is higher than for the AC direction. Although the maximum value of the thermopower is slightly higher in the AC direction than in the ZZ direction due to the larger band gap, see figures S4 and S7, and the transition from direct to indirect band gap for strain is along the ZZ, the increase of electrical conductance is more significant in the ZZ direction due to a narrowing band gap. So, $ZT_{\text{max}}$ is higher in the ZZ direction. For tensile strain higher than $4\%$, strain along the AC direction is more favorable than the ZZ direction because of the drastic reduction of the band gap in the ZZ direction. Compressive strain along the AC direction significantly reduces the band gap so that a semiconductor–metal transition occurs at $\epsilon = -6\%$. This gives rise to the severe reduction of the thermopower and figure of merit. Based on the results, it is clear that strain engineering can be used as a valuable tool to tune the thermal and thermopower properties of the C$_3$N sheet. We believe that the thermoelectric efficiency of the C$_3$N sheet could be greater than the values reported in this work if one uses a quantum mechanical approach to compute the phonon transmission coefficient. Here, we compute the phonon transmission coefficient at the $\Gamma$ point and averaging of it on the $k$-space can significantly reduce $T_\text{ph}$ and, as a result, increase the $ZT$ of the sheet.

Until now, we have studied the transport properties of the C$_3$N sheet under the condition that strain and transport are parallel. In the following, we consider situations in which the transport direction and strain are perpendicular to each other, i.e. the strain is along the $x$-direction (ZZ) while the transport is along the $y$-direction (AC) and vice versa. Figure 8(a) shows the transmission coefficient under different strains along the ZZ direction, while transport is along the AC direction. $T_x$ for the case of $\epsilon = 0$ indicates that the C$_3$N sheet is a semiconductor with a band gap of 0.4 eV from the GGA approximation. The sheet undergoes a transition from semiconductor to metal when a high compressive strain is applied. The result is confirmed for $\epsilon = -10\%$ with a finite value of $T_x$ in the Fermi level. Although the band gap is also reduced under tensile strain, the rate of reduction is slower. The band gap is 0.24 eV for $\epsilon = +10\%$. Electrical conductance, $G_e$, is directly dependent on the nature of the structure so that the metals have a higher $G_e$. At low temperatures, from equations (5) and (8) one can show that $G_e = \frac{2e^2}{h}T_x(E_f)$, so the sheet under a compressive strain of $-10\%$ has the highest value due to the non-zero value of $T_x$ at the Fermi level. An increase of temperature deviates the thermal broadening function, $-\partial f/\partial E$, from a delta function and the transmission coefficient around the Fermi level will be important, leading to the increase of $G_e$ for other cases. The reason for the increase of $G_e$ in the case of $\epsilon = 0$ rater than $\epsilon = +5\%$ is related to the higher value of $T_x$ for $\epsilon = 0$ at $E = E_f = 0.2$ eV.

Unlike electrical conductance, the thermopower of metals is lower than that of semiconductors. The maximum of thermopower is directly related to the band gap, $S_{\text{max}} = E_g / 2eT$ [59]. For that reason thermopower of the sheet for $\epsilon = -10\%$ is negligible, see figure 8(c). In addition, thermopower is related to the derivative of the transmission coefficient at
The asymmetry disturbs the equal contribution of electrons and holes in the charge and heat currents giving rise to an increase of the thermopower. The PF is dependent on both the electrical conductance and thermopower, so just a high thermopower, the case of $\epsilon = 0$, or high electrical conductance, the case of $\epsilon = -10\%$ cannot produce a high PF. The results show that the sheet under compressive strain of $\epsilon = -5\%$ has the optimum PF. For an unstrained sheet, the PF becomes significant at high temperatures, which is related to the increase of $G_e$.

Figure 9 shows $ZT$ versus temperature for strain applied along the ZZ direction and transport along the AC direction. We find that the $ZT$ shows nonlinear behavior for tensile strain so that it decreases for $\epsilon = +2\%$ and then significantly increases for $3\% < \epsilon < 6\%$. The threshold temperature in which $ZT$ is higher than 0.001 is lowered by an increase of strain. In addition, we observe a linear behavior for $ZT$ at high temperatures. Although a greater increase of strain reduces the magnitude of $ZT$, however, it is still higher than for the $\epsilon = 0$ case. Upon applying compressive strain, a substantial increase in $ZT$ is observed that, unlike for the tensile case, it never decreases with an increase of strain magnitude. Our investigations reveal that for $\epsilon = -10\%$ and at 500 K, $ZT$ is 23 times higher than an unstretched sheet at the same temperature.

Figure 10 shows the thermoelectric efficiency of the sheet under conditions where the strain is applied along the AC direction, while transport occurs along the ZZ direction. Unlike the previous case, the $ZT$ of the unstretched sheet is greater at room temperature than that under tensile strain. In addition, the behavior of $ZT$ is nonlinear at high temperatures. On the other hand, compressive strain results in the increase of $ZT$. Finite values of $ZT$ at low temperatures and under high tensile strain are a result of transition from semiconductor to metal because of gapless electrical conductance. The obtained results show that the magnitude of $ZT$ is lower in this case than the strain along the ZZ direction and transport along the AC direction.
direction. The results prove that the thermoelectric abilities of the C$_3$N sheet are strongly dependent on the strain engineering and transport direction, and this phenomenon makes it a promising candidate for thermoelectric applications.

In experiments strain can be applied to the C$_3$N sheet using different techniques. For example, epitaxial growth of the sheet on substrates with different thermal coefficients and cooling the complex after growth can induce large strain on the sheet. The same strategy was used to apply a large compressive strain on the graphene sheet [63]. In addition, one can apply strain on the C$_3$N sheet using the tip of an atomic force microscope (AFM). Lee and co-workers used this strategy to apply strain on a free-standing graphene sheet [64]. Using a flexible substrate and applying mechanical loading is the another way to apply strain on the sheet [65]. Thermopower can be measured using the conducting tip of an AFM and scanning tunneling microscope and measuring the thermoelectric voltage between the tip and the sheet in the presence of a temperature difference. This strategy was used to measure the thermopower of a graphene sheet on the SiC substrate [66]. The thermal conductivity of the sheet can be measured using the optothermal Raman thermometry technique [67] or thermoreflectance technique [68].

4. Conclusion

The polyaniline sheet is a recently synthesized two-dimensional monolayer with a hexagonal unit cell composed of six carbon and two nitrogen atoms with an empirical formula of C$_3$N. We have investigated the electronic and thermal properties of a C$_3$N sheet under external strain using density functional theory combined with the Green function formalism in the linear response regime. We find that the band gap of the sheet decreases with an increase of the strain magnitude and the slope of the reduction is dependent on the strain direction and type (tensile or compressive). Our investigation shows that thermopower is independent of strain direction, along the zigzag or armchair direction, but the power factor and, as a result, the figure of merit are strongly dependent. External strain can reduce the thermoelectric efficiency of the sheet when the strain and electron transport are parallel. We show that the thermoelectric efficiency of the sheet can be noticeably modified with control of the strain and transport direction. The results show that the thermoelectric efficiency increases significantly at room temperature under the conditions that the strain and transport directions are perpendicular to each other.

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