

Engineered Piezoelectricity in Graphene by Chemical Doping

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ABSTRACT

We demonstrate that piezoelectricity can be engineered into nonpiezoelectric graphene by selectively adsorbing atoms on one side, which breaks inversion symmetry. These piezoelectric magnitudes vary depending on the adatom and are found to be comparable to those in 3D piezoelectric materials. This phenomenon is unique to the nanoscale and has potential to bring dynamical control to existing graphene-based devices and other technologies.

Keywords: graphene, piezoelectricity, two-dimensional materials, computational modeling and simulations, nanoelectromechanical systems (NEMS)

1 INTRODUCTION

Among the challenges facing nanotechnology is the ability to dynamically control mechanical motion and deformation at the nanoscale. One way to achieve this control is to use piezoelectric materials, where deformation can be controlled by the application of an electric field. Piezoelectricity is typically thought to be an intrinsic property of a particular material phase, but carbon nanomaterials such as 2D graphene [1] are not intrinsically piezoelectric. One would like to make graphene piezoelectric to enable dynamical control with moderate electric fields on existing graphene-based electronics and other devices.

Graphene is a one-atom thick 2D material where carbon atoms are arranged in a honeycomb lattice. It has a number of extraordinary properties including high carrier mobility,[2] remarkable mechanical strength,[3] and being a zero band gap semimetallic conductor. Recent experiments have shown that application of an electric field normal to the surface can be used to modify bilayer graphene's electronic properties.[4] Furthermore, control over graphene's electronic properties has been shown when applying strain.[5,6]

In this work, we demonstrate that piezoelectricity can be engineered into nonpiezoelectric graphene by selective surface adsorption of atoms. Piezoelectric materials like 2D hexagonal boron nitride (2D-hBN) [7-9] usually belong to a noncentrosymmetric point group (*i.e.*, material without an inversion center). Graphene, however, exhibits inversion

symmetry and therefore is not intrinsically piezoelectric. In order to make graphene piezoelectric, this inversion symmetry element must be broken and this can be accomplished by chemically doping graphene with atoms on one side. Chemical doping of graphene has been extensively studied both experimentally [10,11] and theoretically.[12,13] Experiments have shown that graphene covered completely with either hydrogen or fluorine is chemically stable at ambient conditions.[14-16] Single-sided hydrogen or fluorine covered graphene has also been experimentally realized, among the cases considered here. In addition, alkali metal surface structures and island formation have been examined on both graphene and graphite.[17-20] Patterned adsorption of atoms [21,22] allows one to selectively control the spatial regions endowed with piezoelectricity unlike the case of 2D-hBN. We use density functional theory to calculate piezoelectric coefficients for various atoms on graphene and compare them to other piezoelectric materials. We also examine how these effects change when varying the surface coverage of atoms.

2 RESULTS AND DISCUSSION

Our calculations are performed using DFT implemented within the Quantum-ESPRESSO *ab initio* software package [23] where exchange and correlation effects are treated using the spin-polarized generalized-gradient corrected Perdew-Burke-Ernzerhof (PBE) approximation. We have looked at cases where graphene is uniformly doped on one side with lithium (Li), potassium (K), hydrogen (H), and fluorine (F) atoms. We also considered uniformly doping opposite sides with different atoms, such as H and F, or F and Li. In Figure 1, we show the unit cell and position of the atoms used in this work. In all cases, we use periodic boundary conditions where each unit cell contains two carbon atoms associated with the adatom(s). Based on DFT calculations, we find that Li and K prefer to bind at the center of the honeycomb, known as the hollow site, giving it hexagonal ($6mm$) point group symmetry. Since H and F are known to bond covalently,[15,24] we take H and F to bind on the top site (directly over a carbon atom) resulting in trigonal ($3m$) symmetry. Both two-atom cases result in trigonal ($3m$) symmetry since at least one of the two atoms bind at the top

site. These point group symmetries can be compared to pristine graphene ($6/mmm$) and hexagonal boron nitride (32). Only the $6mm$, 32 and $3m$ point groups are noncentrosymmetric and thus, piezoelectric. Based on the point group symmetry, we can determine which piezoelectric coefficients are nonzero.[25] In this work, we calculate the d_{31} and e_{31} coefficients, which are predicted by symmetry to be nonzero for all six cases depicted in Figure 1. These coefficients relate in-plane strain to electric field and electrical polarization normal to the surface.

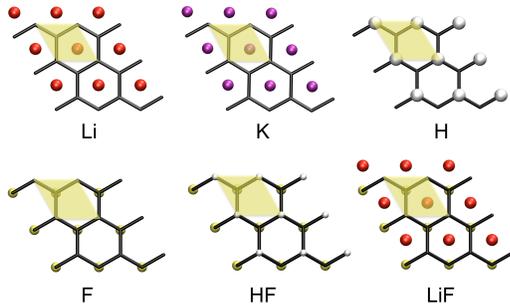


Figure 1: Unit cells for all of the atom cases studied are highlighted in yellow. Periodic boundary conditions are employed in all cases shown.

Figure 2a illustrates how equibiaxial in-plane strain (*i.e.*, equal strain in the 1- and 2-directions) of graphene varies as a function of electric field applied normal to the surface for each case in Figure 1. Our results indicate an approximately linear relationship between the field and strain at field amplitudes between -0.5 to 0.5 V/Å for many of the cases we have examined. The magnitudes of these fields have already been shown to be experimentally achievable.[4] The strain piezoelectric coefficient, d_{31} , for each atom can be determined from the slope. The d_{31} coefficients for all cases are given in Table 1. We find that there are significant variations in the piezoelectric response with respect to the dopant, more than a factor of 3. Both alkali metal atoms that we tested (Li and K) result in moderate changes in piezoelectricity. However, we find that adding F to the top site and Li to the hollow site on the opposite side gives the largest value of d_{31} .

For context, we compare our calculated values to values of known piezoelectric materials. We find that the maximum d_{31} coefficient that we calculated (3.0×10^{-1} pm/V for Li and F) is comparable to a theoretical value of 3.3×10^{-1} pm/V for wurtzite boron nitride (BN) [26] and a factor of 3 smaller than that of wurtzite GaN (-1.0 pm/V).[27] The sign of the d_{31} coefficient depends on the choice of the 3-axis direction. Both wurtzite structures are 4-fold coordinated 3D materials with completely different structures than the 2D materials. Thus, our results show that doped graphene has a sizeable piezoelectric response comparable to other 3D piezoelectric materials.

We have also calculated the e_{31} piezo coefficients by determining the polarization change perpendicular to the surface as a function of equibiaxial in-plane strain (Figure

2b). For strains between -1% to 1%, we find that the relationship is linear for all atoms. The e_{31} piezoelectric coefficient is twice the slope of each line due to the equibiaxial in-plane strain employed. Table 1 shows that Li and K have the highest e_{31} piezoelectric coefficients, almost twice as much as the other atom cases.

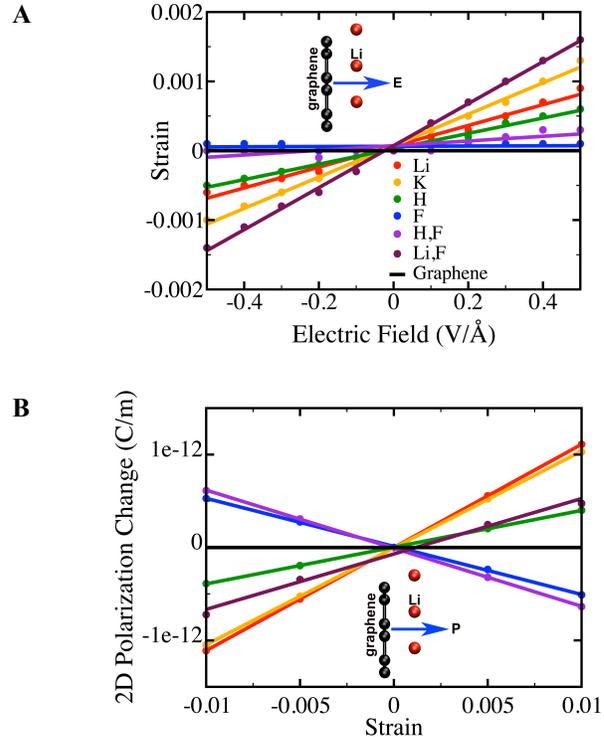


Figure 2: (A) An external electric field applied normal to the surface induces an equibiaxial strain in the plane of the graphene sheet. This leads to a linear relationship between the electric field and strain at low fields, the slope of which gives the d_{31} piezoelectric coefficient. Inset indicates the direction of the positive electric field. (B) Applying an equibiaxial in-plane strain to graphene induces a change in the polarization normal to the sheet. At low values of strain, this relationship is linear where the slope gives twice the e_{31} piezoelectric coefficient. Inset denotes the direction of positive polarization.

Atom(s)	d_{31} (pm/V)	e_{31} (C/m)
Li	1.5×10^{-1}	5.5×10^{-11}
K	2.3×10^{-1}	5.2×10^{-11}
H	1.1×10^{-1}	2.0×10^{-11}
F	1.8×10^{-3}	-2.6×10^{-11}
H,F	3.4×10^{-2}	-3.1×10^{-11}
F,Li	3.0×10^{-1}	3.0×10^{-11}

Table 1: Calculated values for the d_{31} and e_{31} piezoelectric coefficients for all atom cases. Doping with both F and Li give the highest d_{31} piezoelectric coefficient while doping with either Li or K gives the highest e_{31} piezoelectric coefficient.

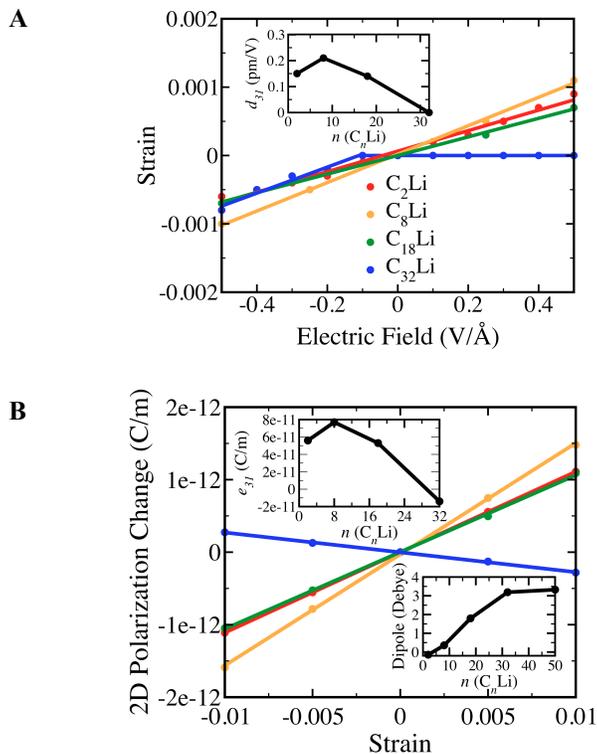


Figure 3: (A) Equibiaxial in-plane strain as a function of electric field applied normal to the plane for different Li coverage densities on graphene. The inset shows that a maximum in the d_{31} piezoelectric coefficient occurs for C_8Li . (B) Change in the polarization normal to the plane as a function of equibiaxial in-plane strain for different Li coverage densities on graphene. The top inset indicates that a maximum in the e_{31} piezoelectric coefficient occurs for C_8Li . The bottom inset shows how the static dipole moment changes as a function of Li coverage.

In order to compare these coefficients to 3D materials like wurtzite BN or GaN, we must account for the difference in dimensionality since the coefficient units for 2D materials are charge per unit length, while for 3D materials, they are charge per unit area. This is done by dividing the e_{31} coefficient of Li-doped graphene by the graphite interlayer spacing of 3.35 Å,[28] giving a value of $e_{31,3D}$ of 0.17 C/m². A similar value of 0.19 C/m² was obtained for $e_{31,3D}$ using the elastic stiffness matrix of graphite.[29] Our calculated $e_{31,3D}$ for Li-doped graphene is smaller by more than a factor of 4 than the $e_{11,3D}$ coefficient (0.731 C/m²) for 2D h-BN.[7] However, these two coefficients are not directly comparable since e_{11} is generally larger than e_{31} . Comparing our calculated $e_{31,3D}$ to those of other 3D materials, we observe it is within a factor of two of the theoretical value[26] of 0.31 C/m² obtained for wurtzite BN and approximately a factor of three less than the experimental value[30] of -0.55 C/m² for wurtzite GaN. We note that the polarization magnitudes in the doped graphene case can potentially be larger than those of wurtzite GaN due to the larger elastic strains achievable in

graphene before elastic failure. Our calculations for both coefficients demonstrate that it is possible to engineer piezoelectricity into graphene that is comparable to known piezoelectric materials.

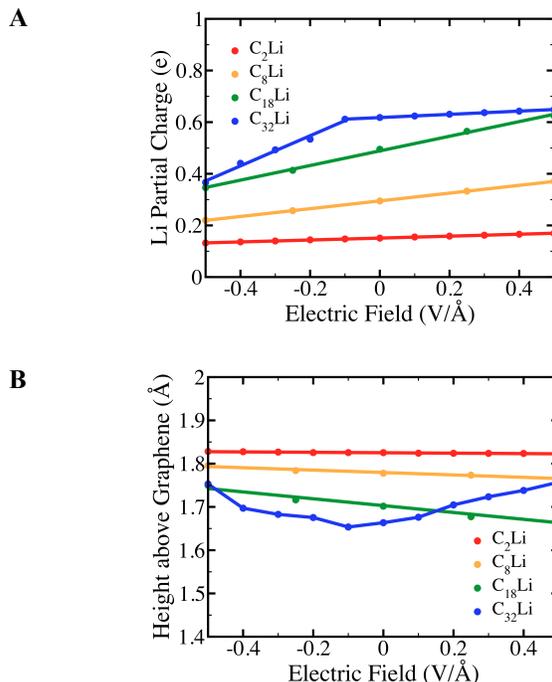


Figure 4: (A) Löwdin analysis for the partial charge on Li as a function of applied electric field at different Li coverage densities on graphene. (B) Li height above graphene as a function of applied electric field for different Li coverage densities.

Since piezoelectric effects might only be observable for sufficiently large dopant concentrations, we have examined how the piezoelectric coefficients change as a function of atom coverage using lithium as an example. We modeled different atomic coverage densities by putting a single Li atom on a 1×1, 2×2, 3×3, and 4×4 graphene periodic supercell. Each case is denoted by the formula unit C_nLi where $n = 2, 8, 18$ and 32, respectively. Figure 3a shows how the equibiaxial in-plane strain of graphene varies with electric field magnitude. In the inset of Figure 3a, we demonstrate how the value of the d_{31} coefficient changes as a function of Li coverage. We see that the piezoelectric coefficient reaches a maximum at C_8Li , which corresponds to one Li atom for every eight carbon atoms. This maximum is likely the result of a competition between an increasing static dipole moment, leading to strong interaction with the field, and a decreasing ratio of Li to C atoms, resulting in diminished interaction with the field. In addition, we find that the piezoelectric coefficient becomes smaller as coverage decreases and eventually reaches near-zero for $C_{32}Li$ or one Li atom for every 32 carbon atoms.

Similar trends are observed for the e_{31} coefficient as shown in Figure 3b. The top inset of Figure 3b shows that e_{31} reaches a maximum for C_8Li or one Li atom for every 8

carbon atoms. At low coverage, values for e_{31} are small, including a possible sign flip. Our study of surface coverage for d_{31} and e_{31} has shown that the magnitude of piezoelectricity in graphene can be engineered by varying the concentration of atoms on the surface.

In Figure 3a, we observe that the case of $C_{32}Li$ exhibits nonlinear behavior in d_{31} . For fields more positive than -0.1 V/Å, the piezoelectric coefficient is approximately zero. However, for fields more negative than -0.1 V/Å, there is an abrupt change resulting in a linear decrease in the strain with a slope of 0.19 pm/V, similar to higher coverage cases. In Figure 4a, we calculate the Löwdin partial charges on Li as a function of applied field for each concentration studied. Fields more positive than -0.1 V/Å indicate the charge remains relatively constant, but for fields more negative than -0.1 V/Å, there is significant charge transfer observed. If we examine how the distance above graphene changes as a function of field (Figure 4b), we find a minimum at -0.1 V/Å for $C_{32}Li$ compared to the other coverages, which are approximately linear. The distance from Li to graphene increases while the charge stays fixed for fields more positive than -0.1 V/Å. The distance also increases for fields more negative than -0.1 V/Å, but charge transfer takes place while the Li moves further away from graphene. Therefore, we find that the nonlinearity for $C_{32}Li$ in Figure 3a is due to the onset of charge transfer between Li and graphene, which begins at -0.1 V/Å.

3 CONCLUSION

The ability to engineer piezoelectricity into an intrinsically nonpiezoelectric material at the nanoscale is fundamentally new and made possible by the 2D nanoscale nature of graphene. Doping graphene on one side with atoms or opposite sides with different atoms breaks inversion symmetry, resulting in piezoelectric magnitudes comparable to known values for other 2D and 3D materials. Our surface coverage study with Li shows that the piezoelectric coefficient reaches a nontrivial maximum for C_8Li . A coverage of $C_{32}Li$ displays nonlinear behavior at fields of -0.1 V/Å, which is due to abrupt charge transfer from graphene to Li. The applied electric fields [4] and chemical doping [10,11] required to observe these effects in the laboratory are readily accessible. Furthermore, the ability to spatially pattern atoms on graphene's surface could lead to devices where strain can be concentrated in specific regions to control local electronic and optical properties. We envision that this designer piezoelectric phenomenon may lead to new nanoscale devices that are not based just on graphene, but other 2D and low-dimensional materials as well.

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