

Electronic Strengthening of Graphene by Charge Doping

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Graphene is known as the strongest 2D material in nature, yet we show that moderate charge doping of either electrons or holes can further enhance its ideal strength by up to $\sim 17\%$, based on first-principles calculations. This unusual electronic enhancement, versus conventional structural enhancement, of the material's strength is achieved by an intriguing physical mechanism of charge doping counteracting the strain induced enhancement of the Kohn anomaly, which leads to an overall stiffening of the zone boundary K_1 phonon mode whose softening under strain is responsible for graphene failure. Electrons and holes work in the same way due to the high electron-hole symmetry around the Dirac point of graphene, while overdoping may weaken the graphene by softening other phonon modes. Our findings uncover another fascinating property of graphene with broad implications in graphene-based electromechanical devices.

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Graphene is a single layer of sp^2 -hybridized carbon atoms arranged in a honeycomb lattice, with in-plane σ bonds forming the skeletons of honeycomb and out-of-plane π bonds forming conjugated 2D electron gas. This unique structure results in various fascinating properties of graphene [1,2]. In particular, mechanically graphene possesses extremely high stiffness and strength and is known as the strongest 2D material in nature [3], which inspires a range of potential applications such as lightweight high-strength materials and composites. Recent theory reveals that the failure mechanism of graphene under tension lies in the softening instability of the zone-boundary K_1 phonon mode occurring at a critical strain of $\sim 15\%$ [4].

The search for and design of hard materials has long attracted great interest with significant technological implications [5,6]. The ideal strength of materials is usually enhanced by structural designs at atomic and molecular level. For example, carbon clathrate (C-46) is found to have a larger ideal strength than diamond because its special cage structure effectively inhibits the instability of the carbon sp^3 to sp^2 transition [7]. Common strategies of material strengthening are to form composites [8] or by alloying and doping, such as high-strength steels formed with different dopants in Fe-C [9]. Here, using first-principles calculations, we demonstrate an unusual electronic enhancement of the material's ideal strength by pure charge doping, in contrast to the conventional structural enhancement. We show that moderate charge doping ($\leq 10^{14} \text{ cm}^{-2}$) of either electrons or holes can increase the strength of graphene by up to $\sim 17\%$. We further show that the strain induced softening of the zone-boundary K_1 mode, which was identified as being responsible for graphene failure [4], is associated with the strain enhanced Kohn anomaly in graphene. The surprising charge strengthening of graphene we discover is caused by doping induced

suppression of the Kohn anomaly, which counteracts the strain effect, and hence hardens the K_1 mode. Electrons and holes work in the same way due to the high electron-hole symmetry around the Dirac point of graphene.

Graphene is often doped either intentionally or unintentionally. When graphene is placed on a substrate [10,11] or adsorbed with foreign atoms and molecules [12,13], it is naturally doped due to charge transfer. In electronic devices, graphene is purposely doped by charge impurities [14,15] or by applying a gate voltage [16,17]. Therefore, understanding the effect of doping on properties of graphene is of both fundamental interest and technological significance. We have performed a systematic first-principles computational study of the effect of doping on graphene's ideal strength through calculations and analyses of phonon spectra of doped graphene under external strain. Our method is based on density-functional theory and density functional perturbation theory in pseudo-potential plane-wave formalism, as implemented in the QUANTUM-ESPRESSO code [18]. We use local density approximation and a plane-wave cutoff energy of 150 Ry. A supercell containing a single layer of graphene and a 15 Å of vacuum is used to eliminate the interaction between the graphene and its periodic images. A $30 \times 30 \times 1$ uniform k point mesh is used for the integration over electronic states, and a $6 \times 6 \times 1$ q point grid is used for the phonon calculations to obtain the dynamic matrices. The Methfessel-Paxton smearing [19] with a smearing width of 0.02 Ry is used for the self-consistent calculations to ensure the convergence of the phonon frequency. The charge doping is simulated by adding or removing electrons to the graphene with a compensating uniform charge background of opposite sign.

Usually, a material's ideal (intrinsic) strength can be traced down to its bond strength. The bond strength,

in principle, can be greatly affected by the amount of charge in the bond. Adding (removing) an electron to (from) the bonding (antibonding) molecular orbital of a diatomic molecule will significantly strengthen its bond, while the reverse action will weaken the bond [20]. However, adding or removing electrons to a solid material (i.e., doping) has negligible effects on the material's strength overall because usually there are many more bonds than electrons. At a typical semiconductor doping level of 10^{18} cm^{-3} , only one electron is added (or removed) every ten thousand bonds.

Consider the case of graphene, a true 2D material one atomic layer thick. In a graphene based field-effect transistor, a doping level up to $4 \times 10^{14} \text{ cm}^{-2}$ for both electrons and holes has been reached by electrical gating [17], which corresponds to one electron being added to or removed from a few tens of bonds. Therefore, one might expect a larger effect of doping on graphene's strength than on bulk materials' strength. However, intuitively, based on bond strength consideration, one would expect charge doping of either the electrons or holes will weaken the graphene strength because electrons or holes would be added (for n doping) to the antibonding states above the Dirac point or removed (for p doping) from the bonding states below the Dirac point, respectively. In contrast, we discover that at the typical level of doping seen in experiments, the ideal strength of graphene is substantially enhanced by either electrons or holes up to $\sim 17\%$. This surprising phenomenon of pure electronic strengthening of materials is associated with the fact that the ideal strength of graphene is

intricately related to the existence of the Kohn anomaly and its strain enhancement, an interesting property unique to graphene.

Figure 1 shows the calculated phonon spectra of intrinsic and doped graphene under different tensile strains, $\varepsilon = a/a_0 - 1$, where a and a_0 are the strained and the equilibrium lattice constants of graphene, respectively. The primitive unit cell containing two C atoms is used for phonon calculations. Specially, we draw the readers' attention to the gradual softening of the K_1 mode with the increasing tensile strain, as shown from Figs. 1(c) and 1(e) and from Figs. 1(f) to 1(i). [Note that when the K_1 mode is completely softened, for convenience, we plot the imaginary part of its frequency as negative values in Figs. 1(b), 1(e), and 1(i).] For intrinsic graphene, our calculated phonon spectra without strain [Fig. 1(a)] agree very well with the previous calculations [21,22]. The frequency of the K_1 mode becomes "negative" (the soft mode) at a critical strain of 14.9% [Fig. 1(b)], signifying the ideal strength of intrinsic graphene, which also agrees well with the previous calculation [4].

Interestingly, when graphene is doped with either electrons or holes, the phonon instability under tension is greatly suppressed. Figures 1(d) and 1(g) clearly show that in the doped graphene, the frequency of the K_1 mode remains positive at the strain of 14.9% in both n - and p -type doped graphene, indicating an enhancement of graphene strength beyond the strain of 14.9%. At a doping level of $7.6 \times 10^{13} \text{ cm}^{-2}$, with the further increase of strain, the K_1 mode will eventually become soft (negative frequency) at a

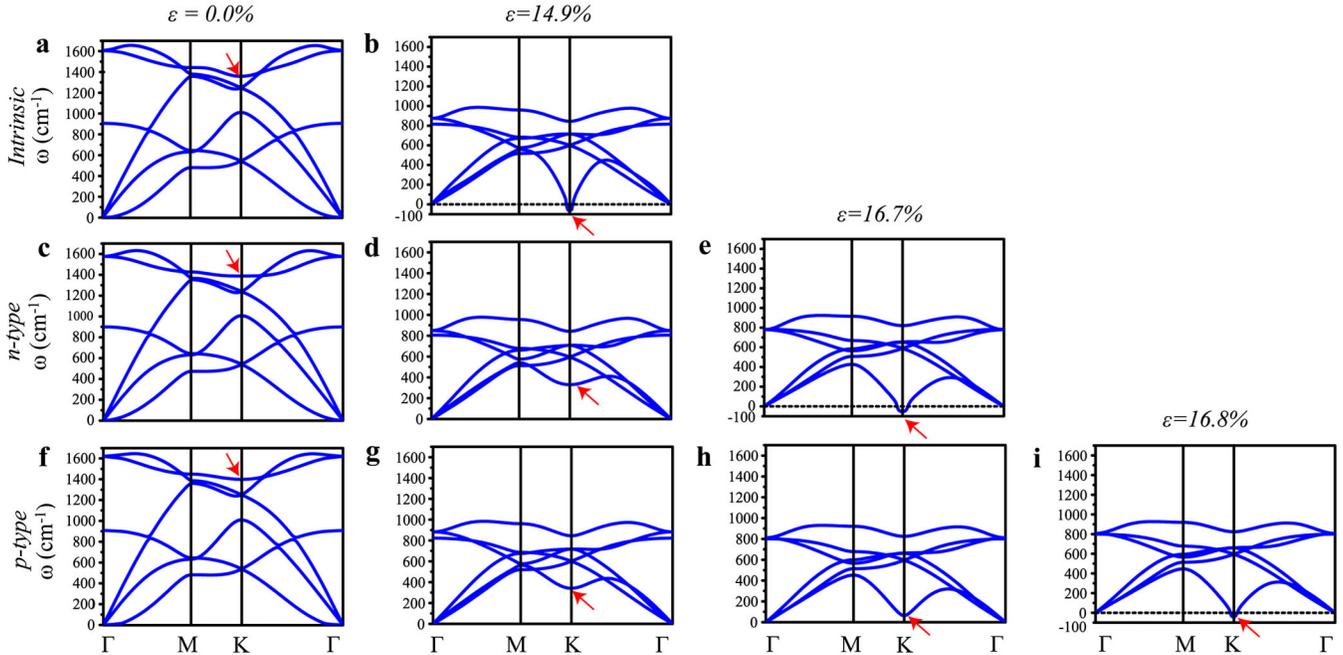


FIG. 1 (color online). Phonon spectra of intrinsic and doped (of $7.6 \times 10^{13} \text{ cm}^{-2}$ carrier density) graphene under different strains. (a) and (b), The intrinsic graphene. (c), (d), and (e), n -type graphene. (f), (g), (h), and (i), p -type graphene. The red arrows indicate the K_1 mode softened under strain.

critical strain of 16.7% in the *n*-type graphene [Fig. 1(e)] and of 16.8% [Fig. 1(i)] in the *p*-type graphene, respectively. This corresponds to an enhancement of graphene's ideal strength by $\sim 13\%$ at this doping level.

The failure of graphene under tensile strain is known to be triggered by the mechanism of strain induced softening of the zone-boundary K_1 phonon mode [4]. However, the underlying reason for the softening of K_1 mode rather than other modes is not fully understood. Here, we show that this is associated with the strain enhancement of the Kohn anomaly in graphene. The Kohn anomaly is a sudden softening of the phonon modes occurring for certain phonons with a wave vector \mathbf{q} connecting two electronic states with wave vectors (\mathbf{k}' , \mathbf{k}) on the Fermi surface, $\mathbf{k}' = \mathbf{q} + \mathbf{k}$ [23]. It arises from the screening effects of electrons on the atomic vibrations, which change the vibrations abruptly at those special \mathbf{q} points. In graphene, due to its peculiar pointlike Fermi surface (Dirac point), the Kohn anomaly can in principle occur for phonon modes at $\mathbf{q} = \Gamma$ (zone center) and $\mathbf{q} = \mathbf{K}$ (zone boundary) [24]. However, the large difference in the electron-phonon coupling strength for the phonon modes at Γ versus \mathbf{K} leads to a notable anomaly only for the K_1 mode [25].

Under tensile strain, the C-C bond length is stretched, resulting in the in-plane phonon modes softening. We propose that the existence of the Kohn anomaly makes the K_1 mode (one of the in-plane modes) much more susceptible to softening under strain and hence responsible for graphene failure under strain. In other words, the failure is caused by a strain enhancement of the Kohn anomaly that accelerates the softening of the K_1 mode. The Kohn anomaly is characterized by a kink (cusp) in the phonon dispersion around the point of the anomaly, i.e., the K_1 point in the present case [24]. We have calculated exactly the phonon frequencies at a series of q points around K_1 as a function of strain, as shown in Fig. 2(a). Clearly, all the dispersion curves are characterized by a cusp, the signature of the Kohn anomaly at the K_1 point. Most interestingly, the cusp becomes deeper (i.e., larger discontinuity in the first derivative of the phonon dispersion) with the increasing tensile strain, indicating a strain enhanced Kohn anomaly, which in turn drives the rapid softening of the K_1 mode under strain.

It is known that charge doping weakens the Kohn anomaly at the K_1 point [25]. Thus, one may expect that charge doping will counteract against strain effect and stiffen the K_1 mode under strain conditions to enhance the graphene strength. Apparently, Fig. 1 already suggests that the doping enhanced graphene's ideal strength is associated with the charge stiffening of the K_1 mode under strain [see Figs. 1(d) and 1(g)]. To further reveal this, we plot in Fig. 2(b) the adiabatic frequency shift of the K_1 mode as a function of the doping level of electrons and holes, in the unstrained and a 14.9% strained graphene. Clearly, we see that the frequency of the K_1 mode in both the unstrained

and strained graphene increases with the increasing carrier concentration of either the electrons or holes. Here, the equilibrium lattice constant of intrinsic graphene is used, giving the electron-hole symmetry. If the lattice constants of doped graphene are used, there will be slight electron-hole asymmetry at high doping levels. We also note that we only calculated the adiabatic frequency shift at the K_1 point. It has been shown that the nonadiabatic dynamic effect is important for the Γ point [26,27], which may affect the K_1 point also, but we expect the effect is only quantitative without qualitatively altering our results and conclusion.

Qualitatively, doping weakens the Kohn anomaly by shifting the Fermi surface away from the Dirac point, so as to move away from the $\mathbf{k}' = \mathbf{q} + \mathbf{k}$ condition and hence stiffening the K_1 mode. In this regard, because of the high electron-hole symmetry of graphene around the Dirac point, both the electron and hole doping will shift the Fermi surface away from the Dirac point in a symmetric fashion [28], resulting in a similar effect. In addition, Fig. 2(b) shows that the doping induced frequency shift of the K_1 mode in the strained graphene is much larger than that in the unstrained graphene. The reason for such a large difference is not fully clear, but it is consistent with the fact that the Kohn anomaly has been enhanced by strain in the strained graphene as shown above [Fig. 2(a)], so correspondingly when the condition of the "enhanced" Kohn anomaly is removed by doping, it may result in a larger shift of the K_1 mode.

To further confirm the above mechanism of the charge doping stiffened zone-boundary K_1 mode responsible for strengthening the graphene, we next determine directly the ideal strength of doped graphene by both electrons and holes, in comparison with intrinsic graphene, by computational tensile testing. To do so, we calculate the stress tensor as a function of biaxial strain using a large unit cell

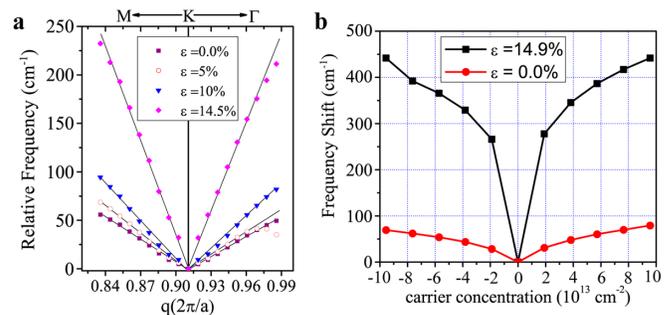


FIG. 2 (color online). The behavior of the K_1 mode under strain and doping. (a) The phonon dispersions around the K_1 mode under different strains: 0.0%, 5%, 10%, and 14.5%. The frequencies of the K_1 modes under different strain are set as the reference of zero frequency. (b) The adiabatic frequency shifts of the K_1 mode (in reference to the intrinsic graphene) as a function of the doping level for the unstrained graphene and strained graphene at the 14.9% strain, respectively.

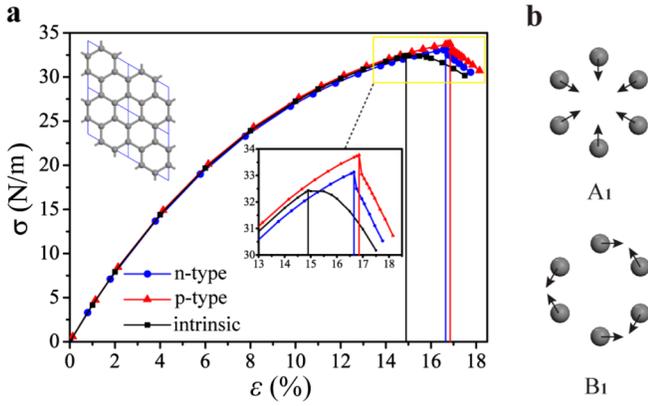


FIG. 3 (color online). (a) The stress (σ) versus biaxial strain (ϵ) for intrinsic, electron- and hole-doped (at a doping level of $7.6 \times 10^{13} \text{ cm}^{-2}$) graphene. The vertical lines denote the locations of structural instabilities. Inset: The graphene supercell used for calculating the stress-strain curve. (b) Atomic displacements of A_1 and B_1 phonon modes.

of graphene with six C atoms [see the left inset of Fig. 3(a)], which is three times the size of the primitive unit cell. This choice of unit cell is made to allow the freedom of lattice distortion representative to the designated K_1 mode as done before for intrinsic graphene [4]. Group theory warrants that the vibration of the K_1 mode is the combination of A_1 and B_1 modes [29], as illustrated in Fig. 3(b), and the A_1 mode is shown to be energetically more favorable [4]. Figure 3(a) shows the results of such a computational tensile testing. By locating the breaking points (discontinuities) in the stress-strain curves, we determine the critical strains where the structural phase transition associated with the K_1 mode softening occurs. They are 14.9%, 16.7%, and 16.9% for the intrinsic, electron-doped and hole-doped graphene, respectively [see the right inset of Fig. 3(a)], which are in excellent agreement with our preceding phonon instability calculations. Above the critical strains, the graphene lattice is seen to be driven to isolated hexagonal rings to start breaking down. Thus, the computational tensile testing results confirm again that the ideal strength of doped graphene is indeed enhanced by either electrons or holes through the charge doping stabilized K_1 phonon mode. On a side note, the stress-strain curves of doped graphene coincide with that of intrinsic graphene below critical strains, indicating that the elastic constant of graphene is almost unaffected by doping.

Finally, we determined the maximum enhancement of graphene strength can be achieved by charge doping. Figure 4 summarizes the calculation results of critical strains, where the phonon instability occurs, as a function of the carrier concentration of electrons and holes (plotted on the negative x axis). Most notably, the electronic strengthening of graphene by doping cannot go indefinitely with the increasing carrier concentration, but exhibits an upper limit. The maximum critical strain for electron

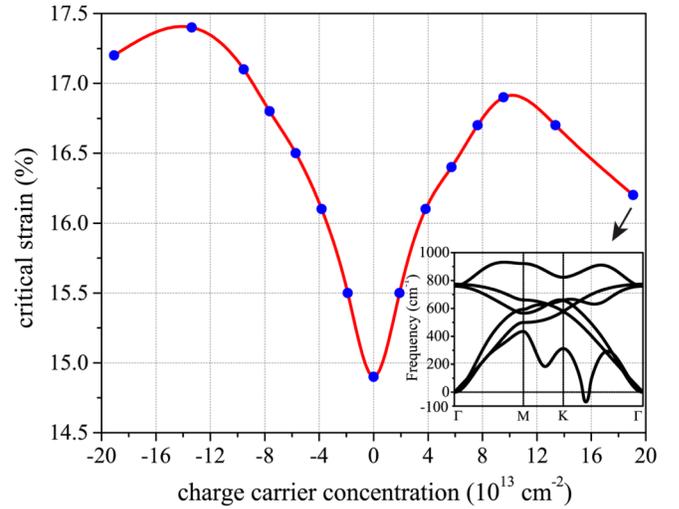


FIG. 4 (color online). The critical strains (where phonon instability occurs) of graphene as a function of carrier concentration of electrons and holes (plotted on the negative x axis). Inset: The phonon spectra of $1.9 \times 10^{14} \text{ cm}^{-2}$ electron-doped graphene under 16.2% strain.

doping is 16.9% at a doping level of $9.6 \times 10^{13} \text{ cm}^{-2}$; for hole doping it is 17.4% at a doping level of $1.34 \times 10^{14} \text{ cm}^{-2}$. This corresponds to a substantial increase of graphene strength by $\sim 13.4\%$ and 16.8% for doping of electrons and holes, respectively. The slight asymmetry in the n - versus p -type graphene at high doping level is caused by the different equilibrium lattice constant of the n - versus p -type graphene. Basically, electron doping induces a lattice expansion while hole doping induces a lattice contraction, determined by the sign of “quantum electronic stress” induced by the electron versus hole [30]. Consequently, the critical strains of p -type graphene are larger than those of n -type graphene, and the difference becomes more pronounced as the doping level increases.

In fact, as the doping increases, the K_1 mode continues to stiffen because the Kohn anomaly at the K_1 point continues to be weakened. Thus, if it were only for the K_1 mode, the graphene strength would be enhanced indefinitely. However, in reality, there are many other phonon modes, and strain may induce softening of another phonon mode different from K_1 to cause failure of the heavily doped graphene. This is clearly seen in the inset of Fig. 4, which shows the phonon spectra of the $1.9 \times 10^{14} \text{ cm}^{-2}$ electron-doped graphene under the 16.2% strain, with a softened mode occurring away from the K_1 point along the K - Γ high symmetry line.

In conclusion, we discover a surprising pure electronic enhancement of graphene strength which is qualitatively different from the common conventional structural enhancement of materials strength. Charge doping changes the electronic structure, resulting in a phonon renormalization of graphene that improves its mechanical properties. It arises from an intriguing mechanism of charge doping

counteracting against strain to affect the degree of Kohn anomaly. It is important to note that the predicted enhancement of graphene strength up to 17% occurs at typical doping levels easily accessible in real experimental samples, such as those used in graphene based field-effect transistor devices [16,17]. It underscores another fascinating property of graphene with broad implications in graphene-based electromechanical devices.

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