First-Principles Analysis of Corrugations, Elastic Constants, and Electronic Properties in Strained Graphyne Nanoribbons

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ABSTRACT: Density functional calculations have been performed to analyze atomic corrugations, Young’s modulus, Poisson’s ratio, and the electronic structure of monolayer graphyne ribbons under uniaxial strains within generalized gradient approximations. Within particular asymmetrical critical compressive ($\epsilon_{cr}^{-}$) and tensile ($\epsilon_{cr}^{+}$) strains, graphyne ribbons will undergo a reversible deformation, which is interpreted within a framework of linear elastic stress–strain response. From the energy-displacement relations, the two-dimensional Young’s modulus is obtained, and it increases along with the width increasing. When the compressive strain is beyond $\epsilon_{cr}^{-}$, unidirectional corrugations perpendicular to the strain direction are formed in narrower ribbons, and transverse and longitudinal corrugations are formed in wider ribbons. When the tensile strains exceed $\epsilon_{cr}^{+}$, all ribbons undergo longitudinal corrugations before fracture. The corrugation wavelength is practically not dependent on the applied strain but on the ribbon width. All these ribbons are semiconductor with controllable band gaps of 0.14–1.22 eV, depending on the width and the applied strain. Furthermore, the band gaps of graphyne ribbons are sensitive to the tensile strain and can be continuously modulated regardless of the critical strain because the bands near the Fermi level are split off 2p$_{z}$ states and mainly composed of $\pi$ orbitals of benzenes in the graphyne sheet.

INTRODUCTION

Graphene, a single atomic layer of carbon sheet, has been one of the first real two-dimensional (2-D) materials to be isolated in nature1 and is therefore structurally more amenable to external modifications including strains.2–6 It is found that graphene can sustain reversible deformations as large as 20%,7,8 and its band structure does not change for realistic strains less than 15%.9,10 It is well-known that, for practical applications of graphene, the opening of a gap is necessary. Besides other ways, it has been shown that a shear combined with an armchair uniaxial strain is a very effective way to fully open the gap.11 As a matter of fact, strain engineering has recently been suggested to modulate the wrinkles,12 electronic structure,13–15 magnetic,16 thermal,17,18 and transport properties19,20 of graphene ribbons for the potential application in future graphene-based electronics.

Recently, graphyne, a new allotrope of carbon which is built from triple- and double-bonded units of two carbon atoms, has been synthesized and attracted extensive interest of the fi community due to its extraordinary electronic properties.21–23 Graphynes possess multiple lattice types, e.g., $\alpha$, $\beta$, $\gamma$, and (6,6,12)-graphynes. Of all the graphynes, $\alpha$-, $\beta$-, and (6,6,12)-graphynes, similar to graphene, also present Dirac-cone-like band structure around the Fermi level.24 In contrast, $\gamma$-graphyne is a semiconductor.25 However, irrespective of the type of the electronic spectrum of the parent graphyne networks, hydrogen26 or fluorine27 adsorbed on sp$_{2}$ carbon atoms leads to the hybridization state from sp$_{2}$ to sp$_{3}$ and will make all of the graphyne sheets behave as semiconductors with a widely tuned band gap. On the other hand, when the adsorbates occur at sp atoms, the graphyne sheets are either semiconductive or metallic due to the hexagonal symmetry breaking.28

In comparison with graphene whose in-plane Young’s modulus is about 340 Nm$^{-1}$,20–22 the $\gamma$-graphyne sheet has a relatively low in-plane Young’s modulus (162 Nm$^{-1}$) due to its porous properties and weaker single bonds in the acetylenic linkages.31 Furthermore, Cranford’s results show that the in-plane Young’s modulus of the $\gamma$-graphyne sheet exhibits a strong anisotropy.32 The Young’s modulus along the reclined-chair direction is 170.4 Nm$^{-1}$,31 while it approaches 224.0 Nm$^{-1}$ in the zigzag direction. The effect of hydrogen adsorption on the mechanical properties of the $\gamma$-graphyne sheet is destructive and results in the in-plane Young’s modulus decreasing to 125 Nm$^{-1}$.33 However, the stiffness of the graphyne sheet may be strengthened by a dopant, and it is shown that some way of incorporating nitrogen atoms in the graphene layer could strengthen the doped system.34

As obtaining graphene nanoribbons from graphene, graphyne ribbons (GyNRs) could be obtained by cutting through an infinite graphyne sheet. In the meantime, the properties of such GyNRs have also been studied.35,36 However, to our best knowledge, a systematic study of corrugations, Young’s modulus, Poisson’s ratio, and the strain-induced electronic
structure changes for \( \gamma \)-GyNRs, so far, is still lacking. In this study we consider four different kinds of \( \gamma \)-GyNRs with various widths, namely, \( n \)-GyNRs with \( n = 2, 3, 4, \) and 5. All the \( \gamma \)-GyNRs are terminated with benzene rings, and all dangling bonds at the edges are saturated with hydrogen atoms. Ab initio strain energy calculations within or beyond the harmonic elastic deformation range are applied. Within particular asymmetrical critical compressive (\( \epsilon_{cr} \)) and tensile (\( \epsilon_{cr} \)) strains, GyNRs will undergo a reversible deformation. When the compressive strain is beyond \( \epsilon_{cr} \), unidirectional corrugations perpendicular to the strain direction are formed in narrower ribbons, and transverse and longitudinal corrugations are formed in wider ribbons. When the tensile strains exceed \( \epsilon_{cr} \), all ribbons undergo longitudinal corrugations before fracture. The results show that all these ribbons are semiconductor with controllable band gaps of 0.14–1.22 eV, depending on the width and the applied strain. Furthermore, its band gap decreases steadily with increasing tensile strain due to the effects of edge bond relaxation.\(^{37} \)

The paper is organized as follows. In Calculation Details, we briefly introduce the computation details that will be used in calculating strained ground-state properties. In the Results and Discussion, we present our self-consistently calculated corrugations, Young’s modulus, Poisson’s ratio, and the changes of the band gaps. The paper ends with the Summary where a short conclusion is given.

### CALCULATION DETAILS

The strain energy—strain relationship of GyNRs under the desired deformation configurations is characterized via ab initio calculations within the density-functional theory package, Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA).\(^{38} \) The generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof is applied for the exchange-correlation potential.\(^{39} \)

The calculation procedure, by taking the GyNR (\( 1 \times 1 \times 2 \)) supercell comprising two unit cells along the \( z \) direction (as shown in Figure 1) as an example, is listed as follows: The simulation invokes the periodic boundary conditions for two in-plane directions (\( x \) and \( z \)) as well as the out-of-plane direction (\( y \)). The vacuum layers in the \( x \) and \( y \) axis are maintained at 20 Å which is much larger than the 3.35 Å interlayer spacing of graphite,\(^{40} \) so each sheet can be laterally isolated from its periodic images. Integration inside the first Brillouin zone is sampled on a \( 1 \times 1 \times 20 \) Monkhorst–Pack meshgrid. The real-space grid cutoff energy is 300 Ry and a Fermi–Dirac distribution function with an electronic temperature of 20 meV is used to populate the energy levels. A linear combination of numerical localized atomic orbital basis sets for the description of carbon valence-band electrons (2s\(^2\)2p\(^3\)) and norm-conserving nonlocal pseudopotentials\(^{41} \) for the atomic core is employed.

We first optimize the equilibrium lattice constant along the \( z \) direction. The total energy as a function of \( z \) spacing is obtained by varying the lattice constants. A least-squares fit of the energy via \( z \) yields the equilibrium lattice constants, \( z_0 = 23.958 \) Å for 2-GyNR and 23.946 Å for 3-, 4-, and 5-GyNRs, which corresponds to the minimum total energy. In this system, there are two different kinds of carbon–carbon bonds inside the carbon chain, which connects to two hexagonal benzene, and they are 1.52 Å as a single \( \sigma \) bond at two ends and 1.20 Å as a \( \sigma + 2\pi \) bond in the middle, respectively. The carbon–carbon bond lengths in the benzene are 1.42 Å as those inside graphene.

The uniaxial strains are imposed by changing lattice constants along the \( z \) direction of the GyNR supercell. The positions of atoms in the supercell are not constrained. Therefore, the atoms in the supercell, as shown in Figure 1, are allowed full freedom (not only in-plane but also out-of-plane degrees of freedom) of motion. A conjugate gradient algorithm is used to relax all atoms into their equilibrium positions (residual maximum forces \( F_{max} \leq 0.02 \) eV/Å) within the deformed supercell that yields the minimum total energy for the imposed strain state of the supercell. Since the calculation of the total energy accounts for the lattice constants \( (z) \), it can be expressed as a function of only the macroscopic deformation gradient; i.e., \( E = E(\epsilon) \), where \( E \) is the total energy in the system, and \( \epsilon = (z - z_0)/z_0 \), where \( z_0 \) and \( z = z_0 + \delta z \) are the equilibrium and stretched lattice constants of GyNRs, respectively. The strain energy is defined as \( E_i = E(\epsilon) - E(\epsilon_0) \), namely, the total energy at a given uniaxial strain \( \epsilon \) minus that at zero strain.

### RESULTS AND DISCUSSION

Wrinkling is a very general physical phenomenon in ultrathin sheets.\(^{42} \) One- or two-dimensional ripples can strongly influence electronic structures of graphene by inducing effective magnetic fields and changing local potentials.\(^{43,44} \) Thus, we first investigated the atomic corrugated deformations of \( \gamma \)-GyNRs under the uniaxial strains along the \( z \) direction (as shown in Figure 1). Four different kinds of GyNRs are taken into account, namely, 2-, 3-, 4-, and 5-GyNRs, the widths of which are increasing along the \( x \) direction. In order to better understand the deformations, the atomic configurations are projected on three different coordinate planes (\( xy, yz, \) and \( xy \)). With increasing uniaxial (compressive or tensile) strains, \( \gamma \)-GyNRs undergo an elastic deformation, where the honeycomb-like structure is maintained and the system returns to its original configuration at \( \epsilon = 0 \) if the uniaxial strain is released below a certain strain known as the critical strain \( (\epsilon_{cr}) \). Beyond \( \epsilon_{cr} \), the planar structures of GyNRs remain unstable and undergo plastic deformations. It means that the system breaks its hexagonal symmetry and all the deformations will not disappear upon the release of the strains. The critical compressive strains \( (\epsilon_{cr}) \) will lead to buckling instability, and
the critical tensile strains ($\varepsilon_{\text{cr}}^t$) also first induce buckling instability and then fracture the systems. This arises from the pressure-induced buckling shape transition that also occurs in the carbon nanotube. In both systems, the energy cost to change (or compress) carbon—carbon bond lengths is about 2 orders of magnitude higher than that to change (or bend) bond angles.

Specifically, beyond $\varepsilon_{\text{cr}}^t$'s, there is one transverse buckling arch for 2-GyNR (as shown in Figure 1(a)) and two transverse buckling arches for 3-GyNR (as shown in Figure 1(b)). When the strain increases to $\varepsilon^* = -0.092$ for 3-GyNR, there is a structural phase transition that the wavelength is twice and the amplitude also becomes larger (as shown in Figure 2). With the width increasing, the buckling arches are not only along the transverse direction but also along the longitudinal direction (as shown in Figure 1(c)). The $\varepsilon_{\text{cr}}^t$'s are $-0.033, -0.054, -0.042,$ and $-0.029$ for GyNRs with $n = 2, 3, 4,$ and 5, respectively, and shown in Table 1. Under the compressive strains, the intrinsic instability in GyNRs does not depend on the width, which is only dominant form of mechanical instabilities for a narrow graphene ribbon under uniaxial tensile strains along the length direction. This can be qualitatively understood in terms of Poisson effect, as stretching along the length direction (say $x$-direction) will cause the compression in the orthogonal direction ($z$-direction) which then induces buckling along the $x$-direction. The $\varepsilon_{\text{cr}}^t$'s are, as shown in Table 1, 0.148, 0.142, 0.192, and 0.196 for GyNRs with $n = 2, 3, 4,$ and 5, respectively.

Comparing the critical compressive and tensile strains, despite the strain-induced mechanical instability in both the buckling forms, there is an asymmetry in the critical strains just like that in graphene ribbons.50 The asymmetry ratios ($\varepsilon_{\text{cr}}^t / \varepsilon_{\text{cr}}^s$) shown in Table 1) are 2–7 and independent of the width. This is because GyNRs and graphene ribbons are both the thinnest films with only one atomic layer thickness. The fact that GyNRs can only maintain their planar structure for a tiny amount of compressive strains has an important practical implication. It means that strain engineering is very unlikely with the application of compressive strains because as soon as the GyNR buckles it relieves the applied compressive strains, mitigating any useful electronic effects associated with the compressive strains. One may consider putting GyNRs onto a substrate to suppress the buckling instability so that larger compressive strains can be applied. Consequently, one has to consider the interaction of substrate on electronic properties of GyNRs in addition to strains.

Further, we investigate the mechanical properties of GyNRs under uniaxial strains in the range $[-0.1, 0.2]$ containing the harmonic elastic deformation range in which GyNRs sustain original atomic configurations and mechanical stabilities. In order to describe the mechanical properties of homogeneous and isotropic materials, two independent elastic parameters are needed. The first one is the Young’s modulus ($Y$), which is a measure of the stiffness. Since the thickness of a monolayer GyNR is ambiguous, it makes more sense to define the in-plane stiffness rather than the classical three-dimensional Young’s modulus. Therefore, the 2-D Young’s modulus can be described as follows: $Y^{2D} = \partial^2 E_s / \partial \varepsilon^2$. In this work, we revealed the relevant Young’s modulus of GyNRs using strain energy calculations. The strain energy as a function of uniaxial strains is shown in Figure 3(a).

With $\varepsilon$ in the range of $[\varepsilon_{\text{cr}}^t / \varepsilon_{\text{cr}}^s]$, the segment undergoes an elastic (i.e., reversible) deformation which implies that

| Table 1. Critical Tensile Strains ($\varepsilon_{\text{cr}}^t$), Compressive Strains ($\varepsilon_{\text{cr}}^c$), and Asymmetry Ratio ($\varepsilon_{\text{cr}}^c / \varepsilon_{\text{cr}}^t$) for GyNRs with Different Widths |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\varepsilon_{\text{cr}}^t$ | 0.148           | 0.142           | 0.192           | 0.196           |
| $\varepsilon_{\text{cr}}^c$ | $-0.033$        | $-0.054$        | $-0.042$        | $-0.029$        |
| $\varepsilon_{\text{cr}}^c / \varepsilon_{\text{cr}}^t$ | 4.885           | 2.631           | 4.571           | 6.759           |

On the other hand, beyond $\varepsilon_{\text{cr}}^c$'s, the tensile strain causes the GyNRs to first buckle in the width direction orthogonal to the direction of the uniaxial tensile strain being applied and eventually causes the GyNRs to break, creating two fracture surfaces (as shown in the down panels (d, e, and f) of Figure 1). This interesting form of instability has been predicted in ultrathin solid membranes97 and observed in graphene.48,49 The instability in GyNRs does not depend on the width, which is different from the graphene ribbon where the fracture is the only dominant form of mechanical instabilities for a narrow graphene ribbon under uniaxial tensile strains along the length direction. This can be qualitatively understood in terms of Poisson effect, as stretching along the length direction (say $z$-direction) will cause the compression in the orthogonal direction ($x$-direction) which then induces buckling along the $x$-direction. The $\varepsilon_{\text{cr}}^t$'s are, as shown in Table 1, 0.148, 0.142, 0.192, and 0.196 for GyNRs with $n = 2, 3, 4,$ and 5, respectively.

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Figure 2. Supercell configurations of GyNRs with width $n = 3$ under the different compressive strains, $\varepsilon^* = -0.058$ (the yellow atoms in panel a), $\varepsilon^* = -0.088$ (the blue atoms in panel a), and $\varepsilon^* = -0.092$ (b).

Figure 3. Schematic illustration of the strain energy (a) and Poisson’s ratio (b) as a function of uniaxial strains ($\varepsilon$) for 2- (red, square), 3- (green, triangle), 4- (blue, dot), and 5-GyNRs (pink, star). The data are self-consistently calculated points, and the lines are fitted with the least-squares method. The parallel purple dashed line means the Poisson’s ratio of the graphene sheet.
formula of an energy potential is a second-order Taylor series in powers of strains. For each strain, the corresponding supercell is fully optimized, and its total energy is calculated. Therefore, a series of grid data is obtained as shown in Figure 3(a). The second-order (quadratic) term leads to a linear elastic response, and the Young’s modulus is obtained by using the least-squares method and shown in Table 2, which are 32.84, 55.59, 70.98, and 95.81 Nm⁻¹ for 2-, 3-, 4-, and 5-GyNRs, respectively. Beyond εc, the system deforms plastically and transforms into a different structure after the yielding point where the strain energy suddenly drops. Within the range of [0−0.1:0.2], the nonlinear stress–strain response must be considered. In comparison with the graphyne sheet, GyNRs are much softer, and the Young’s modulus of 2-GyNR is one-fifth that of the graphyne sheet. In contrast, graphene nanoribbons present higher Young’s modulus than graphene. On the other hand, GyNRs become stiffer and stiffer with increasing width. That is to say, the Young’s modulus of GyNRs can be modulated from 32.84 Nm⁻¹ for 2-GyNR to 170.4 Nm⁻¹ for the graphyne sheet by increasing the ribbon width. However, the Young’s modulus of 5-GyNR just increases to a little more than one-half of that of the graphyne sheet when its width is almost 33.92 Å.

Table 2. Fitted Parameters (E = a × ε² + b × ε + c) Are Calculated by Using the Least-Squares Method (In Units of eV)

<table>
<thead>
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<th>a</th>
<th>b</th>
<th>c</th>
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<tbody>
<tr>
<td>2-GyNR</td>
<td>1175.15 ± 6.16</td>
<td>5.23 ± 0.75</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>3-GyNR</td>
<td>1988.11 ± 7.83</td>
<td>4.69 ± 0.80</td>
<td>0.12 ± 0.03</td>
</tr>
<tr>
<td>4-GyNR</td>
<td>2539.23 ± 24.26</td>
<td>26.19 ± 3.94</td>
<td>0.28 ± 0.15</td>
</tr>
<tr>
<td>5-GyNR</td>
<td>3439.12 ± 20.52</td>
<td>27.58 ± 2.55</td>
<td>0.13 ± 0.09</td>
</tr>
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</table>

The other constant to describe the mechanical properties is Poisson’s ratio (v), the ratio of the transverse strain to the longitudinal strain in the direction of stretching force, which can be defined straightforwardly as v = −Etransverse/Elongitudinal. The transverse strain is also defined as the axial strain (ε = ΔW/W), where W is the width of GyNRs, namely, the transverse distance between terminal carbon atoms. As is well-known, the Poisson’s ratio for graphene is ≈0.17, while that for the graphyne sheet is ≈0.42. Consequently, the graphyne sheet is more incompressible than graphene. From Table 3, it is found that the Poisson’s ratios of GyNRs are the same and independent of the width within the critical strains. The Poisson’s ratios of GyNRs are a bit bigger than those of the graphyne sheet and slightly decrease with increasing strain as shown in Figure 3(b). However, beyond the critical strains, they are close to zero under the compressive strain and 1 under the stretch strain due to the formation of corrugations.

Now we study the variations of band gaps of GyNRs under uniaxial strains. As mentioned above, a 2-D sheet of graphyne is a semiconductor with a direct band gap of 0.52 eV, and its band gap can be continuously modulated by a uniform strain. All of the GyNRs exhibit a semiconducting behavior and have different band gaps varying with widths, which could be also seen from our results in Table 2. The band gaps decrease from 1.22 eV (2-GyNR) to 0.66 eV (5-GyNR), which is consistent with the results of Pan et al. that the band gaps are about 0.75–1.32 eV with widths varying from n = 4 to n = 1. Wu et al. broke the benzene ring structure at the edges and constructed another configuration which has a direct band gap of 0.40 eV with antiferromagnetic coupling between the two edges. However, other than widths and edge types, it is worth asking what the effect is of uniaxial strains on their band gaps. Figure 4 shows the energies of the conduction band minimum and valence band maximum with respect to uniaxial strains. More interestingly, the band gap can be continuously modulated by the tensile strain, although the critical tensile strain induces the longitudinal bulking of GyNRs. In contrast, there is a sudden change of the band gap under the critical compressive strains.

Table 3. Young’s Modulus, Poisson’s Ratio, and Band Gap of GyNRs in Comparison with Other Values for Graphyne Sheet and Hydrogenated Graphyne (H-Graphyne)

<table>
<thead>
<tr>
<th></th>
<th>2-GyNR</th>
<th>3-GyNR</th>
<th>4-GyNR</th>
<th>5-GyNR</th>
<th>graphyne</th>
<th>H-graphyne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (Nm⁻¹)</td>
<td>32.84</td>
<td>55.59</td>
<td>70.98</td>
<td>95.81</td>
<td>170.4</td>
<td>125</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.47</td>
<td>0.49</td>
<td>0.46</td>
<td>0.45</td>
<td>0.417</td>
<td>0.23</td>
</tr>
<tr>
<td>gap (eV)</td>
<td>1.22</td>
<td>0.92</td>
<td>0.77</td>
<td>0.68</td>
<td>0.52</td>
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Figure 4. Energies of conduction band minimum and valence band maximum of γ-GyNRs as a function of strains (ε). (a) 2-GyNR; (b) 3-GyNR; (c) 4-GyNR; and (d) 5-GyNR.
certain compressive strain ($\varepsilon = -0.013$). The atomic orbital components of the energy bands around the Fermi level are almost completely composed of the $p_z$ orbital, which can be seen from Figure 6. This is also reported by ref 56. The band gap variation occurs due to the same nature of bands around the conduction band minimum (shown in Figure 7(a)) and valence band maximum (shown in Figure 7(b)) exhibiting the similar shifts with strain. Dramatic variation in the band gap with the strain suggests that GyNRs can be used as a strain gauge at nanoscale.

**SUMMARY**

We have studied the mechanical instability, Young’s modulus, and electron properties of $\gamma$-graphyne ribbons under uniaxial compressive/tensile strains, using density functional theory. We demonstrate that the GyNRs exhibit an asymmetry in tensile versus compressive strain induced mechanical instability which implicates that strain engineering of GyNR devices is only viable with application of tensile strain but difficult with compressive strain. All these ribbons are semiconductor with controllable band gaps of $0.139 - 1.216 \text{ eV}$, depending on the width and the applied strain. Furthermore, its band gap decreases steadily with increasing the tensile strain. Therefore, by applying moderate strains, the electronic properties of GyNRs can be readily engineered.

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**Notes**

The authors declare no competing financial interest.

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