A Novel Hyperbolic Two-Dimensional Carbon Material with an In-Plane Negative Poisson’s Ratio Behavior and Low-Gap Semiconductor Characteristics

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ABSTRACT: Poisson’s ratio is one of the fundamental parameters of a mechanical property of materials, which reflects the transverse strain response to the applied uniaxial load. The Poisson’s ratio is defined as $\nu = -\varepsilon_t/\varepsilon_a$, where $\varepsilon_t$ is an applied strain along the $a$ direction and $\varepsilon_a$ is the resulting stress in the transverse $b$ direction. Generally, materials are prone to expand (contract) in a perpendicular direction when a compressive (tensile) strain is performed in one certain direction, resulting in a positive Poisson’s ratio. In addition, previous studies verified that the Poisson’s ratios of elastic materials generally fall in the range of $0 < \nu < 0.5$. Notably, there are several materials with a negative Poisson’s ratio (NPR), which are allowable in elastic theory and rare in nature. The NPRs for materials mean that the materials will expand under stretching, and they will contract when there is compressive stress. Materials with a NPR are known as auxetic materials, exhibiting unusual mechanical behaviors and rendering them much more promising applications in mechanical nanodevices.

1. INTRODUCTION

Poisson’s ratio is one of the fundamental parameters of a mechanical property of materials, which reflects the transverse strain response to the applied uniaxial load. The Poisson’s ratio is defined as $\nu = -\varepsilon_t/\varepsilon_a$, where $\varepsilon_t$ is an applied strain along the $a$ direction and $\varepsilon_a$ is the resulting stress in the transverse $b$ direction. Generally, materials are prone to expand (contract) in a perpendicular direction when a compressive (tensile) strain is performed in one certain direction, resulting in a positive Poisson’s ratio. In addition, previous studies verified that the Poisson’s ratios of elastic materials generally fall in the range of $0 < \nu < 0.5$. Notably, there are several materials with a negative Poisson’s ratio (NPR), which are allowable in elastic theory and rare in nature. The NPRs for materials mean that the materials will expand under stretching, and they will contract when there is compressive stress. Materials with a NPR are known as auxetic materials, exhibiting unusual mechanical behaviors and rendering them much more promising applications in mechanical nanodevices. Foams with negative Poisson’s ratios were first produced from conventional low-density open-cell polymer foams by causing the ribs of each cell to permanently protrude inward in 1987.

Primeval NPR phenomena are generally observed in engineered three-dimensional (3D) bulk structures, including natural and man-made materials. Many cubic metals, and $\alpha$-cristobalite are reported to show NPR behaviors. Especially, the NPRs of some materials are derived from the phase transition. The unusual auxetic effect and concomitant enhancements in material properties offer enormous potential applications in many technologically important fields, such as biomedicine, sensors, fasteners, and protective equipment. Thus, the design and synthesis of multifunctional auxetic materials are urgently desired.

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configurations, and luckily is confirmed by both theoretical and experimental methods. Notably, the reported largest NPR among 2D auxetic materials is $-0.267$ for monolayer $\beta$-P. The NPRs of other 2D materials are relatively small. In addition, the 2D materials show the out-of-plane and in-plane NPRs. For example, one state-of-the-art theoretical calculation predicted that monolayer $\text{ABP}_6\text{X}_6$ ($\text{A}=$Ag, Cu; $\text{B}=$Bi, In; $\text{X}=$S, Se) are to a new class of auxetic materials with an out-of-plane NPR. However, a novel auxetic material, penta-silicene, is recently reported with an in-plane NPR.$^7$

Up to now, 2D materials still attract lots of research interest since the discovery of well-known graphene because they show various excellent properties with many potential applications in electronics, optoelectronics, and energy conversion. For example, 2D BN and MoS$_2$ have much higher piezoelectricity, and thus they are beneficial for efficient mechanical-to-electrical energy conversion.$^{30,31}$ The black phosphorone with an NPR shows excellent ferroelasticity and is a candidate for nonvolatile memory devices. Taking together, 2D materials display lots of excellent features, and auxetic materials also show unique mechanical properties. The unusual auxetic behavior in combination with other remarkable properties of 2D materials will lead to novel multifunctionalities.$^8$ Thus, it is highly recommended to design and synthesize special functionalized 2D materials simultaneously with NPRs.

Geometric considerations are predominantly reported in the literature to understand the auxetic phenomenon and design novel auxetic materials.$^7,8$ Herein, we proposed a novel 2D material with a hyperbolic geometry, called graphene-like structure (GLS), via state-of-the-art theoretical calculations. The GLS shows an interesting anisotropy NPR behavior and semiconductor characteristics. The values of NPRs depend on the orientation of applied strain. In addition, the geometry of the GLS is shown in Figure 2. The applications of molecules are novel hyperbolic configurations, and luckily is conformed by both theoretical and experimental methods.$^7$ The GLS is the first 2D structure with a hyperbolic geometry leading to an interesting NPR behavior and some excellent properties. This new mechanism of the auxetic phenomenon will extend the scope of auxetic nanomaterials and can serve as principles for future design of auxetic materials. We hope that these interesting findings would motivate further experimental and theoretical efforts to 2D materials with excellent auxetic behaviors.

2. COMPUTATIONAL METHODS

All of the first-principles calculations were carried out based on the Kohn–Sham density functional theory (DFT) with the Vienna ab initio simulation package (VASP). The generalized gradient approximation as parameterized by Perdew, Burke, and Ernzerhof (PBE) for exchange-correlation functional is used to relax the geometries. The plane-wave basis set with a kinetic energy cutoff of 400 eV is used to expand the valence electron wave functions. The convergence criteria for the energy in electronic SCF iterations and the force in ionic step iterations are $1.0 \times 10^{-6}$ and $5.0 \times 10^{-7}$, respectively. The non-periodic direction was set along the $c$ direction, and an at least 20 Å vacuum slab was added in order to eliminate the interactions between the layers of GLS. The reciprocal space is sampled with $k$-grid densities of 331, 551, 771, and 991, and finally a k point of 771 was selected with consideration of accuracy and efficiency. Furthermore, the geometries and electronic density for conduction band minimum (CBM) and valence band maximum (VBM) of the GLS were conducted with VESTA software.$^7$

The Poisson’s ratio of the GLS was calculated from its definition $\nu_{ab} = -\frac{\epsilon_{ab}}{\epsilon_{aa}}$, where $\epsilon_{ab} = \Delta L_{ab}/L_0$ is the resulting stress in the transverse $b$ direction. In our calculations of uniaxial strain (for example, along the $a$ direction), the lattice constant $L_a$ of the $a$ direction was manually set and fixed, and then the lattice constant $L_b$ was obtained via optimizing the structure, which corresponds to the lowest energy of the considered system. Finally, the Poisson’s ratio $\nu$ can be obtained in each strain percentage.

3. RESULTS AND DISCUSSIONS

3.1. Stability of the GLS. First, the optimization of the lattice parameters ($a$ and $b$ directions) with a constant $c$ of 25 Å was carried out. As shown in Figure 1a,b, the results of the relationship between the potential energies and the changing $a$ and $b$ parameters indicate that the optimal lattice parameters of the GLS ($C_{48}H_{8}$) for $a$ and $b$ directions are 18.45 and 12.33 Å, respectively. The geometry of the GLS belongs to the $P_1$ point group (space group no. 1) with much lower symmetry. In addition, the geometry of the GLS is shown in Figure 2. The novel hyperbolic configuration of the GLS can be seen from the left view and main view. The applications of molecules are determined by their features, which seriously rely on the geometries. A previous work on polymerized phenanthrene molecules forming porous graphene had shown a tunable Poisson’s ratio on the nanoscale.$^7$ Thus, it is inferred that the GLS with a unique hyperbolic configuration possesses interesting Poisson’s ratio behaviors, which would be revealed as follows.

In order to evaluate the lattice dynamic stability of the GLS, the phonon bands of the unit cell of the GLS were calculated using VASP combined with Phonopy.$^{39,40}$ As shown in Figure S1, although there are few imaginary frequencies, the maximum imaginary frequency for the unit cell of the GLS is less than $50 \text{ cm}^{-1}$. Considering the huge system and phonon band simulations for the primitive cell of the GLS, we thought that the imaginary frequency in Figure S1 is rational and would be
absent when the phonon band calculations were carried out for a supercell of the GLS. Given that any \textit{ab initio} calculations of phonons with high accuracy are far beyond our current computational capabilities, we hope that more researches could explore it. Besides, in the experiment, variable and complex substrate environment and categories would probably further stabilize the GLS.

In addition, the formation energy for molecule is a good method to evaluate the thermodynamic stability. If the formation energy of a compound is negative, this compound will be thermodynamically stable. The formation energy of the GLS (C48H8) per atom is

$$\Delta E(C_{M}H_{N}) = \frac{E(C_{M}H_{N}) - N\mu_{C} - M\mu_{H}}{M + N}$$

where $\Delta E(C_{M}H_{N})$ is the formation energy per atom of C48H8, $E(C_{M}H_{N})$ is the total energy ($-441.697$ eV) of C48H8 calculated on PBE, and chemical potentials ($\mu_{C}$ and $\mu_{H}$) of C and H atoms are the cohesive energies of graphene ($-7.906$ eV) and one-dimensional metallic hydrogen ($-1.75$ eV), respectively.61,62 The formation energy of C48H8 is $-0.861$ eV/atom, implying that the GLS is thermodynamically stable.

Furthermore, for any mechanically stable 2D materials, a necessary but not a sufficient condition must be satisfied: $C_{11}C_{22} - C_{12}^2 > 0$ and $C_{66} > 0$.12,47,63 The stiffness matrix of the GLS is given in Table S1. Especially, the calculated four elastic stiffness constants of GLS are $C_{11} = -100.85$ GPa, $C_{22} = -63.04$ GPa, $C_{12} = -12.73$ GPa, and $C_{66} = -6.80$ GPa. Clearly, the results of $C_{11}C_{22} - C_{12}^2 > 0$ with slightly negative $C_{66}$ verified the defective mechanical stability of the GLS. Again, the low stability originates from the absence of a proper substrate or chemical environment. The previous reports also demonstrated that materials with negative shear moduli would be stable if confined.64,65 Furthermore, we also calculated the Young’s modulus of the GLS, and comparing with the Young’s modulus of other 2D materials, including graphene (1023 GPa), BP ($E_{p} = 168$ GPa, $E_{s} = 38$ GPa), and $\alpha$-2D silica (178.56 GPa),12 there are some deviations between the Young’s modulus of the GLS and the values of classical 2D materials due to the defective mechanical stability. In the future, we will try to remold and stabilize the GLS with hydrogenation or other chemical modifications.

Furthermore, the dynamic stability of the GLS was also explored with molecular dynamics, and the relationship between the changing potential energy and increasing time within 3 ps is shown in Figure 3. After carefully checking the dynamic data, the maximum energy difference is 0.43 kJ/mol, which means that the structure of the GLS would hardly fluctuate with changing time. In other words, the GLS shows good dynamic stability.

According to the above discussion on the stability of the GLS, we thought that the GLS would be a potential 2D material with interesting mechanic features. Although there is experimental information on the GLS proposed in the present work, there are several reasonable experimental methods, including chemical vapor deposition (CVD),66 close-spaced vapor transport (CVT),67 flux growth,68 high-pressure flux method,69 and epitaxial growth,70 proposed to generally synthesize 2D materials. All of these general experimental methods will be the promising candidates to synthesize the GLS theoretically proposed here with a hyperbolical structure.

**3.2. Electronic Structures of the GLS.** As shown in Figure 4, the energy eigenvalues of VBM and CBM for the GLS are $-0.40$ and $0.38$ eV, respectively. There is no energy level traversing the Fermi level, and a band gap of GLS is $0.78$ eV with weak semiconductor features at the PBE level, indicating that the

Figure 2. Geometries of a supercell and the top view, left view, and main view of the GLS.

Figure 3. Relationship between the potential energy and time.

Figure 4. Energetical band structure of the GLS along high symmetry points and the density of states, the partial density states of s and p orbitals of carbon atoms, and the partial density state of s orbitals of hydrogen atoms.
GLS has a potential application for designing the nano-electro-optical devices with infrared absorption. A small band gap of 0.66 eV also occurs in δ-P. In addition, there are also several 2D materials with NPR behaviors showing semiconductor features. Furthermore, the total density of states (DOS) and partial density of states (PDOS) are shown in Figure 4. We considered the contributions of s and p orbitals of carbon and s orbitals of hydrogen to DOS. It is clear that the main contribution for DOS is from the p orbitals of carbon atoms. Around the $E_f$, the p orbital contributes significantly, indicating the origin of the semiconducting behavior of the GLS.

Similarly, VBM and CBM are mainly contributed by p orbitals of carbon atoms. As shown in Figure 5a,b, the populations of VBM and CBM cover all of the molecules with several nodes. Thus, there is no clear difference between electrons and holes, which is consistent with a small band gap. These nodes represent the alternative triple and single bonds along the whole carbon skeleton. The alternative triple and single bonds are also confirmed by bond lengths of 1.21 and 1.40 Å for the carbon skeleton except for benzene. The benzenes in the GLS show a little distortion, although six carbon atoms are in the same plane. Specifically, a bond length of 1.40/1.44 Å is for benzene, and it is clearly distinguished for the standard benzene with 1.40 Å, attributing to unequal carbon atoms.

3.3. Mechanical Properties of the GLS. Clearly, as shown in Figure 2, the GLS possesses features of hyperbolic geometry and reentrant polygon, which will lead to an NPR behavior. In the $ab$ plane, the geometry of the GLS consists of reentrant hexagons, one of the present configurations for auxetic materials. In addition, the geometry of the GLS shows layered and wave configurations in the $bc$ plane and $ac$ plane, respectively. The thickness of the GLS is around 3.10 Å. Due to these unique geometrical features, the GLS possesses unique mechanical properties.

The relationship between $-\varepsilon_a$ and $\varepsilon_b$ is shown in Figure 6, where $\varepsilon_a$ ($\varepsilon_b$) is the applied strain along the $a$ ($b$) direction and $-\varepsilon_b$ ($-\varepsilon_a$) is the resulting strain along the $b$ ($a$) transverse direction. As shown in Figure 6, Poisson’s ratio phenomena of the GLS are complex along different directions, leading to distinguished Poisson’s ratio, which coincides with the anisotropy of the GLS. Clearly, when the GLS is stretched along the $a$ direction, as shown in Figure 6a, the GLS shows a positive Poisson’s ratio. However, the GLS shows characteristics of auxetic materials when it is compressed along the $a$ direction, indicating an interesting mechanical behavior of the GLS. The result of linear fitting within 0.1–10% tension reveals that the NPR of the GLS is $-0.25$ ($\nu_a(-) = -0.25$). Notably, the NPR of the GLS is $-2.36$ when the tension is within 0.1–0.5% along the $a$ direction. This interesting NPR behavior is similar with the graphene, in which the Poisson’s ratio evolves from positive to negative when the applied tensile strain exceeds about 6%.

Remarkably, the NPR of the GLS along the $a$ direction with tension is quite higher compared with penta-graphene ($\nu = -0.068$), borophene ($\nu_a = -0.04, \nu_b = -0.02$), Be$_5$C$_2$ ($\nu_a = -0.04, \nu_b = -0.16$), HiB$_2$ ($\nu_a = -0.174$), VB$_2$ ($\nu_a(-) = -0.253$), and TaB$_2$ ($\nu_a = -0.224$).

Here, we also applied constraint uniaxial strain, within $-8\%$ to $+3\%$, along the $b$ direction for investigating the anisotropic mechanical properties. As shown in Figure 6b, the GLS presents a lower NPR for both compressive and tensile strains along the $b$ direction. The result of linear fitting reveals that the values of NPRs for GLS along the $b$ direction are around $-0.0576$ to $-0.087$, which are similar to penta-graphene ($\nu = -0.068$), though there are positive Poisson’s ratios when the compressive strain along the $b$ direction is less than 2%. Clearly, the mechanical property of the GLS is complex.

Generally, the Poisson’s ratios of the material with the reentrant structure are functions of the strains, especially for the large deformation, instead of a constant. Therefore, the relationship between the Poisson’s ratios and the strains is shown in Figure S2. It can be seen that with increasing the compressive strain along the $a$ direction from 0.1 to 2%, the NPR drastically decreases from $-6.208$ to $-0.691$. Consequently, it
converges to a constant value of −0.26 with the compressive strain (εb) further increasing (Figure S2a). The relationship between the Poisson’s ratios and the strains along the b direction (εb) is much more complicated. Roughly, the Poisson’s ratios are of small negative values in the regions of higher compressive strains with |εb| > 20% and those of tensile strains εb > 0, while in the small value of compressive strains (|εb| > 10%), the Poisson’s ratios are positive (Figure S2b). Although the whole negative Poisson’s ratio of the 2D GLS is not good enough, there are still evident negative Poisson’s ratio (NPR) effects along the given directions. Yu et al.11 revealed that the differences between NPRs along different directions represent an anisotropy auxetic material in 2017. Besides, our result is similar to single-layer graphene, which shows a positive Poisson’s ratio at a small strain while a negative Poisson’s ratio at a large strain.72 Therefore, it can be induced that the GLS with a hyperbolic geometry also shows an anisotropy Poisson’s ratio, which shows different behaviors along a certain direction. The hyperbolic configuration, which results in similar NPR behaviors derived from the reentrant and hinged geometries, is still expected to be a second key factor for a novel 2D material with NPR performance. In detail, the hinged structures will lead to changes in the material stiffness, and the magnitude of the Poisson’s ratio increases as the contrast between the unit cell stiffness increases. Furthermore, the increasing stiffness will enhance the deformation along one certain direction but inhibit the deformation along another direction, which is the main cause behind the achieved Poisson’s ratio of hinged structures.73 This novel hyperbolic structure with the auxetic phenomenon will extend the scope of auxetic nanomaterials.

It is known that the negative Poisson’s ratio of nanostructures and even metamaterials originates from the hidden degree of freedom (DOF). Those DOF parameters are hinged bonds (angles) and rotated bonds (angles). This hidden DOF can be released by the external strain, lifted temperature, pressure, and (angles) and rotated bonds (angles). This hidden DOF can be released by the external strain, lifted temperature, pressure, and volume.8,12,58 The negative Poisson’s ratio of our GLS is derived from the warping effect of carbon ribbons. An external strain could release the hidden degree of freedom when the system possesses buckling and warping.71 Furthermore, a previous report showed that chemical functionalization could enhance the auxeticity of graphene. Also, it is notable to expect more excellent auxetic nanomaterials with a hyperbolic configuration and suitable chemical functionalization.71 In order to clearly show the mechanism of NPRs for the GLS, we plot the local skeleton geometry of the GLS, as shown in Figure S3. The detailed structural information is shown in Table S2, including one optimal GLS without strain, which would be compared with, for example, two deformations of GLS with 30% strain along a and b, respectively. According to Table S2, while there are applied strain along a, the negative Poisson’s ratio of the GLS is derived from the change of dihedral angle for C17–C18–C19–C20 and C9–C10–C11–C12. In other words, the dihedral angles rather than the bond length along b stretch under a tensile force along a, which is the similar case for the auxetic materials semi-fluorinated graphene and δ-phosphorene.11,68 Furthermore, the negative Poisson’s ratio of the GLS along b originated from the slight change of the bond lengths of C13–C14, C14–C15, and C15–C16 and the change of the bond angles of C13–C14–C15 and C14–C15–C16.

3.4. Optical and Electronic Properties of the GLS. As a multifunctional material, we also explored the optical and electronic properties of the GLS. The dielectric function of the material is defined as ε(ω) = ε1(ω) + iε2(ω), with the real part (ε1(ω)) and imaginary part (ε2(ω)),74 when there is electromagnetic radiation. The relationships between the dielectric function and energy of electromagnetic radiation along different directions are shown in Figure 7.

![Figure 7. Relationships between the real part and imaginary part of the dielectric function for the GLS and energy of electromagnetic waves.](https://dx.doi.org/10.1021/acsomega.0c00182)
4. CONCLUSIONS

We proposed a novel 2D material (GLS) with a hyperbolic configuration via state-of-the-art theoretical methods, and the results confirm that the GLS has excellent thermodynamic and dynamic stabilities as well as acceptable lattice dynamic and defective mechanic stabilities. The GLS with a small band gap of 0.78 eV exhibits semiconductor characteristics, meaning that the GLS has a potential application for designing the nano-electro-optical devices with infrared absorption as well as δ-P. The density of states and partial density of states show that the valence band maximum and conduction band minimum are mainly from p orbitals of carbon atoms. The GLS shows an interesting negative Poisson’s ratio behavior along certain directions due to the novel hyperbolic configuration. This kind of hyperbolic configuration is expected to be a novel geometry leading to negative Poisson’s ratios of materials and a second principle for future designing auxetic materials. In addition, the GLS has an ideal electronic conductivity depending on the wavelength and can absorb and reflect the certain wavelength of ultraviolet and infrared light. Accordingly, we highly expect that these interesting findings would motivate further theoretical and experimental efforts in 2D auxetic carbon nanomaterials.

ASSOCIATED CONTENT

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00182.

Phonon band of the unit cell of GL, stiffness matrix of GL coefficients, geometry of GLS for the NPR mechanism study, the relationship between the Poisson’s ratios and the strains along a (and b) directions, and the geometrical parameters of GLS shown in Figure S3 without strain (GLS0) and deformation of GLS with strain along a (GLSa) and b (GLSb), respectively (PDF)

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Author Contributions

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Notes

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