PCF-Graphene: A 2D sp²-Hybridized Carbon Allotrope with a Direct Band Gap

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Supporting Information

ABSTRACT: Motivated by the recent progress in synthesizing graphene by using aromatic benzene molecules as precursors, herein, we propose a new two-dimensional (2D) carbon allotrope by using nonaromatic molecule cyclooctatetraene as the precursor from a bottom-up approach. In this structure, all the carbon atoms are threefold coordinated, similar to the sp²-hybridized atoms in graphene; thus, we name the poly-cyclooctatetraene framework as PCFgraphene. First-principles calculations reveal that although PCF-graphene is metastable compared with graphene, it is thermally, mechanically, and dynamically stable. Different from graphene with a single-atomic thickness and zero band gap, PCF-graphene has a finite thickness of 2.45 Å and is a



semiconductor with a direct band gap of 0.77 eV. It exhibits anisotropies in mechanical properties, carrier mobility, and optical adsorption because of its anisotropic lattice. This study not only sheds insights into the design of 2D carbon materials from some simple organic molecules but also expands the 2D purely three-coordinated carbon family from a single-atomic layer to a finite thickness. PCF-graphene can be used as a rung in the ladder to stabilize three-dimensional three-coordinated carbon system that remains elusive currently.

1. INTRODUCTION

Graphene has a honeycomb lattice structure with one-atom thickness and exhibits many novel properties such as high electron mobility,^{1,2} ambipolar effect,³ Klein tunneling, massless Dirac fermions,⁵ and anomalous quantum Hall effect,⁶ showing great potential for applications in high-speed electronic,⁷ radio frequency logic devices,^{8,9} thermally and electrically conductive reinforced composites,¹⁰ sensors,¹¹ and transparent electrodes.^{12,13} These findings have stimulated tremendous interest in exploring other two-dimensional (2D) carbon structures including phagraphene,¹⁴ T-graphene,¹⁵ octagraphene,¹⁶ penta-graphene,¹⁷ supergraphene,¹⁸ twin graphene,¹⁹ DHP-graphene,²⁰ Haeckelite,²¹ QPHT-gra-phene,²² and popgraphene.²³ These theoretically proposed graphene allotropes have many intriguing properties; however, none of them has been experimentally synthesized so far. One of the main reasons is lacking of precursors for chemical synthesis or lacking of layered three-dimensional (3D) counterparts for the exfoliation, even if these structures are energetically stable as proved by global structure search, dynamically stable proved by phonon spectra, and thermally stable by molecular dynamics simulations. Different from these 2D carbon allotropes, graphene has been synthesized by using not only the top-down approach via the exfoliation of graphite but also the bottom-up approach via the chemical synthesis from molecular precursors.²⁴ For instance, recently, Lopes and

co-workers²⁵ reported a facile room temperature synthesis of large graphene sheets using simple molecules such as benzene or *n*-hexane as precursors, which is simple, cheap, innovative, efficient, and reproducible. Li et al.²⁶ proposed to use *s*indacene molecule for the design and synthesis of ψ -graphene that exhibits robust metallicity against external strain. Furthermore, the metallic ψ -graphene shows the potential as an anode material for lithium-ion batteries because it contains active sites for Li adsorption.²⁷ These advances encourage to design and synthesize new 2D carbon allotropes by using appropriate molecular precursors.

In this study, inspired by the nonaromatic nature of cyclooctatetraene (COT, C_8H_8) and the cycloaddition reactions of unsaturated hydrocarbon molecules, we propose a COT-based 2D carbon allotrope, PCF-graphene, which is composed of purely sp²-hybridized carbon atoms. On the basis of the state-of-the-art first-principles calculations, we show that PCF-graphene is stable, possesses a direct band gap, and exhibits anisotropic optical adsorption, carrier mobility, and Young's modulus.

Received:December 19, 2018Revised:January 22, 2019Published:January 30, 2019

2. COMPUTATIONAL METHODS

All first-principles calculations and AIMD simulations in this study are performed using the Vienna ab initio simulation package (VASP).^{28,29} The interaction between valence electrons and ions is described by the projector-augmented wave approach.³⁰ Plane waves with an energy cutoff of 600 eV are adopted to expand the wavefunctions of valence electrons. The Perdew-Burke-Ernzerhof functional for the general gradient approximation³¹ is used to treat the exchangecorrelation interaction unless otherwise stated, whereas the Heyd–Scuseria–Ernzerhof (HSE06) functional^{32,33} is used to obtain more accurate electronic structures. The first Brillouin zone is sampled by using $9 \times 9 \times 1$ meshes for structure relaxation and properties study and by using $15 \times 15 \times 1$ for the self-consistent calculations. A vacuum space of 22.5 Å along c axis is employed, and the convergence thresholds of total energy and atomic force are set to 10^{-8} and 10^{-6} eV, respectively. Structure relaxations are performed with no symmetrical constraint. In AIMD simulations, the threshold for total energy is set to 10^{-4} eV, and temperature is controlled by the Nosé-Hoover thermostat.³⁴ Phonon-related properties are calculated by using the finite displacement method as implemented in Phonopy.³⁵

3. RESULTS AND DISCUSSION

3.1. Geometric Structure. COT is a nonaromatic molecule with the formula C_8H_8 , where all carbon atoms are threefold coordinated. When dehydrogenated, the resulting C_8 can be used as the structural unit to construct the 2D carbon sheet, termed as PCF-graphene, as shown in Figure 1a. The



Figure 1. (a) Self-assembly of PCF-graphene by using the COT framework. (b) Perspective and (c) top and side views of the atomic configuration of PCF-graphene. The dashed rectangle represents the unit cell.

chemical bonding between adjacent COT frameworks (which are painted in different colors) resembles that in the product of a cycloaddition reaction. Because the simultaneous addition and dehydrogenation processes can occur in cycloaddition reactions to maintain the feature of threefold coordination in the carbon framework,³⁶ it would be feasible to synthesize PCF-graphene from COT and/or its analogues. The optimized lattice parameters for the orthorhombic unit cell of PCF- graphene are a = 4.915 Å and b = 5.487 Å. The space group of the optimized lattice is *Cmmm* (space group no. 65), and the carbon atoms occupy two nonequivalent Wyckoff positions of 8m (0.25, 0.25, 0.4727) and 8n (0, 0.3744, 0.4511), which are classified as C_1 and C_2 , respectively. As shown in Figure 1b, the atomic ratio of C1 and C2 is 1:1, and the nonequivalent bond angles $\angle C_1 - C_2 - C_1$, $\angle C_1 - C_1 - C_2$, $\angle C_1 - C_2 - C_2$, and $\angle C_2 - C_2$ $C_1 - C_2$ are denoted as θ_1 , θ_2 , θ_3 , and θ_4 , respectively. Note that this structure can be viewed as an ordered arrangement of C1 and C_2 dimers along the (001) and (010) directions because the bond lengths of C_1-C_1 and C_2-C_2 bonds are 1.367 and 1.378 Å, respectively, both falling into the region of C-C double bonds, while the bond length of C_1-C_2 bond is 1.506 Å. For comparison, C–C bond lengths in graphene are all 1.42 Å, while those in COT are 1.35 and 1.47 Å, respectively. PCFgraphene possesses a buckling height (denoted as h in Figure 1c) of 2.447 Å, and a sandwich-like structure where C_1 atoms are in between the two layers of C2 atoms. The top view of PCF-graphene shows a nanoporous structure with a pore diameter d of 3.6 Å, as illustrated by the dashed circle in Figure 1c, which is larger than that of graphene.

3.2. Structural Stability. We first perform ab initio molecular dynamics (AIMD) simulations to check the thermal stability of PCF-graphene. A (3×3) supercell is adopted to reduce the possible errors introduced by periodic boundary conditions. As shown in Figure 2a, no significant reconstruction occurs during the heating process at 500 K for 10 ps with a time step of 1 fs, and the total potential energy fluctuates around a steady level, indicating that PCF-graphene is thermally stable at 500 K. We then calculate the phonon band structure of PCF-graphene to examine its dynamical stability, as shown in Figure 2b, where the absence of imaginary modes in the entire Brillouin zone confirms the dynamical stability of PCF-graphene. A further analysis of the phonon density of states (PhDOS) finds that the contributions from C₁ and C₂ atoms to the partial PhDOS in the region of low frequencies share a similar pattern, as their peaks and peak widths coincide with each other, while differ in the region of high frequencies, as the contribution from C_1 has two close peaks, differing from that of C_2 with a sharp peak. It is reasonable to attribute the distinct contribution of C1 and C2 atoms to PhDOS at ~43 THz to C_1 - C_1 and C_2 - C_2 bonds, whose Raman activities are found at 1481, 1438, and 1400 cm^{-1} (equivalent to phonon frequency of ~43 THz) and well coincide with the measuring results of unsaturated bonds in COT.³

3.3. Mechanical Properties. We then systematically study the mechanical properties of PCF-graphene after confirming its stability. All the elastic mechanical properties of a crystalline material can be deduced from its stiffness tensor **C**, which contains at most 21 independent components (often known as elastic constants). For a 2D material with an orthorhombic lattice, the number is reduced to four, namely, C_{11} , C_{22} , C_{12} , and C_{66} under Voigt notation, which can be treated as a partial derivative of stress with respect to strain.³⁸ For our system, the resulted elastic constants C_{11} , C_{22} , C_{12} , and C_{66} are 353.3, 199.8, 89.5, and 116.2 N m⁻¹, respectively. These results well satisfy Born–Huang criteria for 2D materials, which requires $C_{11}C_{22} > C_{12}^2$ and $C_{66} > 0$,³⁹ confirming the mechanical stability of PCF-graphene. The in-plane Young's moduli along the (100) and (010) directions (E_a and E_b) are 331.1 and 159.6 N m⁻¹, and the Poisson's ratios are 0.25 and 0.45, respectively. The difference between mechanical properties



Figure 2. (a) Energy fluctuation of PCF-graphene during AIMD simulation at 500 K. Inset image shows the geometry of PCF-graphene at the end of the simulation. (b) Phonon dispersion and PhDOS of PCF-graphene.



Figure 3. (a) In-plane Young's modulus and Poisson's ratio of PCF-graphene. (b) Stress-strain relationship of PCF-graphene.

along various directions indicates a significant mechanical anisotropy in PCF-graphene and is mostly due to the orthorhombic nature of its lattice. It is interesting to note that the in-plane Young's modulus E_a (331.1 N m⁻¹) of PCF-graphene is comparable to that of graphene (345 N m⁻¹).⁴⁰

To study the crystal orientation dependence of mechanical properties, we apply the tensor rotation matrix T to the stiffness tensor C of PCF-graphene based on the equation

$$\mathbf{C}' = \mathbf{T}^{-1} \cdot \mathbf{C} \cdot \mathbf{R} \cdot \mathbf{T} \cdot \mathbf{R}^{-1} \tag{1}$$

where $\mathbf{R} = \text{diag}(1, 1, 2)$ is the bridge between engineering strain and tensor strain. As illustrated in Figure 3a, the in-plane Young's modulus of PCF-graphene has a maximum at the (100) direction (0°) and a minimum at (010) (90°), while the minimum Poisson's ratio of PCF-graphene is found at ~36° near the (110) direction. We also examine the ideal strength of PCF-graphene by calculating its stress—strain relationship under in-plane biaxial tensile strain. The stretched lattice parameters are fixed during structural optimization to simulate the effect of strain. To examine whether the periodic boundary condition can cause any error, a (2 × 2) supercell of PCFgraphene is considered along with the unit cell. As illustrated in Figure 3b, the results from the supercell well fit those from the unit cell, and the ideal strength of PCF-graphene is 19.3 N m⁻¹ under a 19% biaxial tensile strain (denoted by the red arrow).

To further understand the mechanical anisotropy of PCFgraphene, we turn to a classic interpretation of strain energy, where strain energy U in stretched/compressed PCF-graphene sheets can be evaluated by the deviation of bond lengths (Δd) and bond angles ($\Delta \theta$) in a parabolic form

$$U = \sum_{i} K_{i}^{d} \Delta d_{i}^{2} + \sum_{i} K_{i}^{\theta} \Delta \theta_{i}^{2}$$
⁽²⁾

near its equilibrium state. For a purely sp²-hybridized structure, K_i^{θ} can be approximately treated as a constant, so that the quadratic sum of the deviation of bond angles $(\sum_i \Delta \theta_i^2)$ is a

reasonable parameter to evaluate the strain energy contributed by the distortion of bond angles. We perform structural optimizations to obtain PCF-graphene structures under uniaxial tensile/compressive strain of 1% along the (100) and (010) directions and examine the bond parameter changes in these structures (see Table 1). The uniaxial strain along the

Table 1. Bond Lengths d (in Å) and Bond Angles θ in the Relaxed and Stretched PCF-Graphene Structures

bond parameters	relaxed	+1% strain along (100)	+1% strain along (010)	-1% strain along (100)	-1% strain along (010)
$d(C_1 - C_1)$	1.367	1.368	1.368	1.367	1.367
$d(C_2-C_2)$	1.378	1.381	1.381	1.376	1.376
$d(C_1 - C_2)$	1.506	1.514	1.511	1.498	1.501
$ heta_1$ (°)	109.37	110.06	108.84	108.62	109.86
θ_2 (°)	111.02	110.80	110.86	111.30	111.22
θ_3 (°)	116.96	116.74	117.39	117.16	116.50
$ heta_4$ (°)	137.97	138.41	138.27	137.39	137.56

(010) direction causes less bond length changes and a smaller $\sum_i \Delta \theta_i^2$ value than that along (100), which can explain the lower stiffness of PCF-graphene in the (010) direction.

3.4. Electronic Properties. We calculate the electronic band structure and density of states (DOS) of PCF-graphene at the HSE06 level (see Figure 4a). A narrow direct band gap of 0.77 eV is found, indicating the absence of a lattice-wide conjugated system, and the valence band maximum (VBM) and the conduction band minimum (CBM) are both located at the Γ point. A further analysis of the electronic structure reveals that the DOS around the VBM and CBM are contributed from the p orbitals of C₁ and C₂ atoms, respectively, [namely, $\pi(C_1-C_1)$ and $\pi(C_2-C_2)$ bonds], which is further confirmed by the band-decomposed charge density of the highest occupied and lowest unoccupied bands



Figure 4. (a) Electronic band structure and corresponding total and partial DOS of PCF-graphene. Band-decomposed charge density of the (b) highest occupied and (c) lowest unoccupied band. The positions of slices are shown in (d).

of PCF-graphene (see Figure 4b,c), where they resemble the bonding orbital of $\pi(C_1-C_1)$ and antibonding orbital of $\pi(C_2-C_2)$. Note that the two bands are spatially separated, which is uncommon because the VBM and CBM of 2D semiconductors are usually contributed by the bonding and antibonding states of adjacent bonds with common atoms.^{17,41} The semiconductive electronic configuration of PCF-graphene differs from the metallic ones reported in various threefold hybridized 2D carbon allotropes and is similar to that of twin graphene, from which we can speculate that the buckling between adjacent unsaturated bonds is necessary but insufficient for breaking the lattice-wide conjugated system and that an extra condition is needed, namely, the different dispersion directions of π bonds between adjacent unsaturated bonds.^{14,15,19,23,26}

It is worth noting that PCF-graphene is not a *single-atomic layer* like graphene, in which the finite thickness would cause differences in properties as compared to that of a single-atomic layer. To see the effect of thickness on electronic structures, we chemically exfoliate a *single-atomic layer* from PCF-graphene, which becomes metallic and remains stable and planar when fully optimized (see Figure S1a,b for the atomic configuration and electronic band structure), different from the semiconducting feature of PCF-graphene.

To see the effect of stress on electronic properties, we also calculate the electronic configurations of PCF-graphene under biaxial compressive strain to check whether the semiconductive nature is robust. Similar to previously reported strain-induced band gap changes in 2D materials,^{42,43} the band gap of PCF-graphene declines with respect to the biaxial compressive strain and is closed at Γ point under a 5%-strain (see Figure S2), indicating a limited window of strain for the semiconductive properties.

We further investigate the carrier mobility of PCF-graphene. The carrier mobility along a given transport direction d in 2D materials can be described as

$$\mu_{\rm d} = \frac{2e\hbar^3 C_{\rm 2D}}{3k_{\rm B}Tm_{\rm d}^*m_{\rm e}^*E_1^{\ 2}} \tag{3}$$

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where m_d^* is the effective mass of carrier in the direction d, $m_e^* = \text{Sqrt}(m_a^*m_b^*)$ is the mean effective mass, and C_{2D} and E_1 are the in-plane elastic constant and the deformation potential under uniaxial strain along d, respectively.⁴⁴ All the parameters listed above can be calculated. The transport directions along the crystal orientations (100) and (010) are considered in accordance to the symmetry of PCF-graphene, and C_{11} and C_{22} are substituted into C_{2D} , respectively. The anisotropic mobility is found in both holes and electrons, and the results are summarized in Table 2. While the effective mass of electrons

Table 2. In-Plane Young's Modulus C_{2D} (in N m⁻¹), Deformation Potential E_1 (in eV), Effective Mass m_d^* (in m_e), and Mobility μ_d (in 10^2 cm² V⁻¹ s⁻¹) of Holes and Electrons in PCF-Graphene Sheet at 300 K

transport direction	carrier	C_{2D}	E_1	$m_{\rm d}^*$	$\mu_{\rm d}$
(100)	hole	353.3	-13.0	-0.338	2.27
(100)	electron	353.3	-4.52	0.414	14.0
(010)	hole	199.8	-8.16	-0.441	2.50
(010)	electron	199.8	-4.46	0.431	7.82

and holes are comparable, the low deformation potential of CBM under the strain along the (100) direction (see Figure 5a,b) together with the high C_{11} results in a significant electron mobility of 1.40×10^3 cm² V⁻¹ s⁻¹ at 300 K, which is superior to that of MoS₂ (predicted theoretically to be ~400 cm² V⁻¹ s⁻¹ and measured as ~200 cm² V⁻¹ s⁻¹).^{45,46} The favorable electron mobility in PCF-graphene indicates the potential applications in electronic devices.

3.5. Optical Properties. We then study the optical properties of PCF-graphene. The frequency-dependent complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ of a material is closely related to the DOS, as its real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$ are given by the following equations

$$\varepsilon_2(\omega) = \frac{4}{\pi\omega^2} \sum_{nn'} \int |P_{nn'}(k)|^2 \frac{\mathrm{d}S_k}{\nabla\omega_{nn'}(k)} \tag{4}$$

and

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega')}{{\omega'}^2 - \omega^2} d\omega'$$
(5)

All linear optical properties can be deduced from $\varepsilon(\omega)$,⁴⁷ that is, the absorption coefficient

$$I(\omega) = \sqrt{2}\,\omega[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)]^{1/2} \tag{6}$$

the refraction index

$$n(\omega) = \frac{\sqrt{2}}{2} \left[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} + \varepsilon_1(\omega) \right]^{1/2}$$
(7)

and the reflectivity

$$R(\omega) = \left| \frac{\varepsilon(\omega)^{1/2} - 1}{\varepsilon(\omega)^{1/2} + 1} \right|^2$$
(8)

As illustrated in Figure 6a, $\varepsilon_2(\omega)$ has a negligible value for photons with less energy than ~3 eV, indicating that little transition can occur under such stimulation, while the following peaks in $\varepsilon_2(\omega)$ at around 3.8 and 4.2 eV can be



Figure 5. Energy of the VBM and CBM as a function of uniaxial strain along the (a) (100) and (b) (010) directions.



Figure 6. (a) Optical absorption $\varepsilon_2(\omega)$, (b) absorption coefficient *I*, (c) refraction index *n*, and (d) reflectivity *R* of PCF-graphene. The visible region of light is denoted by the two dashed lines.

well explained by the onsets of DOS. Because little absorption occurs beneath 3 eV, transparency of PCF-graphene can be expected, while the increasing absorption coefficient beyond the stimulation energy of 3 eV indicates a considerable absorption of the near ultraviolet (UV) region of light (see Figure 6b). Note that an optical band gap of 3.1 eV is deduced from the absorption onset in *yy* direction, which is larger than the energy band gap. Figure 6c illustrates a remarkable increase in the refraction index in yy direction within the visible and near UV region of light, indicating the significant dispersion. A similar trend is found in the reflectivity of PCF-graphene and a reflection rate of over 20% in the near UV region of light is expected in yy direction (see Figure 6d). The transparency of PCF-graphene along with its significant absorption and reflection in the near UV region of light indicate the potential application as a coating material for protection against UV luminance.

4. CONCLUSIONS

In this study, we have proposed to use COT as the molecular precursor via a bottom-up approach to design PCF-graphene, which is composed merely of sp²-hybridized atoms in two nonequivalent Wyckoff positions. Different from the aromatic feature of a benzene molecule, the nonaromatic nature of COT makes PCF-graphene semiconductive rather than semimetallic as graphene does. In addition, the buckled geometry of COT endows PCF-graphene with anisotropies in mechanical properties, optical absorption, and carrier mobility. Equally interesting, in the carbon materials family with all carbon atoms in sp²-hybridized configuration, PCF-graphene is in between the two extreme situations: 2D single-atomic graphene and 3D K₄ carbon,⁴⁸ while the latter was found to be dynamically unstable.⁴⁹ Currently, it remains elusive for the existence of stable 3D carbon structures merely consisting of sp² hybrid carbon atoms. In this sense, PCF-graphene would be an important rung in the ladder to reach stable 3D 3coordinated carbon structures. We hope that this study would

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stimulate experimental effort on the synthesis of PCF-graphene to richen the 2D carbon materials with sp² hybridizations.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b12205.

Atomic configuration and electronic band structure of the exfoliated PCF-graphene and energy of the VBM and CBM as a function of biaxial strain and POSCAR file of PCF-graphene (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is partially supported by grants from the National Natural Science Foundation of China (NSFC-21773004), the National Key Research and Development Program of China (grant nos. 2016YFE0127300 and 2017YFA0205003), and the High Performance Computing Platform of Peking University, China.

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