Tetragonal Mexican-hat dispersion and switchable half-metal state with multiple anisotropic Weyl fermions in penta-graphene

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Abstract
Due to the paired valence electrons configuration, all known two-dimensional (2D) carbon allotropes are intrinsically nonmagnetic. Based on the reported 2D carbon structure database and first-principles calculations, herein we demonstrate that inherent ferromagnetism can be obtained in the prominent allotrope, penta-graphene, which has a unique Mexican-hat valence band edge, giving rise to van Hove singularities and electronic instability. Induced by modest hole-doping that is achievable in electrolyte gate, the semiconducting penta-graphene can be transformed into different ferromagnetic half-metals with room-temperature stability and switchable spin directions. In particular, multiple anisotropic Weyl states, including type-I and type-II Weyl cones and hybrid quasi Weyl nodal loop, can be found in a sizable energy window of spin-down half-metal under proper strains. These findings not only identify a promising carbon allotrope to obtain the inherent magnetism for carbon-based spintronic devices, but highlight the possibility to realize different Weyl states by combining the electronic and mechanical means as well.

1. Introduction

As the king of elements, carbon has abundant allotropes in different dimensionalities due to its bonding flexibility with itself [1-4]. The best-known and well-studied carbon forms include three-dimensional (3D) graphite and diamond [3], two-dimensional (2D) graphene [5], one-dimensional (1D) nanotube [6], and zero-dimensional fullerene [7]. In the past decades, the ever-expanding library of carbon allotropes has become more and more colorful. Naturally, the structural diversity gives rise to a broad range of exotic properties [8-25], such as semiconductivity [8-11], metallicity [12-15], superhardness [16-21], and topological states [22-25], which are anticipated to realize the desirable applications in microelectronic devices, Li/Na/K ion batteries, industrial cutting, and topological quantum computation, respectively.

Owing to the paired valence electrons configuration, all known carbon allotropes are intrinsically nonmagnetic, which formidable hinders their applications in spintronics. To generate local magnetic moments, some schemes such as transition-metal doping [26-30], cutting into nanoribbon [31, 32], and functionalization [33] have been introduced in different carbon materials, especially in the nanostructures. Experimentally, however, precise control of these external modulation methods still remains challenging. In this context, it would be very meaningful to achieve inherent magnetism in carbon allotropes.

Recently, it is revealed that some 2D intrinsic semiconducting materials (e.g. GaS/GaSe/InSe [34], α-SnO [35], α-PhO [36], and InP [37]) harbor Mexican-hat band edges (MHBEs). Since the novel band dispersion can induce the van Hove singularities with $1/\sqrt{E}$ divergence in the density of states (DOS) [35], the 2D materials with MHBEs have attracted more and more attentions due to their potential applications in...
multiferroics [35, 36, 38], thermoelectronics [39, 40], and superconductivity [41]. What is more, it has been proposed that magnetism can be viewed as an inherent property in 2D semiconductors with Mexican-hat bands [35]. In these kinds of materials, since the caused van Hove singularities can lead to electronic instability, the much-desired ferromagnetism will be readily induced by modest carriers doping [35–38]. As a consequence, such materials are naturally advantageous to realize electrical tuning of the magnetic state [35] via gate voltage. Then, an interesting question rises—whether the fascinating Mexican-hat bands exist in the pristine 2D carbon allotropes? If so, what kind of exotic electronic states would emerge under carriers doping?

Bearing the feature of Mexican-hat bands in mind, herein we first screen the electronic bands of all the known 2D carbon allotropes in the ‘2D carbon structure database’ [42]. We find that the prominent penta-graphene [9] is the only system exhibiting Mexican-hat dispersion in its frontier bands near the Fermi level. Using first-principles calculations, a Mexican hat-like dispersion with van Hove singularity is identified in the valence band edge of penta-graphene. When penta-graphene is doped by holes with modest density, robust long-range ferromagnetic (FM) states with room-temperature stability can be obtained, including spin-down half-metal (d-HM), bipolar semiconductor (b-SC), and spin-up half-metal (u-HM). Remarkably, multiple anisotropic Weyl states (e.g. type-I and type-II Weyl cones, and quasi hybrid Weyl loop holding both type-I and type-II linear dispersions) are induced near the Fermi level of d-HM state under proper strain. With the advantage of electronic and mechanical tuning, the switchable half-metallicity and anisotropic Weyl fermions of penta-graphene hold promise for carbon-based spintronic devices.

2. Computational details

We carried out state-of-the-art first-principles calculations based on density functional theory (DFT), as implemented with Vienna ab initio simulation package (VASP) [43]. The generalized gradient approximation with Perdew–Burke–Ernzerhof (PBE) functional [44] is adopted to deal with the exchange-correlation interactions. For the description of ion-electron potential, the projector augmented wave method [45] is employed by taking a cutoff energy of 600 eV for the plane-wave basis. A large vacuum layer (25 Å) is added to the perpendicular direction of penta-graphene, so as to avoid the spurious interactions between the adjacent periodic images. A Monkhorst-Pack k-point mesh with uniform spacing of 2π × 0.02 Å−1 is used to sample the 2D Brillouin zone. The convergence criteria of 10−8 eV and 0.001 eV Å−1 are used for the electronic iteration and Hellmann-Feynman force, respectively.

3. Results and discussion

3.1. Mexican-hat dispersion of the valence band edge

Like the Cairo pentagonal tiling [46], penta-graphene is made up entirely of carbon pentagons (see figure 1(a)). Its atomic structure holds P42_1m (D_{4h}^5) symmetry in a tetragonal lattice. The optimized lattice constant is a = b = 3.637 Å, close to previously reported value of 3.64 Å [9]. In every unit cell, six carbon atoms can be classified into two categories: C1 (yellow) and C2 (grey), holding four-coordinated sp^3 and three-coordinated sp^2 bonding environment, respectively. The electronic band structure plotted in figure 1(b) reveals that penta-graphene is an indirect semiconductor with a bandgap of 2.21 eV at PBE level [3.28 eV using HSE06 functional (see figure S1 in the supplemental material), being well consistent with 3.25 eV in [9]]. Interestingly, the valence band edge of penta-graphene has a small local minimum at the Fermi point, which makes it shaped as a shallow inverted Mexican-hat (see figure 1(c)). Such remarkable band feature corresponds to a sharp van Hove singularity divergence (see figure 1(b)) with 1/\sqrt{E} on the DOS [35–37]. From partial DOS, one can find that the Mexican-hat band primarily originates from C2 atoms.

To provide a quantitative description for the Mexican-hat band of penta-graphene, we propose a modified dispersion function ‘E_{vi}(k)’ similar to the case of hexagonal GaS monolayer [34, 47]. Taking angular dependence (quadrupole rotational symmetry) into account, the dispersion function is written as,

\[ E_v(k, \theta) = E_0 + A k^2 + B k^4 + F k^6 \cos(4\theta) \]  \hspace{1cm} (1)

in the 2D polar-coordinate system, or expressed as,

\[ E_v(k_x, k_y) = E_0 + F \left( k_x^4 + k_y^4 \right) - 6F k_x^2 k_y^2 + A \left( k_x^2 + k_y^2 \right)^2 + B \left( k_x^2 + k_y^2 \right)^2 \]  \hspace{1cm} (2)

in the Cartesian coordinate system. Thereinto, k = |k| = \left( k_x^2 + k_y^2 \right)^{1/2}. Based on the DFT-calculated valence band surface (see figure 1(c)), the dispersion function (2) is fitted in a square area of k space centered at \Gamma point with the side length of 0.4 rad/bohr. The values of \( E_0, A, B \) and \( F \) are obtained as \(-0.28944 \text{ eV}, \)
Figure 1. Structure and electronic bands of penta-graphene: (a) top and side view for the optimized structure, (b) electronic band structure and the corresponding DOS, (c) 3D plot together with its contours of the Mexican-hat valence band from DFT–PBE calculations, (d) energy contours of the fitted 3D Mexican-hat valence band using equation (2). For all the bands, the Fermi energy is set to 0 eV.

0.88301 eV Å⁻², −7.90467 eV Å⁻⁴, and 2.00059 eV Å⁻⁴, respectively. Figure 1(d) depicts contour plot of the Mexican-hat band obtained from the dispersion function (2) with the fitted $E_0$, $A$, $B$ and $F$ parameters. Comparing with the contour plot in figure 1(c), one can see that the proposed dispersion function $E_v(k)$ reproduces the DFT data well. Furthermore, our detailed analysis reveals a saddle point $(k_x = 0.145 \text{ Å}^{-1}, k_y = 0.145 \text{ Å}^{-1}, E_v = -0.270 \text{ eV})$ in the valence band along the $\Gamma \rightarrow M$ path (i.e. $\theta = 45^\circ$ direction) in the $k$-space. Owing to its presence, the aforementioned 1D van Hove singularity in the DOS emerges. Moreover, a Lifshitz transition [34, 47] would occur when the Fermi level is modulated to cross the critical energy of the saddle point. This is due to the change of topology of the Fermi surface, i.e. from four isolated small rings, to interconnected rings (see the green lines in figure 1(d)), then to one big ring.

3.2. Magnetic properties and switchable half-metal states

Apart from pristine penta-graphene, it would be more interesting to explore penta-graphene with $p$-type doping. As mentioned above, 1D van Hove singularity is an important indication of electronic instabilities, providing the opportunity to generate different phases [35–37, 48, 49], such as ferromagnetism and superconductivity. Indeed, previous experiments have confirmed that high doping level of electron or hole carriers up to $10^{15} \text{ cm}^{-2}$ can be achieved in 2D materials with an electrolyte gate [50–52]. For these, we first assess the impact of hole doping on penta-graphene. With different hole densities, the atomic structures of $p$-type penta-graphene have been fully re-optimized using spin-polarized DFT calculations. The results show that three-coordinated C2 atoms are in the intermediate hybrid state between $sp^2$ and $sp^3$ hybridization, and gradually tend to form the planar $sp^2$ hybridization with increasing densities, which enlarges the $\angle$C1C2C1 angle and lattice constants (see figure 2(a)). Indeed, such effect is equivalent to applying an effective biaxial tensile strain $\varepsilon_{eff}$ (up to 11.8%) to penta-graphene. The relationship between $\varepsilon_{eff}$ and hole density can be well characterized by a third-order polynomial fitting as: $\varepsilon_{eff} = 0.009 \sigma^3 - 0.089 \sigma^2 + 0.338 \sigma - 0.176$. In [9], the authors have systematically assessed the structural stability of penta-graphene under different strains by calculating phonon dispersion. The results indicate that penta-graphene can still maintain its stability under much larger mechanical strains (up to 17.2%). In this sense, hence, we can conclude that the hole doped penta-graphene structures should also be dynamically stable. To further examine this, we perform the calculation of phonon dispersion for the doped penta-graphene with the hole density of $7.36 \times 10^{14} \text{ cm}^{-2}$ as a representative, which will be the focus in the following discussion. As illustrated in figure S2 (see the...
supplemental material), the phonon dispersion has no virtual frequency, confirming that this doped system is dynamically stable.

In addition to doping-induced structural changes, increasing hole doping also breaks the time-reversal symmetry and leads to FM state in penta-graphene. As plotted in figure 2(b), the localized magnetic moment of per hole reaches up to 1 $\mu_B$/hole at the hole density ranging from $5.60 \times 10^{14}$ cm$^{-2}$ to $1.28 \times 10^{15}$ cm$^{-2}$. The corresponding spin charge density reveals that all magnetic moments are mainly contributed by the C2-C2 dimers, which can be viewed as one magnetic unit (see inset of figure 2(b)). Because of this, we construct a $2 \times 2$ supercell, and then calculate their total energy in different collinear magnetic orders, including FM state, possible antiferromagnetic states (AFM1 and AFM2, see figure S3 in the supplemental material), and nonmagnetic state NM. The relative energies of AFM1, AFM2 and NM with respect to FM state are displayed in figure 2(c). Evidently, FM order is always the magnetic ground state for p-type penta-graphene for all the considered hole densities. To examine the effect of exchange-correlation, the relative energies of FM, AFM1, AFM2 and NM for penta-graphene with hole density of $7.36 \times 10^{14}$ cm$^{-2}$ are also calculated by HSE06 (see table S1). The results also reveal that FM state is the magnetic ground state.

After confirming the magnetic ground state, it is highly necessary to examine its thermal stability, which is essential for practical spintronic applications. We estimate the Curie temperature ($T_C$) of p-type FM penta-graphene with different hole densities. By considering the nearest-neighbor ($J_1$) and next-neighbor ($J_2$) exchange parameters, the Hamiltonian of penta-graphene in a classical Heisenberg model can be expressed as:

$$H = -\sum_{i,j} J_1 M_i M_j - \sum_{k,l} J_2 M_k M_l. \quad (3)$$

Here, $M_x$ ($x = i, j, k, l$) denotes the magnetic moment on different sites, denoting every C2-C2 dimer in magnetic penta-graphene. From the total energies of different magnetic states, $J_1$ and $J_2$ parameters can be evaluated by:

$$J_1 = \frac{E(\text{AFM1}) - E(\text{FM})}{8M^2}, \quad (4)$$

$$J_2 = \frac{E(\text{FM}) + E(\text{AFM1}) - 2E(\text{AFM2})}{-8M^2}. \quad (5)$$

Figure 2. (a) Optimized lattice constants and the corresponding effective strains, (b) magnetic moment per hole, (c) relative energies to FM state, (d) Curie temperature of penta-graphene as a function of the doping densities $\sigma$. The inset in (b) is the spatial distribution of spin-polarized electron density at hole density of $7.36 \times 10^{14}$ cm$^{-2}$, while that in (d) displays the temperature-dependent magnetic moments and heat capacity ($C_v$) for penta-graphene at hole density of $7.36 \times 10^{14}$ cm$^{-2}$.
Figure 3. Electronic band structures of penta-graphene with hole doping at different densities: (a) $7.36 \times 10^{14}$ cm$^{-2}$ with one hole per primitive cell, (b) $1.28 \times 10^{15}$ cm$^{-2}$ with two holes per primitive cell, and (c) $1.35 \times 10^{15}$ cm$^{-2}$ with 2.25 holes per primitive cell. (d) Schematic diagram of electrolytic gate and band structures for different spin-polarized states: $u$-HM, $b$-SC, and $d$-HM.

Based on the Wolff algorithm [53], Monte Carlo simulations are carried out on a 16 $\times$ 16 lattice by using the Mcsolver code [54]. Overall, the obtained $T_C$ increases with the increasing of hole density (see figure 2(d)) due to the enhanced exchange energy ($\Delta E_{FM} = E_{NM} - E_{FM}$, see figure 2(c)). Specifically, (i) $T_C$ first increases to a maximum of 972 K at $1.28 \times 10^{15}$ cm$^{-2}$, and then decreases, consistent with the tendency of relative energies of different magnetic states (see figure 2(c)); (ii) all the $T_C$ values for the hole densities ranging from $7.36 \times 10^{14}$ cm$^{-2}$ $\sim$ $1.37 \times 10^{15}$ cm$^{-2}$ are larger than room temperature (see figures S4 and S5 in the supplemental material), ensuring that the FM order is robust enough for applications in the ambient environment.

Besides the robust FM order, three appealing electronic states with distinct conduction behavior are observed in the calculated band structures of $p$-type penta-graphene (see figure S6 in the supplemental material), including $d$-HM, $b$-SC, and $u$-HM. Among them, 100% spin-polarized $d$-HM state is formed at hole densities from $1.9 \times 10^{14}$ cm$^{-2}$ $\sim$ $1.17 \times 10^{15}$ cm$^{-2}$, in which the transport carriers are purely spin-down holes. Figure 3(a) presents a typical example of $d$-HM at the density of $7.36 \times 10^{14}$ cm$^{-2}$. One can see that there is a half-filled spin-down band across the Fermi energy. When the density increases to $1.28 \times 10^{15}$ cm$^{-2}$, penta-graphene transforms into a non-conducting $b$-SC (figure 3(b)), in which the conduction and valence bands have opposite spin directions, exhibiting bipolar characteristics [55]. Since there is no conduction carrier, such $b$-SC should be regarded as an indispensable off-state in device application. As for larger density of $1.37 \times 10^{15}$ cm$^{-2}$, penta-graphene is switched to conductive half-metal again. However, the transport carriers become spin-up holes instead of spin-down ones, corresponding to the $u$-HM state, as shown in figure 3(c). In experiments, as hole density can be tuned by the electrolytic gate [50–52] (see schematic diagram in figure 3(d)), $p$-type penta-graphene should be an ideal platform to achieve switchable and reversible spintronic devices, in which the transformation among $d$-HM $\leftrightarrow$ $b$-SC $\leftrightarrow$ $u$-HM states can be readily realized by electrical means, as illustrated in figure 3(d).

3.3. Strain induced multiple Weyl states

According to the dispersion feature of conduction bands around the Fermi level, there exists linear crossing along the $\Gamma \rightarrow X$ path in the spin-down channel of penta-graphene at hole densities of $5.6 \times 10^{14}$ cm$^{-2}$ $\sim$ $9 \times 10^{14}$ cm$^{-2}$ (see figure S6 in the supplemental material). However, the effective energy window with linear bands is rather small, which will hinder experimental detection of the corresponding massless fermions. Then, an interesting question arises: can the linear energy window and the band dispersion be modulated by a feasibly external method? To explore this, taking the penta-graphene at $7.36 \times 10^{14}$ cm$^{-2}$ as an example, we recalculate its band structures under different mechanical strains, which has been confirmed as an accessible approach for engineering the electronic properties of 2D materials [56, 57]. As seen from the
band structures in figure S7 in the supplemental material, the crossing bands are sensitive to both the tensile and compressive strains. Hereafter, we focus on the following two cases, i.e. at the compressive strain of −2% and at tensile strain of 8%.

Under −2% strain, a double degenerate Weyl state (figure 4(a)) with a sizable linear energy window (≈140 meV) can be found along the Γ → X path at the Weyl point of W1 (0.30936, 0.00000). The computed 3D band structure reveals that this Weyl point is isolated in the 2D Brillouin zone, and the two low-energy bands around the Fermi level form a tetragonal symmetric type-I Weyl cone (figure 5(a)) with weak transport anisotropy, whose Fermi velocities along different k directions range from 1.55 × 10^5 m s$^{-1}$~1.90 × 10^5 m s$^{-1}$ (see figure S8(b) in the supplemental material). To explore the origin of such Weyl state, we further analyze the orbital-resolved bands. As displayed in figure 4(c), the wavefunctions around W1 are mainly contributed by px and py orbitals, and there is an evident inversion of energy order between px and py bands. Such band inversion is an important signal of the topological semimetal [58–60]. Additionally, to elucidate how the Weyl state forms, we perform symmetry analysis for the two crossing bands using the IRVSP code [61]. Around W1, the obtained irreducible representations of the two linear bands in the high symmetry path are G1 and G2 (figure 4(c)), respectively. Using Bilbao Crystallographic Server [62], it is found that the corresponding symmetrical element is dual rotational axis C2. Therefore, the Weyl state around W1 is formed by the band inversions between px and py of carbon atoms with the protection of C2 rotational symmetry.

Interestingly, when 8% tensile strain is applied to penta-graphene, the original type-I Weyl cone evolves into a tilted type-II Weyl cone, in which the slopes of the two crossing bands in some k-paths share the same sign around W2 (see figure 4(b)). This stems from that the kinetic component T(k) is larger than the potential component U(k) in the energy spectrum of $E_{2d}(k) = T(k) \pm U(k)$ for a Weyl state [63]. A visualized image can be seen in the 3D bands with a small k-plane centered at W2 point, as shown in figure 5(b). There coexist electron and hole pockets on the energy isosurface of W2, as presented in the lower inset. Moreover, band dispersion of the Weyl cone, unlike the case of figure 5(a), is highly anisotropic (see figure 7(c) in the supplemental material). Along the kz direction, the Fermi velocity reaches up to 2.7 × 10^5 m s$^{-1}$, while in the $\theta = 72.74^\circ$ direction, the Fermi velocity is reduced to a minimum value of 2.5 × 10^5 m s$^{-1}$ due to the weak band dispersion.

Besides W2, another Weyl crossing point, i.e. W3 (0.16638, 0.00000) along Γ → M, also emerges under 8% tensile strain. Unlike W2, however, it is not a strict degeneracy point because of the existence of a tiny bandgap of 9 meV (see inset in figure 4(b)). This can be understood by the mechanism of band repulsion [64], namely, when there is no symmetry (see figure S9 in the supplemental material), the two crossing bands will hybridize with each other and maintain a gap in-between. Even so, considering the thermal effect in practical environment, such a tiny bandgap should be ignored at temperatures higher than 100 K. In this regard, W3 can be considered as a massive Weyl point. Then, multi-crossing Weyl points are reminiscent of the FM Weyl nodal lines [65, 66], which is composed of consecutive Weyl points. To explore the complete pattern of Weyl points in the 2D Brillouin zone, we plot the corresponding 3D band structure. As presented in figure 5(c), there are four equivalent and strict Weyl points protected by C2 symmetry, and infinite

![Figure 4](image-url)
number of massive Weyl points, like $W_3$. The colorized contour plot (figure 5(d)) of the energy gap between the two bands further reveals that all the ‘Weyl points’ form a closed quasi nodal line shaped as a rounded square centered at $\Gamma$ point. Moreover, in the view of band dispersion, the quasi nodal line should be referred to as a hybrid nodal loop — there exist both type-I and tilted type-II Weyl dispersions along the transverse directions of the nodal line, as displayed in the bands along $\Gamma \rightarrow M$ and $\Gamma \rightarrow X$, respectively. As proposed, such type of hybrid nodal loop may lead to unconventional magnetic responses [67], such as the effect of zero-field magnetic breakdown and the peculiar anisotropy in the cyclotron resonance.

In summary, using first-principles calculations, we show that the prominent penta-graphene is the only system harboring the novel MHBE among all known 2D carbon allotropes. An analytical dispersion function with quadruple rotational symmetry is proposed to describe the Mexican-hat band. Owing to the van Hove singularities and electronic instability, the desirable room-temperature FM half-metal states with switchable spin directions can be readily obtained by hole doping. Remarkably, both weak and strong anisotropic Weyl states, including type-I/type-II Weyl cones and quasi hybrid Weyl nodal loop, are found in the $d$-HM state under modest strains. As is proposed, the possible route for synthesizing penta-graphene is chemical exfoliation from the layered $T12$-carbon phase [9]. Moreover, in view of some pentagon-based 2D materials have been synthesized [68–70], and the accessibility of high-density carrier doping by electronic means, we believe that the robust FM half-metal states identified in penta-graphene would be promising in carbon-based spintronic devices. Additionally, our findings highlight the strategy to obtain different Weyl fermions by combining the electronic and mechanical modulations.

NOTE: In this work, the focus is on the 2D carbon structure with MHBEs because of the existence of a van Hove singularity in the DOSs at the Fermi level, which can lead to electronic instability. Whether the desirable magnetism can be induced by carrier doping with achievable density in the non-Mexican hat carbon allotropes and what is the mechanism are unknown. This is an interesting question to be studied in future.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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Author contributions

J Z and Z L designed the research. N J and Y S contributed equally to this work. N J, Y S, J Q and Z L prepared the manuscript with notable inputs from all authors.

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