Highly Anisotropic Dirac Fermions in Square Graphynes


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ABSTRACT: We predict a family of 2D carbon (C) allotropes, square graphynes (S-graphynes) that exhibit highly anisotropic Dirac fermions, using first-principle calculations within density functional theory. They have a square unit-cell containing two sizes of square C rings. The equal-energy contour of their 3D band structure shows a crescent shape, and the Dirac crescent has varying Fermi velocities from 0.6 × 10^9 to 7.2 × 10^9 m/s along different k directions. Near the Fermi level, the Dirac crescent can be nicely expressed by an extended 2D Dirac model Hamiltonian. Furthermore, tight-binding band fitting reveals that the Dirac crescent originates from the next-nearest-neighbor interactions between C atoms. S-graphynes may be used to build new 2D electronic devices taking advantages of their highly directional charge transport.

Since the discovery of graphene, 2D materials have attracted more and more attention. Especially the 2D Dirac materials, exhibiting ballistic charge transport, enormously high carrier mobility, and topological phases, offer potential applications for high performance electronic and spintronic devices. It has been also shown that highly anisotropic charge transport can be beneficial to graphene-based 2D devices. The highly anisotropic band dispersion around Fermi surface was also predicted in the VO2–TiO2 nanoheterostructures, characterized with a semi-Dirac band. Currently, there have been continued efforts in search of 2D materials including those with highly anisotropic Dirac states.

Among all the 2D Dirac materials, carbon (C) allotropes take up the largest portion, including graphene, rectangular graphenes, and graphynes. Different from graphene, graphynes contain both sp and sp^2 hybridized C atoms, being the biggest C allotrope family. It was first proposed by Baughman et al. in 1987, and recent calculations show that similar to graphene, some graphynes are Dirac materials, including α-, β-, δ-, 6,6,12-, 14,14,14-, 14,14,18-, 6,6,18-, and h-12,12,20-graphyne. On the other hand, some other 2D C structures, such as S-graphene, D-graphene, and E-graphene, were predicted to be Dirac materials, even though they have a nonhexagonal rectangular symmetry. However, it has been pointed out that no square symmetry C allotropes have been found to be Dirac materials.

In this work, we investigate the electronic properties of a family of square graphynes (S-graphynes) by using the first-principle calculations. We find that S-graphynes, containing two sizes of square C rings in one unit cell, turn out to be Dirac materials and exhibit highly anisotropic Dirac crescent near the Fermi level (E_F). They are characterized by a strongly varying Fermi velocity from 0.6 × 10^9 to 7.2 × 10^9 m/s along different k directions. Near the Dirac point, the highly anisotropic Dirac crescent can be nicely described by an effective 2 × 2 Dirac Hamiltonian. Finally, by fitting the tight-1

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layer is used and all atoms are fully relaxed until the residual forces on each atom are smaller than 0.001 eV/Å. The phonon frequencies are calculated by using a supercell approach as implemented in the PHONOPY code.32,33

Figure 1a and b show the schematic structures of two kinds of S-graphynes. One C4 ring and one C12 ring in the unit cell are indicated, which are connected with each other to form S-graphynes. In 4,12,2-graphyne (Figure 1a), two C rings are connected directly; in 4,12,4-graphyne (Figure 1b), two C rings are connected by an acetylene bond. There are three kinds of C bonds, which are marked by red color. Their bond lengths are about 1.45, 1.39, and 1.22 Å for 1, 2, and 3, respectively. Both S-graphynes have the plane group \( p4mm \), with lattice constant \( a_1 = 7.39 \) Å and formation energy \( E_1 = 9.03 \) eV/atom for 4,12,2-graphyne and \( a_2 = 10.99 \) Å and \( E_2 = 8.89 \) eV/atom for 4,12,4-graphyne, respectively. Their formation energies are comparable with graphdiyne, which has been synthesized in experiment.19 Some large molecules containing C4 and C12 rings have been synthesized,34–36 which may be used as the building blocks for S-graphynes. We also calculated phonon-dispersion curves of these two S-graphynes, as shown in Figure 1c and d, which show the absence of imaginary frequencies.

The calculated band structures and projected density of states (PDOS) of 4,12,4-graphyne are shown in Figure 2a. The main feature is a Dirac point at B point. Two linear bands cross at the \( E_F \) and located at an off-symmetry point \( [(0.5,0.1706)\times 2\pi/a_2] \) between M and X (right inset in Figure 2a). The PDOS (right panel of Figure 2a) show that the Dirac states near the \( E_F \) are predominantly contributed by \( p_z \) orbital of C. To see the band structure more clearly, we plot the 3D valence and conduction bands around the Fermi level for 4,12,4-graphyne.

It has been shown that acetylenic linkages in graphynes mainly mediate effective hopping between vertex \( p_z \) orbitals, which determine the existence/absence of Dirac cones in graphynes.17 Here, to describe such highly anisotropic Dirac crescent, we propose an effective 2 \( \times \) 2 Hamiltonian \( H(k) = \hbar(k) \cdot \tilde{\sigma} \)

\[
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\]

where \( \hbar(k) = (k^2/2m - v_x k_x v_y k_y 0) \), \( \tilde{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \). Then we have the dispersion relation of the S-graphynes as

\[
E = \pm \sqrt{\left(\frac{k_x^2}{2m} - v_x k_x\right)^2 + (v_y k_y)^2}.
\]

The 3D plot of the low-energy dispersion of this model is shown in Figure 3a, which captures the highly anisotropic properties of the band structures for 4,12,4-graphyne. Figure 3c and d show that this extended Dirac model Hamiltonian (red circles) provides a perfect description of the First-principles band structures (black line). The dispersion is linear along one direction \( (k_y = 0, \text{Figure 3d}) \) and also linear along the perpendicular direction \( (k_x = 0, \text{Figure 3c}) \) for small momentum \( (k_x \sim 0, \text{see Supporting Information Figure S2}) \) but is parabolic for large \( k_x \) (Figure 3c). This is slightly different from that of the semi-Dirac materials,9,16 which is linear along one direction and completely quadratic in the perpendicular direction. From the linear dispersions at the Dirac point, we obtain the effective mass and Fermi velocities to be \( m = 0.13 m_0, v_x = 0.8 \times 10^5 \) m/s and \( v_y = 7.2 \times 10^3 \) m/s for 4,12,4-graphyne and \( m = 0.16 m_0, v_x = 0.6 \times 10^5 \) m/s and \( v_y = 5.8 \times 10^3 \) m/s for 4,12,2-graphyne (Supporting Information Figure S3). Due to the particular crescent-like band structures of S-graphyne, highly directional transport of the electron beam...
is expected (highly anisotropic group velocities are shown in Supporting Information Figure S4 and S5).

To understand the physical origin of such high anisotropy, we tried to fit the DFT bands structure over a large energy window by incorporating different interactions in a tight-binding (TB) model. For the electronic states around the Fermi level are predominantly contributed by pₖ electrons and single-orbital hoppings are included. The TB Hamiltonian could be generally written as

$$H = \sum_{(i,j)} t_{ij}(C_i^\dagger C_j + h. c.)$$

where the operators $C_i^\dagger$ and $C_j$ are the creation and annihilation operators of electrons at site $i$, $(ij)$ denotes the sum over neighbors within the unit cell, and $t_{ij}$ stands for the hopping magnitude between sites $i$ and $j$. Considering the fact that a large number of C atoms are involved, to minimize the number of fitting parameters, we assume that the hopping magnitude scales with interatomic C–C distance as

$$t_{ij} = t_0 e^{-r_{ij} / r_0}$$

where $r_{ij}$ stands for the distance between sites $i$ and $j$, $r_0$ is the C–C bond length of graphene ($r_0 = 1.413$ Å).

Interestingly, we find that only if the next-nearest-neighbor hopping is included, we can get the accurate band structures in agreement with the first-principles results (see Supporting Information Table S1 and Figure S6). In Figure 4, we compare the 2D constant-energy contour of the TB model for 4,12,4-graphyne with the first-principles results as that in (a) but only considering the nearest-neighbor hopping interaction, whereas the nearest-neighbor interaction alone only produces a Dirac ring. Our findings enrich the Dirac physics founded in other 2D carbon allotropes and offer a new design mechanism for creating Dirac band by tuning the interaction range. We envision that this new type of Dirac crescent may be exploited in carbon-based electronic devices for manipulating anisotropic electron propagation.

**REFERENCES**


