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New nanoporous graphyne monolayer as nodal line semimetal: Double Dirac points with an ultrahigh Fermi velocity

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ABSTRACT

Two-dimensional (2D) carbon materials play an important role in nanomaterials. We propose a new carbon monolayer, named hexagonal-4,4,4-graphyne ($H_{4,4,4}$-graphyne), which is a nanoporous structure composed of rectangular carbon rings and triple bonds of carbon. Using first-principles calculations, we systematically studied the structure, stability, and band structure of this new material. We found that its total energy is lower than that of experimentally synthesized β-graphdiyne and it is stable at least up to 1500 K. In contrast to the single Dirac point band structure of other 2D carbon monolayers, the band structure of $H_{4,4,4}$-graphyne exhibits double Dirac points along the high-symmetry points and the corresponding Fermi velocities ($1.04-1.27 \times 10^6$ m/s) are asymmetric and higher than that of graphene. The origin of these double Dirac points is traced back to the nodal line states, which can be well explained by a tight-binding model. The $H_{4,4,4}$-graphyne forms a moiré superstructure when placed on top of a hexagonal boron nitride substrate. These properties make $H_{4,4,4}$-graphyne a promising semimetal material for applications in high-speed electronic devices.

1. Introduction

Monolayer graphene was first realized in 2004 [1] and since then two-dimensional (2D) carbon material research has played a crucial role in nanomaterials. Many kinds of 2D carbon allotropes have been proposed due to the huge flexibility of the carbon bonding. Graphdiyne [2], a special structure of graphyne, has been realized experimentally. Topological defects [3–5], which include non-hexagonal carbon rings, have been observed in graphene. Many more new 2D carbon allotropes have been predicted theoretically with novel crystal structures that can be classified into two general classes. The first are carbon monolayers that include some non-hexagonal carbon rings [6–8], such as Haeckelite $H_{5,6,7}$ [9]/phagraphene [10]/ψ-graphene [11] (5-6-7 rings), *T* graphene [12] (4-8 rings), and penta-graphene [13] (5 rings). These structures exhibit sp^2/sp^3 hybridization of the carbon atom. The second one are the carbon monolayers that have the triple bonds of carbon (-C≡C-) due to the *sp* hybridization of the carbon atom, such as $\alpha/\beta/\gamma/\delta$/6,6,12-graphyne [14–16], in which the carbon atoms (sp^2 hybridization)/hexagonal carbon rings are connected by -C≡C-. These 2D carbon allotropes show different fundamental physical and chemical properties. Not only their band structure changes from metal/semimetal to semiconductor, but also they can be used in many energetic and environmental applications, such as for gas separation [17], and for water desalination [18]. The abundant new 2D carbon structures also provide efficient inspiration for structural predictions of other elements [19], leading to many more new lattice structures with excellent properties. Although many 2D carbon allotropes have been predicted, combining structural properties of the above two classes have been scarce up to now [20–22].

The topologically nontrivial materials, such as topological semimetals, have attracted broad interest. There are three distinct kinds of topological semimetals: Dirac, Weyl, and nodal line semimetals [23]. For the nodal line semimetals, the band crossing points form a continuous Dirac loop with a relatively higher density of states at the Fermi level [24], which is an advantage for high-speed electronic devices. Many kinds of three-dimensional (3D) nodal line bulk materials, such as $PtSn_4$ [25], $PbTaSe_2$ [26], and ZrSiS [27,28], have been realized experimentally. Theoretically, $TlTaSe_2$ [29], 3D-honeycomb graphene networks [30], Ca_3P_2 [31,32], LnX

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(Ln = La, Gd; X = Cl, Br) [33], Cu_3PdN [34], and body-centered orthorhombic C_{16} [35], have been predicted to show nodal line states [36]. In contrast to the extended literature on 3D nodal line semimetals, the study of semimetal nodal line states in 2D materials is still in its infancy. This has only been confirmed experimentally in a Cu_2Si monolayer [37] and theoretical predictions of a nodal line band structure have been made for several 2D materials, such as Be_2C/BeH_2 [38], MX (M = Pd, Pt; X = S, Se, Te) [24], and A_3B_2 compound (A is a group-IIB cation and B is a group-VA anion, such as Hg_3As_2) [39]. Therefore, there is a need for more predictions of new 2D nodal line semimetals that are stable and can be realized experimentally.

In this work, we constructed a new graphyne monolayer with a hexagonal lattice using rectangular carbon rings and triple bonds of carbon. According to the naming rule of graphyne and its lattice feature, $H_{4,4,4}$-graphyne is obtained. Using first-principles calculations, we systematically investigated the structure, energy, stability, and electronic band structure of the $H_{4,4,4}$-graphyne monolayer. This monolayer shows a nanoporous structure and its total energy is almost equal to that of β-graphyne. The phonon spectrum provides convincing evidence for the dynamical stability of $H_{4,4,4}$-graphyne and our molecular dynamics (MD) calculations show that the monolayer is stable up to a high temperature. Different to the band structure with a single Dirac point as found in most other carbon monolayers, $H_{4,4,4}$-graphyne owns a band structure consisting of double Dirac points along the high-symmetry points with high Fermi velocities, which we confirm using different calculation methods. From an analysis of the orbital-projected band structure, we found that the p_z atomic orbitals of the carbon atoms are responsible for the double Dirac points in the $H_{4,4,4}$-graphyne monolayer. Using the p_z atomic orbitals, a tight-binding (TB) model was constructed, which not only reproduces the double Dirac points, but also shows that the physical origin of the double Dirac points can be traced back to the nodal line states. Finally, we show that the $H_{4,4,4}$-graphyne/hexagonal boron nitride (h-BN) moiré superstructure is a possible way of realizing the $H_{4,4,4}$-graphyne monolayer experimentally.

2. Calculation method

Our first-principles calculations were performed using the Vienna *ab initio* simulation package (VASP) code [40–42], implementing density functional theory (DFT). The electron exchange-correlation functional was treated by using the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE) [43]. The atomic positions and lattice vectors were fully optimized using the conjugate gradient (CG) scheme until the maximum force on each atom was less than 0.01 eV/Å. The energy cutoff of the plane-wave basis was set to 520 eV with an energy precision of 10^{-5} eV. The Brillouin zone (BZ) was sampled by using a $9 \times 9 \times 1$ Γ-centered Monkhorst-Pack grid. The vacuum space was set to at least 15 Å in all the calculations to minimize artificial interactions between neighboring slabs. The phonon spectrum was calculated using a supercell (4×4) approach within the PHONOPY code [44].

3. Results and discussions

3.1. Structure

The investigated graphyne monolayer is shown in Fig. 1(a). Its hexagonal framework structure is composed of rectangular carbon rings, connected by the triple bonds of carbon. The carbon atoms in the rectangular carbon rings are close to sp^2 hybridization, because the angle of the two neighboring single bonds of carbon (-C–C-) is not equal to 120° while the carbon atoms in the -C≡C- are close to *sp* hybridization, because the four carbon atoms (-C–C≡C–C-) are not located in a strict straight line. According to the naming rule of graphyne [45], the new graphyne should be named as 4,4,4-graphyne. To distinguish the rectangular graphyne (R-graphyne) [46], which can also be called as 4,4,4-graphyne using the naming rule of graphyne, we call our proposed graphyne hexagonal-4,4,4-graphyne ($H_{4,4,4}$-graphyne). Most new predicted graphyne structures are based on the hexagonal graphene structure by inserting triple bonds of carbon, such as 6,6,12-graphyne [16], 14,14,14-graphyne [47], and α-graphyne (α-2/α-3/α-4 graphyne) [48,49], while those with non-hexagonal carbon rings are rather exceptional [20–22,46]. Here, we provide a novel structure model in which the rectangular carbon rings and triple bonds of carbon can coexist, providing a novel structure model for new stable carbon monolayers.

The lattice of the $H_{4,4,4}$-graphyne is not only a hexagonal lattice, but also a kagome lattice [39], which is formed by all the centers of the rectangular carbon rings. Its lattice constant is 11.82 Å. There are four kinds of bond lengths, which are labeled l_1, l_2, l_3, and l_4, as shown in Fig. 1(a). The $l_1 = 1.247$ Å is the length of the carbon triple bond, which is formed by two carbon atoms close to *sp* hybridization and the value of l_1 is close to that of the other graphyne structures [14]. All the other carbon atoms are close to sp^2 hybridization with bond lengths, $l_2 = 1.351$ Å, $l_3 = 1.453$ Å, and $l_4 = 1.489$ Å. Since $H_{4,4,4}$-graphyne can be regarded as inserting -C≡C- into the -C–C- of graphenylene that are shared by 6 and 12 carbon rings [17], the graphenylene bond lengths (1.367/1.474/1.473 Å) are close to those of our structure ($l_2/l_3/l_4$). The nanoporous graphenylene membrane has been theoretically predicted to achieve efficient $^3He/^4He$ separation for industrial applications [17], while the graphyne membrane has been proposed for water desalination [18]. Besides these carbon monolayers, the C_2N-*h*2D [50] and g-C_3N_4 [51] membranes have also been proposed for separation applications, depending on their nanoporous structure. The diameter $d = 9.30$ Å of the circumcircle (red dotted line in Fig. 1(a)) of the 24 carbon ring of $H_{4,4,4}$-graphyne is much larger than the one of other monolayers (5.49 Å for graphenylene [17], 6.90 Å for graphyne-3 [18], 5.51 Å for C_2N-*h*2D [50], and 4.76 Å for g-C_3N_4 [51]) and is comparable to that of the well-known covalent organic frameworks, which have been shown to have potential for a wide range of applications in gas/liquid separation [52].

3.2. Energy and stability

Introducing *sp*-hybridized carbon atoms can increase the system total energy (E_t in units of eV per carbon atom) of carbon allotropes. Graphene shows the lowest E_t in all the carbon allotropes while the graphyne structures have a higher E_t due to the presence of *sp*-hybridized carbon atoms [15]. Setting n (N) as the number of *sp*-hybridized carbon atoms (total carbon atoms) in the unit cell, we calculated the ratio n/N. For γ-graphyne, β-graphyne, and α-graphyne, E_t increases with the value of this ratio (Table 1). However, $H_{4,4,4}$-graphyne shows the same ratio (0.50) as γ-graphyne, but its E_t is higher than that of γ-graphyne and comparable to that of β-graphyne. This can be ascribed to the special structure of $H_{4,4,4}$-graphyne. In contrast to fully sp^2-hybridized carbon atoms of γ-graphyne in which the three angles of the two neighboring single bonds are all 120° [14], the three angles in our structure are 140.1° (belonging to the 24 carbon ring), 129.9° (belonging to the 12 carbon ring), and 90° (belonging to the 4 carbon ring), which leads to an increase of E_t. Similar situations can apply to the *sp*-hybridized carbon atoms, where the angle between single bond and triple bond of $H_{4,4,4}$-graphyne becomes 170.1° (belonging to the 12 carbon ring) instead of 180° of γ-graphyne. Although $H_{4,4,4}$-graphyne