The roles of π electrons in the electronic structures and optical properties of graphyne

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The electronic structures and optical properties of graphyne consisting of sp - and sp^2 -hybridized carbon atoms are studied using first-principles calculations. A tight-binding model of the $2p_z$ orbitals are proposed to describe the electronic bands near the Fermi level. The results show that the natural band gap of graphyne originates from the inhomogeneous π bindings between differently-hybridized carbon atoms. The interlayer interactions of bulk graphyne narrow the band gap to 0.16 eV and result in redshift of the optical spectral peaks as compared to single-layered graphyne.

graphyne, electronic structure, tight-binding model, first-principles calculation

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The successful fabrication of graphene [1] has aroused increasing interest worldwide due to its intriguing electronic properties and promising applications in electronics [2,3]. Graphene-based electronics promise to overcome the limitations of silicon technologies [4], and may even replace silicon in future solid state devices [5]. However, semimetallic graphene requires modification to open up a band gap which is essential for logic circuits [6] and other electronic device applications. Different attempts, such as hydrogenating graphene to graphane [7–9], patterning graphene into nanoribbon [10], forming graphene quantum dots [11], and applying uniaxial strain on graphene [12], have been made to reach this goal. Up to now, tuning the band gap of graphene in a wide range remains challenging. Therefore, searching for novel carbon allotropes with layered structures and a natural band gap is desirable.

Graphyne is another hypothetical carbon allotrope proposed by Baughman et al. [13], which consists of sp - and sp^2 -hybridized carbon atoms. It is well-known that π -conjugated molecules are promising candidates for molecular-based electronics [14,15]. In contrast to graphene with

identical π bindings, graphyne has three types of π bindings, $C(sp^2)-C(sp^2)$, $C(sp)-C(sp^2)$, and $C(sp)-C(sp)$, as shown in Figure 1. A number of theoretical calculations on graphyne monolayer [13,16–19] and graphyne-related nanomaterials [20–22] have been performed to reveal their unique properties and potential applications. First-principles calculations showed that single-layered graphyne is semiconducting with a small direct band gap of ~ 0.5 eV at M point [16]. The natural band gap feature has also been found

Figure 1 (Color online) Top view of single-layered graphyne in a 2×2 supercell. The dashed lines indicate a unit cell. C_1 and C_2 represent the sp^2 - and sp -hybridized carbon atoms, respectively.

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in other two-dimensional carbon-based materials, such as polyphenylene [23]. However, the origination of the natural band gap in graphyne remains unclear. How the inhomogeneous π bindings in graphyne network affect the electronic and optical properties of graphyne has never been addressed in previous works. Compared with the great successes of tight-binding (TB) model in reproducing the electronic properties of graphene, the TB model of graphyne which is very important for revealing its unique properties has not been proposed to date. Theoretical works on these issues are quite interesting from the points of view of basic research and potential applications of graphyne in building nano-devices.

In this contribution, based on first-principles calculations and tight-binding model, we demonstrate that the features of the bands in proximity to the Fermi level of graphyne are mainly dominated by the π electrons, which possess two band gaps locating at M ($1/2, \sqrt{3}/6)(2\pi/a_0)$ and M^* ($4/9, 0$) ($2\pi/a_0$) points (a_0 is the lattice constant of graphyne), respectively. The weak π binding between $C(sp)-C(sp^2)$ compared to other π binding opens a small band gap at M point, while the band gap at M^* is the feature of graphyne lattice. These two band gaps are responsible for the highest peaks in the absorption spectrum at low energy region. The interlayer interactions in bulk graphyne narrow the band gap and result in redshift of optical spectral peaks, compared to the single-layered graphyne. The dual-band-gap feature of the π electrons in graphyne may find applications in future electronic and optoelectronic devices.

1 Methods and computational details

We performed first-principles calculations using the plane wave basis Vienna *ab initio* simulation package known as VASP code [24], implementing the density functional theory (DFT) and the projector-augmented wave (PAW) pseudopotentials [25,26]. The electron-electron interaction was treated within the generalized gradient approximation (GGA) in the form of PW91 exchange-correlation functional [27]. The positions of all the atoms and the size of the supercell were fully optimized without any symmetric restrictions, using conjugate gradient (CG) procedures. The energy cut-off adopted for plane wave expansion of electron wave functions of C atoms is 400 eV. Two-dimensional periodic boundary conditions were applied to the single-layered graphyne while a vacuum spacing of 20 Å was set along the direction perpendicular to the graphyne basal plane to avoid the mirror interaction. For structural optimization, the Brillouin zone (BZ) was sampled on grids of $6 \times 6 \times 1$ k -points within the Monkhorst-Pack scheme [28]. Forces were converged to 0.02 eV/Å and the total energy was obtained with 0.1 meV precision. Based on the optimized configurations, band structures were calculated using $10 \times 10 \times 1$ Monk-

horst-Pack k -grid. For three-dimensional (3D) graphyne, the structural optimization and band structures were calculated using $6 \times 6 \times 6$ and $10 \times 10 \times 10$ Monkhorst-Pack k -grid, separately.

2 Results and discussion

The atomic structure of graphyne can be described by replacing one-third of the carbon-carbon bonds in graphene by $-C \equiv C-$ linkage. Obviously, there are two nonequivalent carbon atoms in graphyne network. One is sp^2 -hybridized (labeled as C_1) forming hexagons and another is sp -hybridized (labeled as C_2) connecting the hexagons, as shown in Figure 1. In the optimized configuration, the bond length between two sp^2 -hybridized carbon atoms is 1.42 Å, suggesting that the π -conjugate feature of graphene is kept in the hexagons. The short distance between sp -hybridized carbon atoms (1.22 Å) in the chain indicates that a $C \equiv C$ triple bond is formed between them. It is noteworthy that the bond length between C_1 and C_2 atoms (1.40 Å) is much shorter than that of the typical single bond (~ 1.5 Å), implying the π binding between them. The optimized lattice constant a_0 is 6.86 Å, in good agreement with other DFT calculations [16]. Due to the existence of two-fold coordinated (sp -hybridized) carbon atoms in graphyne, it is energetically unfavorable than graphene by about 0.63 eV/atom. However, our results indicate that graphyne is energetically more stable than the already-synthesized graphdiyne [29] by about 0.19 eV/atom.

The carbon-carbon bond length distribution in graphyne suggests that the coupling between $C(2p_z)$ orbitals forms conjugate π orbitals on the graphyne basal plane. How the π -conjugated orbitals dominate the electronic structure of graphyne becomes quite interesting. Figure 2 shows the

Figure 2 Calculated band lines of single-layered graphyne along high symmetry points in the region near the Fermi level. The Fermi level is indicated as the dot line. The second maximum (minimum) of the valence band (conduction band) is located at M^* . VB_1 (CB_1) and VB_2 (CB_2) represent the nearest and the second nearest valence (conduction) band to the Fermi level, respectively.

calculated band structure of single-layered graphyne. Different from zero-band-gap graphene, graphyne has a small band gap of 0.46 eV at M ($1/2, \sqrt{3}/6$)($2\pi/a_0$) point and a large band gap at M^* ($4/9, 0$)($2\pi/a_0$) point which is one-third from the K ($2/3, 0$)($2\pi/a_0$) to the Γ ($0, 0$)($2\pi/a_0$) point. The effective masses of the valence (m_v) and conduction (m_c) bands at these two points along different directions are: $m_c(\Gamma-M) = 0.25 m_0$ and $m_v(\Gamma-M) = 0.28 m_0$, $m_c(K-M) = 0.11 m_0$ and $m_v(K-M) = 0.12 m_0$, $m_c(K-M^*) = 0.19 m_0$ and $m_v(K-M^*) = 0.22 m_0$, $m_c(\Gamma-M^*) = 0.13 m_0$ and $m_v(\Gamma-M^*) = 0.15 m_0$, respectively, where m_0 is the mass of a free electron. The anisotropic effective masses are very small compared to typical semiconductors, indicating high carrier mobility of this material. This is in good agreement with the experimental findings in graphdiyne [29].

It is interesting to see that although both graphene and graphyne have conjugated π electrons, their electronic band structures differ significantly. To reveal the origination of such difference, we plotted the valence electron density isosurfaces of graphene and graphyne in Figure 3(a) and (b). It is clear that the valence electrons in graphene are dispersive, whereas those in graphyne are somewhat localized, especially in the region between C_1 and C_2 . To illustrate this difference more clearly, we plotted the isosurfaces of the charge density projected onto the VB_1 and CB_1 states at M point, and onto the VB_2 and CB_2 states at M^* point in Figure 3(c)–(f), where VB_1 (CB_1) and VB_2 (CB_2) represent the nearest and the second nearest valence (conduction) band to the Fermi level, respectively. Obviously, these states originate from the $C(2p_z)$ orbitals perpendicular to the graphyne plane. The VB_1 state arises from the π interaction between the sp^2 -hybridized atoms (in hexagons) and between sp -hybridized carbon atoms (the two atoms connecting the hexagons), whereas the CB_1 state comes from π interaction between $C(sp^2)$ and $C(sp)$. Similar features have also been found for the VB_2 and CB_2 states at M^* point. This suggests that the π binding strengths are no longer identical in graphyne, which may be responsible for the opening of the small band gap at M point.

To address the origination of the dual-band-gap feature

Figure 3 (Color online) The isosurfaces of the total charge density of graphene (a) and single-layered graphyne (b). Isosurfaces of the charge density of the states corresponding to the VB_1 , CB_1 at M point and VB_2 , CB_2 at M^* point are plotted in (c)–(f), respectively. The isovalues of (a), (b) and (c), (f) are 0.25 and 0.01 $e/\text{\AA}^3$, respectively.

of graphyne, we present a simple TB model. Because DFT calculations have shown that the band lines in the vicinity of Fermi level are mainly contributed by the $C(2p_z)$, only the p_z orbitals are taken into account in this TB model for simplicity. According to nearest-neighboring approximation, the electron hopping between adjacent sites can be characterized by three parameters: t_1 , t_2 , and t_3 , which correspond to the hopping integrals between $C(sp^2)-C(sp^2)$, $C(sp^2)-C(sp)$, and $C(sp)-C(sp)$, respectively, as shown in Figure 4(a). A Hamiltonian with a 12×12 dimensionality can be constructed. By diagonalizing this Hamiltonian at different wave vectors (k), band structures are obtained, as shown in Figure 4(b) and (c). Obviously, the profiles of the band lines depend on the nearest-hopping integrals: t_1 , t_2 , and t_3 . The hopping integral t_1 between $C(sp^2)$ atoms is 2.7 eV in graphene [30], but the values of t_2 and t_3 have not been reported. If the π bindings throughout graphyne are identical, i.e. $t_1=t_2=t_3$, the valence (π) and conduction (π^*) bands touch at M point, as shown in Figure 4(b), whereas the band gap at ($4/9, 0$)($2\pi/a_0$) point still exists. However, when t_2 and t_3 are different from t_1 , corresponding to inhomogeneous π - π interaction, a small band gap appears at M point, as shown in Figure 4(c). The different bond lengths between $C(sp^2)-C(sp^2)$, $C(sp^2)-C(sp)$, and $C(sp)-C(sp)$ revealed by first-principles calculations suggest that t_1 , t_2 , and t_3 are different. The band gaps and band line profiles of first-principles calculations can be well fitted by our TB model using the parameters: $t_1=2.7$ eV, $t_2=2.6$ eV, and $t_3=2.97$ eV. The TB band gaps are 0.45 and 1.51 eV, in good agreement with the results of first-principle calculations, 0.46 and 1.44 eV. Moreover, our TB model shows that the band gaps increase with increasing differences between t_1 and t_2 , and between t_1 and t_3 . Similar phenomenon also appears in finite-width armchair graphene nanoribbon [31], where the hopping parameter (resulting from the added chemical groups) can significantly affect the electronic properties. For example, for the ribbon width $n=3p+1$, the energy gap of hopping parameter $t_1=t=2.7$ eV is zero, which becomes independent of ribbon width n . But for $t_1=1.2t$, the energy gaps open and gradually decrease as the increase of ribbon width. Both first-principles calculations and TB model demonstrated that the states contributed by the π interaction of $2p_y$ orbitals on the graphyne basal plane between $C(sp)-C(sp)$ are highly localized and the corresponding band lines are away (>2 eV) from the Fermi level.

Figure 5 shows the electron density of states (DOS) of graphyne in the vicinity of Fermi level. In this region, the valence bands and conduction bands can be characterized as several peaks (labeled V_1 , V_2 , V_3 , and V_4 and C_1 , C_2 , C_3 , C_4 , and C_5 , respectively). The appearance of the band gaps and the peaks in DOS will affect the optical properties of graphyne. In this contribution, we study the optical properties of graphyne by calculating the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. A knowledge of $\epsilon_2(\omega)$ allows us to obtain $\epsilon_1(\omega)$ using the Kramers-Kronig relation and $\epsilon_2(\omega)$

Figure 4 (a) t_1 , t_2 and t_3 represent the hopping integral between $C(sp^2)-C(sp^2)$, $C(sp^2)-C(sp)$, and $C(sp)-C(sp)$, respectively. Calculated band lines using homogeneous hopping integrals: $t_1=t_2=t_3=2.7$ eV (b), and inhomogeneous hopping integrals: $t_1=2.7$ eV, $t_2=2.6$ eV, $t_3=2.97$ eV (c).

Figure 5 Calculated DOS of single-layered graphyne. The Fermi level is indicated as the dot line.

can be written as [32]

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega) \times \langle u_{ck+e_{\alpha}q} | u_{vk} \rangle \langle u_{ck+e_{\beta}q} | u_{vk} \rangle^*,$$

where the indices c and v refer to conduction and valence band states respectively, and u_{ck} is the cell periodic part of the wavefunctions at the k -point $\mathbf{k}$. Figure 6(a) and (b) represent the real part $\varepsilon_1(\omega)$ and imaginary part $\varepsilon_2(\omega)$, respectively. Due to the interband transition, the peak of real part reduces and approaches to the minimum at about 1.48 eV, as shown in Figure 6(a). Unlike graphene with negligible static dielectric constant $\varepsilon_1(0)$, the $\varepsilon_1(0)$ of graphyne is found to be 7.3. It is also much higher than that of C_{60} with a direct band gap of 1.34 eV, which is 4.4 [33].

The imaginary part $\varepsilon_2(\omega)$ of the dielectric function reflects the optical absorption properties of graphyne. Our calculations show that the first prominent peak of $\varepsilon_2(\omega)$ locates at about 0.58 eV, corresponding to the small band gap at M point, which is the threshold for direct optical transitions between the valence band maximum (VBM) and the conduction band minimum (CBM). The absorption intensity decreases with increasing photon energy with no noticeable absorption beyond 8 eV. The spectrum consists of seven

Figure 6 Calculated real part of the dielectric function of single-layered graphyne (a), and imaginary part of the dielectric function of single-layered and bulk graphyne (b). Seven absorption peaks are labeled as A, B, C, D, E, F, and G, respectively. The ε_2 of single-layered graphyne is enlarged to ten times for clearly seen.

major structures (labeled A, B, C, D, E, F, and G), which can be assigned to the direct transition between occupied states and empty states as follows: A, the gap; B, $V1 \rightarrow C1$; C, $V2 \rightarrow C1$; D, $V4 \rightarrow C1$; E, $V1 \rightarrow C5$; F, $V3 \rightarrow C3$; G, $V2 \rightarrow C4$. The corresponding energies are shown in Table 1 for comparison. The energies of the peaks agree well with that of the transition energies.

To reveal the effects of interlayer coupling on the electronic and optical properties of graphyne, we calculated a

Table 1 The energies of absorption peaks and those of the transitions from valence bands to conduction bands

Absorption peaks	Energy (eV)	Transitions	Energy (eV)
A	0.58	Band gap	0.46
B	1.41	V1→C1	1.43
C	2.61	V2→C1	2.78
D	3.62	V4→C1	3.59
E	4.95	V1→C5	5.05
F	5.82	V3→C3	6.01
G	6.20	V2→C4	6.10

bulk graphyne by applying three-dimensional periodic conditions. The supercell contains two graphyne layers with AB stacking sequence, which has been predicted as the most stable configuration of bulk graphyne [20]. Our calculations show that bulk graphyne has a small band gap of only 0.16 eV. The isosurfaces of the charge density projected onto the VBM and the CBM exhibit the same features as those of single-layered graphyne. The smaller band gap of bulk graphyne than that of single-layered graphyne is due to the interlayer interaction in bulk graphyne. Similar results have also been found in graphite where the interlayer interactions result in band overlap and semimetallic behaviors of graphite [34]. The interlayer interactions also affect the optical properties of graphyne. The dotted line in Figure 6(b) represents the $\varepsilon_2(\omega)$ of bulk graphyne on the basal plane. It is evident that the $\varepsilon_2(\omega)$ of bulk graphyne has similar profile as that of single-layered graphyne, but the intensity of the first-peak is greatly increased compared to others. There is redshift of about 0.3 eV for the first-two peaks, which can be attributed to the interlayer coupling. It is noteworthy that in the present DFT calculations, neither generalized gradient approximation nor local density approximation functional can reproduce the binding energy and interlayer distance of layered materials [35,36], due to their faults in describing the van der Waals' forces between layers. However, the variation trend of band gap of bulk graphyne in response to interlayer interaction revealed in this work is expected to be reasonable.

3 Conclusions

In summary, our first-principles calculations and TB model show that both single-layered and bulk graphynes are semiconductors with a moderate gap. The band gap originates from the inhomogeneous π - π binding between differently-hybridized carbon atoms. The effective masses of graphyne in the region near the band gaps are considerably small compared to typical semiconductors. The two main peaks in the $\varepsilon_2(\omega)$ spectrum can be attributed to the direct transition between occupied and empty states at the small and large band gaps. The interlayer interactions in bulk graphyne narrow the band gaps, resulting in redshift of the two main peaks of $\varepsilon_2(\omega)$ spectrum.

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- Novoselov K S, Geim A K, Morozov S V, et al. Electric field effect in atomically thin carbon films. *Science*, 2004, 306: 666–669
- Schedin F, Geim A K, Morozov S V, et al. Detection of individual gas molecules adsorbed on graphene. *Nat Mater*, 2007, 6: 652–655
- Silvestrov P G, Efetov K B. Quantum dots in graphene. *Phys Rev Lett*, 2007, 98: 016802
- Lin Y M, Dimitrakopoulos C, Jenkins K A, et al. 100-GHz transistors from wafer-scale epitaxial graphene. *Science*, 2010, 327: 662
- Geim A K, Novoselov K S. The rise of graphene. *Nat Mater*, 2007, 6: 183–191
- Appelhaus D J, Lin Z B, Lusk M T. Two-dimensional carbon semiconductor: Density functional theory calculations. *Phys Rev B*, 2010, 82: 073410-1
- Elias D C, Nair R R, Mohiuddin T M G, et al. Control of graphene's properties by reversible hydrogenation: Evidence for graphane. *Science*, 2009, 323: 610–613
- Li Y F, Chen Z F. Patterned partially hydrogenated graphene (C_4H) and its one-dimensional analogues: A computational study. *J Phys Chem C*, 2012, 116: 4526–4534
- Li Y F, Zhou Z, Shen P W, et al. Structural and electronic properties of graphane nanoribbons. *J Phys Chem C*, 2009, 113: 15043–15045
- Han M Y, Ozyilmaz B, Zhang Y B, et al. Energy band-gap engineering of graphene nanoribbons. *Phys Rev Lett*, 2007, 98: 206805
- Ma W L, Li S S. Electrically controllable energy gaps in graphene quantum dots. *Appl Phys Lett*, 2012, 100: 163109
- Ni Z H, Yu T, Lu Y H, et al. Uniaxial strain on graphene: Raman spectroscopy study and band-gap opening. *ACS Nano*, 2008, 2: 2301–2305
- Baughman R H, Eckhardt H, Kertesz M. Structure-property predictions for new planar forms of carbon: Layered phases containing sp^2 and sp atoms. *J Chem Phys*, 1987, 87: 6687–6699
- Joachim C, Gimzewski J K, Aviram A. Electronics using hybrid-molecular and mono-molecular devices. *Nature*, 2000, 408: 541–548
- Carroll R L, Gorman C B. The genesis of molecular electronics. *Angew Chem Int Ed*, 2002, 41: 4378–4400
- Narita N, Nagai S, Suzuki S, et al. Optimized geometries and electronic structures of graphyne and its family. *Phys Rev B*, 1998, 58: 11009–11014
- Tahara K, Yoshimura T, Sonoda M, et al. Theoretical studies on graphyne substructures: Geometry, aromaticity, and electronic properties of the multiply fused dehydrobenzo [12] annulenes. *J Org Chem*, 2007, 72: 1437–1442
- Narita N, Nagai S, Suzuki S. Potassium intercalated graphyne. *Phys Rev B*, 2001, 64: 245408
- Zhang H Y, Zhao M W, He X J, et al. High mobility and high storage capacity of lithium in sp - sp^2 hybridized carbon network: The case of graphyne. *J Phys Chem C*, 2011, 115: 8845–8850
- Narita N, Nagai S, Suzuki S, et al. Electronic structure of three-dimensional graphyne. *Phys Rev B*, 2000, 62: 11146–11151
- Coluci V R, Braga S F, Legoas S B, et al. Families of carbon nanotubes: Graphyne-based nanotubes. *Phys Rev B*, 2003, 68: 035430
- Bu H X, Zhao M W, Zhang H Y, et al. Isoelectronic doping of graphdiyne with boron and nitrogen: Stable configurations and band gap modification. *J Phys Chem A*, 2012, 116: 3934–3939
- Li Y F, Zhou Z, Shen P W, et al. Two-dimensional polyphenylene: Experimentally available porous graphene as a hydrogen purification membrane. *Chem Commun*, 2010, 46: 3672–3674
- Kresse G, Furthmüller J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys Rev B*, 1996, 54: 11169–11186
- Blöchl P E. Projector augmented-wave method. *Phys Rev B*, 1994, 50: 17953–17979

- 26 Kresse G, Joubert D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys Rev B*, 1999, 59: 1758–1775
- 27 Perdew J P, Wang Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys Rev B*, 1992, 45: 13244–13249
- 28 Monkhorst H J, Pack J D. Special points for Brillouin-zone integrations. *Phys Rev B*, 1976, 13: 5188–5192
- 29 Li G X, Li Y L, Liu H B, et al. Architecture of graphdiyne nanoscale films. *Chem Commun*, 2010, 46: 3256–3258
- 30 Reich S, Maultzsch J, Thomsen C. Tight-binding description of graphene. *Phys Rev B*, 2002, 66: 035412
- 31 Wang Z F, Li Q X, Zheng H X, et al. Tuning the electronic structure of grapheme nanoribbons through chemical edge modification: A theoretical study. *Phys Rev B*, 2007, 75: 113406
- 32 Gajdoš M, Hummer K, Kresse G, et al. Linear optical properties in the projector-augmented wave methodology. *Phys Rev B*, 2006, 73: 045112
- 33 Ching W Y, Huang M Z, Xu Y N, et al. First-principles calculation of optical properties of C60 in the fcc lattice. *Phys Rev Lett*, 1991, 67: 2045–2048
- 34 Partoens B, Peeters F M. From graphene to graphite: Electronic structure around the K point. *Phys Rev B*, 2006, 74: 075404
- 35 Fan Y C, Zhao M W, Wang Z H, et al. Tunable electronic structures of graphene/boron nitride heterobilayers. *Appl Phys Lett*, 2012, 98: 083103
- 36 Marom N, Bernstein J, Garel J, et al. Stacking and registry effects in layered materials: The case of hexagonal boron nitride. *Phys Rev Lett*, 2010, 105: 046801

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