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Confinement massless Dirac Fermions in graphene matrix induced by the B/N heteroatoms

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this work, the systems are constructed with the defect lines of B-B or N-N dimers embedded in graphene matrix using density function theory. It is found that the Dirac-cone dispersions appear at the Fermi level in the bands introduced by the B or N heteroatom, linear B-B or N-N dimers, demonstrating that the carriers mobility are $\sim 10^6$ m/s which are comparable with the pristine graphene. Most importantly, such dimer lines act as the quasi-1-D conducting nanowires which the charge carriers are confined around the linear defects with these dimers while the charge carriers in pristine graphene are dispersed two-dimensionally. Such systems suggest that heteroatoms in graphene can indeed make their contribution to Dirac cone. In addition, the type of carriers (*p*-type or *n*-type) can be manipulated using the B or N heteroatoms, respectively. This will greatly enrich electronic properties of Dirac semimetals.

Introduction

As microelectronic devices continue to diminish in size to achieve higher speeds, the design parameters of the devices have pushed the current used materials to the limits. To maintain the rate of device shrinkage without scarifying the overall performance goals, the conventional field effect transistors in semiconductor devices will eventually reach a natural performance limit associated with the fundamental issues in energy loss and heat dissipation etc.¹ Graphene has been recognized as a potential candidate to replace the silicon for next-generation material in the semiconductor technology.²⁻⁴ Based on *k*-*p* theory,⁵ the performance of semiconductor devices can be improved significantly by reducing the effective mass of electrons. The intrinsic band structure of pristine graphene has linear energy dispersion at the Fermi level, implying that the charge carriers are 2-D massless fermions. It indicates that the carriers in graphene have an effective 'speed of light' of $\sim 10^6$ m/s. In order to engineer the graphene transistor into the integrated circuits, it is important to develop graphene containing heteroatoms besides carbon with interesting electronic properties than pristine graphene to improve the performance of graphene-based electronics significantly.

By only changing geometric structure of graphene, the electronic properties can be tailored. However, the Dirac point disappears when the perfect bipartite symmetry of honeycomb lattice in 2-D graphene is broken, for example, in 0-D quantum graphene dots and 1-D graphene nanoribbons.^{6,7} Thus, in order to develop the high quality devices, Prof. Louie and his co-

operators have created a graphene superlattice with an external periodic potential,⁸ which leads to the anisotropic behaviours of massless Dirac fermions depending on the potential barrier height and width. Although this route can control the propagation of charge carrier along a particular direction, the distribution of spatial charge carriers is not confined to the narrow space. The structure of 5-5-8 line defect, which is formed by stitching the two graphene domains with a C-C dimer line, has been prepared experimentally.⁹ Such linear defect can act as a metallic-like nanowire in graphene. It raised a question in whether this nanowire can be further developed to tunnel the charge carriers by enhancing their mobility significantly.

Recently, some other 2-D graphene allotropes possessing Dirac cones can be created according to electronic structure calculations.^{10,11} It is believed that the symmetry of hexagonal lattice are not the fundamental requirement for the Dirac dispersion of carriers. Although 2-D graphynes containing heteroatoms are also exhibited to feature Dirac points in their band structure, such heteroatoms do not contribute to Dirac cone at all.¹⁰ A question of fundamental interest is whether heteroatom can indeed make its contribution to Dirac cone. Doping B or N into the graphene is commonly used to modulate the electronic and transport properties of graphene.¹² This is because B or N atom has one less or more electron than C atom with comparable atomic size. For B/N doped graphene, the band gap could be opened since the density of state near the Fermi level is suppressed.¹³ Such B or N dopant in graphene can be regard as an acceptor or a donor dopant, thus a *p*-/*n*-type

doping behaviour is exhibited while maintaining considerably good mobility and conductivity.^{14,15} Therefore, B/N doped graphene has shown a range of applications in *p*-/*n*-type graphene-based field-effect transistors,¹⁶ electrochemical biosensors,¹⁷ and so on. The structure of 5-5-8 line defect in graphene is easily attacked by N dopant.^{18,19} The magnetization can be induced or annihilated by the suitable doping, and the magnetic moment depends on the doping sites. In this work, we investigated the electronic structures in the systems that the linear defect of C-C dimers is replaced by the B-B and N-N dimers, respectively, using density functional theory (DFT). The holes or electrons introduced by the B or N dopants can be attracted by the ionic B- or N+ and also the coordinated zigzag edges,¹² thus pulling away the localized states near the Fermi level from the lower energy zone. Such a phenomenon is associated with the correlation effect and Dirac character to re-appear at the Fermi level. As the confinement effect, it opens the band-gap of the rest part of graphene, thus confining the new carriers (holes or electrons) to move along the linear defects with an ultra-high mobility.

Methods and Models

In this work, the calculations of geometrical optimization and electronic bands were conducted using DFT by DMOL3 code.²⁰ In the DFT calculations, the all-electron Kohn–Sham wavefunctions were expanded in the double numerical polarized atomic orbital basis, and the generalized gradient approximation with the Perdew–Burke–Ernzerh of describing the exchange and correlation energy was employed.²¹ Self-consistent field procedure was done until the change of energy was less than 10^{-6} Hartree, and the geometrical optimization of the structure was done with an energy convergence criterion of 10^{-5} Hartree. For band structure calculations, the sampling of was carried out with $0.001\text{\AA}^{-1}$ between consecutive *k*-points on the reciprocal space path. Calculations using CASTEP²² code were performed for electronic orbitals induced by the bands close to Fermi level at the low-energy zone (range about from ~ -0.4 eV to ~ 0.4 eV), containing occupied and unoccupied orbitals. In addition, VASP²³ code was also employed to understand the behavior of electronic orbitals at the Dirac point.

It is well known that the standard DFT underestimates the band gap for semiconductor and insulator substantially. The so-called screened exchange, or sX-LDA scheme, may be required to understand the properties of semiconductors and insulators. Their calculations are exceedingly expensive in terms of memory usage and time. However, for semimetal materials (e.g. graphene, graphyne, janugraphene, chlorographene and other graphene allotropes),^{10,11,24} Dirac cones could be predicated by standard DFT calculations. All stable structures in this work were achieved by sufficient relaxation including cell lattices. The band structures with and without relaxing cell lattices were also compared in ESI Fig. S1. The difference between their energy bands is tiny, which indicates that such electronic structures originate in special atomic arrangement.

The dynamic stability of new structures had also been examined by the molecular dynamic in DMOL3 code.²⁰ The constant temperature and volume (NVT) ensemble was used with time steps of 3fs for a total simulation time of 3ps at 300 K.

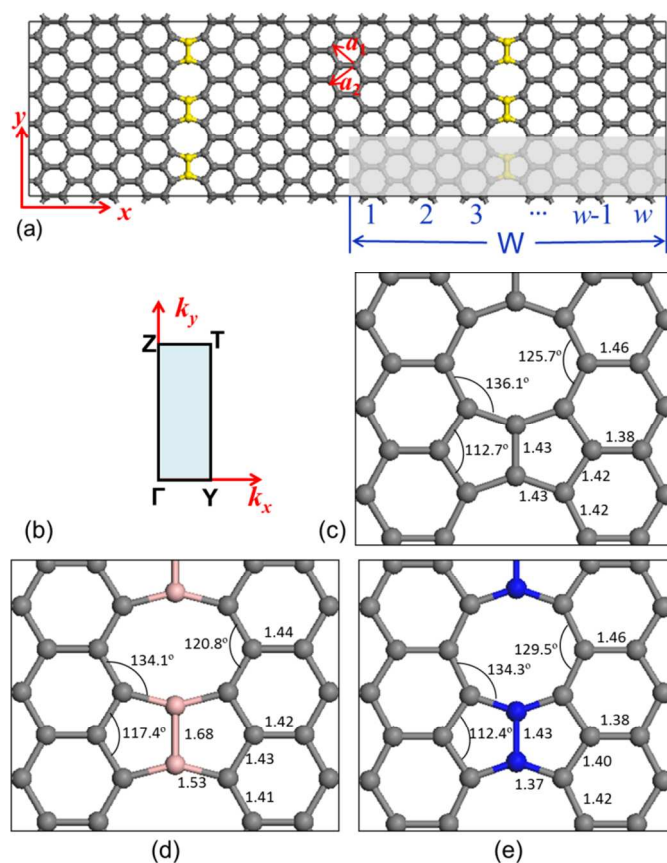


Fig. 1 (a) Schematic illustration shows the structure of linear C-C dimer in graphene. (b) The special high symmetry points for energy dispersion calculations in the Brillouin zone. The DFT relaxed geometries of the (c) C-C dimer, (d) B-B dimer, and (e) N-N dimer systems, including bond lengths (in $\text{\AA}$) and bond angles, are exhibited.

In order to investigate the energy band structure, the system with C-C dimer lines periodically embedded in graphene was illustrated in Fig. 1(a). The C-C dimers are denoted by yellow balls. These linear topological defects contain 5-5-8 rings, and the structure exhibits translational symmetry along the defect. The shadow zone is the primitive cell, and its width (*W*) is defined by the number of hexagon along its width. The high symmetric path is Γ -Z-T-Y-G for the calculations of energy bands as shown in Fig. 1(b). It is noted that the two zigzag edges on both sides of the linear defects of C-C dimers are three-fold-coordinated without any unsaturated dangling bond. The lattices of two graphene domains stitched by the C-C dimers linearly are translated by a fractional vector of $1/3(a_1+a_2)$,⁹ where a_1 and a_2 are the unit cell vectors of graphene. In order to study the individual dimer line, the interaction of electronic orbitals between two dimer lines should be eliminated. Therefore, in our works, the primitive cell with $W=8$ is sampled because the interval distance between

periodical linear defects is $\sim 35.3 \text{ \AA}$ and it is large enough to ensure negligible interaction between two nearest-neighbour dimer lines. The parameters of fully relaxed geometry along the C-C dimer line are shown in Fig. 1(c). They are in a good agreement with the structural details in Ref. 9, indicating that our methods are robust.

Results and discussion

Electronic properties

The electronic structures of pristine graphene and the system with C-C dimer lines embedded in graphene are shown in Fig. 2(a)(b), respectively. It exhibits that the linear valence and conduction bands [cyan lines in Fig. 2(a)] of graphene meet at a point of Fermi level, which can be characterized by the Dirac cone. Therefore, the charge carriers in graphene can be considered as the massless Dirac fermions. For the system with the linear defects of C-C dimers, the bands of graphene matrix [black solid lines in Fig. 2(b)] open the gap near the Fermi level, thus resulting in the semiconducting matrix due to trapping effect. Note that some extra bands (pink dashed lines) introduced by the linear C-C dimers are inserted in this gap. It indicates that the defect line possesses the metallic characteristic. In addition, these extra bands at the shallow energy zone are partially flat. Therefore, the electronic states in proximity of Fermi level are transferred from the extended states [Fig. 2(c)] to the localized states [Fig. 2(d)]. Apparently, such localized states contain valence and conduction band edge states.²⁵ The movement of charge carriers is confined within the quasi 1-D nanowire along the C-C dimer line.

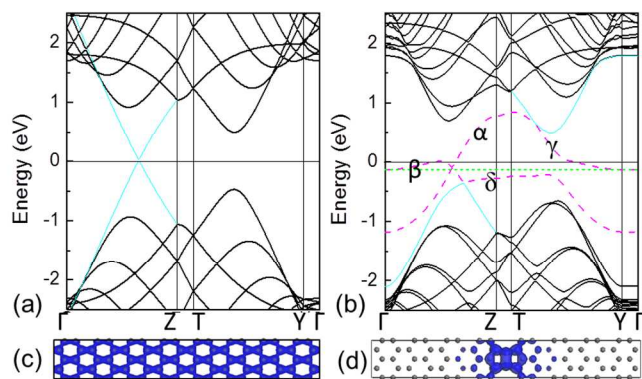


Fig. 2 The electronic bands: (a) pristine graphene and (b) C-C dimer system. The electronic orbitals colored in blue are: (c) pristine graphene and (d) C-C dimer system. They are mainly induced by the bands close to Fermi level at the low-energy zone, containing occupied and unoccupied orbitals. The solid line at 0 eV is Fermi level of the graphene matrix exclusive the linear defect while the dashed green line is the Fermi level of the entire system.

The electronic structures show that these extra bands induced by the linear defect produce a local doping in a narrow strip. Such a self-doping phenomenon leads to the aggregation of electrons, from graphene matrix, surround the linear defect. This processing leaves a number of holes in the matrix. Alike to the p-doping, the Fermi level of the system labelled by the dashed green line is lowered to underneath of the Fermi level of

the graphene matrix, as indicated with the solid black line at 0 eV in Fig. 2(b). In addition, similar to the zigzag edged graphene nanoribbon,²⁶ the corresponding zigzag edges in this system introduce partially flat states closed to the Fermi level, thus attracting the charges.¹² Although the conductive 1-D nanowire has been achieved inside of 2-D graphene, its electronic band structures in proximity of Fermi level are not characterized by the Dirac cone. This demonstrates its metallic character and its carrier mobility is much lower than that of pristine graphene. To enhance the carrier mobility without changing the configuration of the 1-D conductive nanowire that is embedded in 2-D graphene matrix, tailoring extra bands at the low-energy zone by doping B or N in the C-C dimers is expected to be a strategic approach.

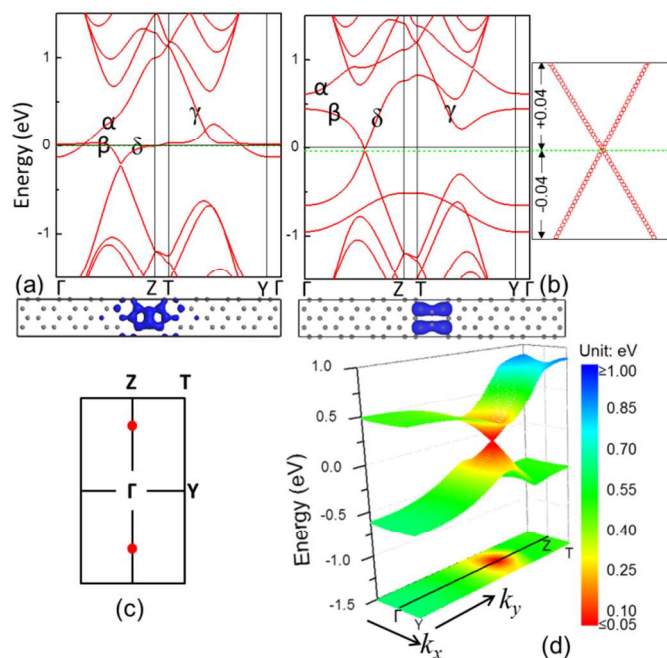


Fig. 3 The electronic bands (top) and orbitals (bottom) for (a) B-C and (b) B-B dimer systems are exhibited. The spectra in the right panel of (b) is the linear dispersion relation in the vicinity of the Dirac point, and the unit of energy is eV. The Fermi levels of system and graphene matrix are denoted by green dashed and black solid lines, respectively. (c) First Brillouin zone: the red dots are the position of Dirac point for B-B dimer system. (d) Energy of charge carriers in the B-B dimer system: the first band dispersion above and below the Dirac point, and projection of first band below the Dirac point.

In this approach, we used B to replace a C to form the B-C dimer first and the band structure of the system with linear B-C dimers is shown in Fig. 3(a). Compared to the system with the C-C dimers, the α and δ bands in the system with linear defect of B-C dimers are raised. In general, the doping holes push the Fermi level down, whereas the Fermi level of the entire system (graphene matrix + B-C dimer line) is very close to the one of graphene matrix. This is because the amount of the holes induced by the B substitution approximately equals to that of the localized electrons surround the linear defect, which are aggregated from the graphene matrix. However, there is no linear electronic band presenting at the Fermi level in the system with B-C dimers. The B substitutions only altered the

flat electronic bands near the Fermi level in the reciprocal space partially. This gives rise in whether the flat bands at the Fermi level can be diminished by further increasing the B concentration. For example, to double the B doping level forms the linear defects with B-B dimers to stitch the two domains of graphene. Fig. 3(b) exhibits the corresponding band dispersion of such a system. Compared with the B-C dimer system in Fig. 3(a), it is surprised to find that the β and δ bands of the system with B-B dimers are further raised to cross in a single point along the Γ -Z path at the Fermi level. Around the cross point, both the valence and conduction bands are linear and can be characterized by the Dirac cone. This cross point of the valence and conduction bands can be defined as the Dirac point (K point). In order to verify the Dirac character, the band dispersion with a large number of k -points around the K-point was calculated. The spectra on the right panel of Fig. 3(b) demonstrate that the band dispersion has a linear relationship with k . In this system, there are two Dirac points appeared in its first Brillouin zone as shown in Fig. 3(c). However, due to the rectangular symmetry ($pm\bar{m}$), only one is independent.

In this case, the Fermi level of the entire system can be manipulated by controlling the concentration of B dopants. It evidences that the charge carrier is the hole in the system with B-B dimers. In addition, due to the large width of the primitive cell, the 3-D band dispersion is very narrow along the k_x in the reciprocal space [Fig. 3(d)]. The energy range of the linear spectra along the k_y is ~ 0.9 eV and along the k_x is ~ 0.6 eV. The color-coded constant-energy isolines in xy projection demonstrate that the Dirac cone is nearly isotropic (the quantitative value will be reported below). In order to investigate the spatial distribution of charge carriers, the electronic orbitals at the Dirac point, containing occupied and unoccupied orbitals, are calculated and shown in the bottom panel of Fig. 3(b). It is discernable that such electronic orbitals are also confined near the dimer defect. Different from the systems with C-C and B-C dimers, the linear bands in the system with linear defect lines of B-B dimers possess a massless Dirac fermion character to the charge carriers. Therefore, when the charge carriers (holes) move in these electronic orbitals, they may transport at the speed of $\sim c/300$ (c is the speed of light) with a few order magnitudes higher than the metallic-like nanowire in the C-C dimer system.

Following our finding by using the B-B to substitute the C-C dimers in linear defects, it is interested to understand the physical behaviour of the substitution with the N element that have one more negative charge than C element. Fig. 4(a) shows the band structure of the system with the linear defects, which the C-C dimer was substituted by C-N dimer. Similar to the system with B-C dimers, there is no linear electronic band presenting at the Fermi level, and there are some partially flat bands closed to the Fermi level. Different from the B-C dimer system, the α , γ and δ bands fall in the band structures. This is because N dopants contribute more electrons to the zigzag edges than the graphene matrix. These electrons occupy the empty states in the extra bands at the low-energy zone, thus shifting the Fermi level up (green dashed line) by referring to

the Fermi level of the graphene matrix (black solid line at 0 eV) in Fig. 4(a). For a similar reason to the B-B substitution, we doubled the N doping concentration. As shown in Fig. 4(b)(c), the system with the linear defects of N-N dimers possesses two Dirac points with an independent one at the boundary of the first Brillouin zone due to the further lowering of α and γ bands. Thus, the charge carriers in this system are attributed to massless Dirac fermions and can propagate at an effective 'speed of light' of $\sim 10^6$ m/s. In contrast to the B-B dimer system with the charge carriers of holes, this system with the charge carriers of electrons raised the Fermi level of the system up. In the bottom panel of Fig. 4(b), the electronic orbitals at the Dirac point, containing occupied and unoccupied orbitals, indicates that the charge carriers (electron) in these orbitals are also confined round the dimer defect in a real space.

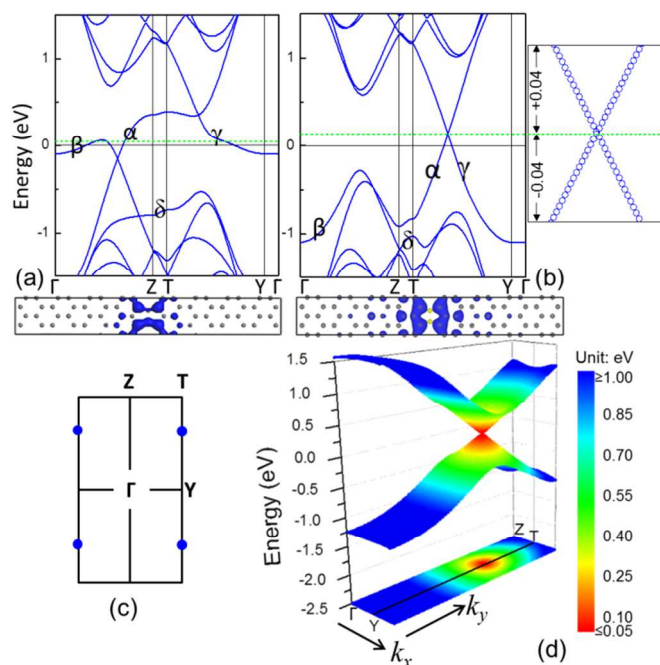


Fig 4 The electronic bands (top) and orbitals (bottom) for (a) C-N and (b) N-N dimer systems are exhibited. The spectra on the right panel of (b) is the linear dispersion relation in the vicinity of the Dirac point, and the unit of energy is eV. The Fermi levels of system and graphene matrix are denoted by green dashed and black solid lines, respectively. (c) First Brillouin zone: the blue dots are the position of Dirac point for N-N dimer system. (d) 3-D energy spectrum of N-N dimer system: the first band dispersion above and below the Dirac point, and projection of first band below the Dirac point.

It is interested to note that the charge carrier of N-N dimer system is less localized than that of B-B dimer system. The N-N dimer system has a larger energy range of the linear bands than the B-B dimer system. This is because the electron attracted by the ionic N^- dopant is much less than the holes attracted by the B^+ dopant.²⁷ The 3-D band dispersion in Fig. 4(d) exhibits that the Dirac cone is nearly isotropic for the N-N dimer system. The energy range of the linear spectrum along the k_y is ~ 2.0 eV and along the k_x is ~ 0.9 eV. In particular, the linear energy dispersion has a wider energy range compared with the B-B dimer system. Combined with the color-coded

constant-energy isolines in xy projection [Fig. 3(d) and 4(d)], the slope of Dirac cone (Fermi velocity) in the system with the linear defects of N-N dimers is larger than that in the system with B-B dimers. In addition, the linear bands gradually become flat when they are approaching to the boundary of Brillouin zone, as shown in Fig. 3(b) and 4(b); also see the ESI Fig. S1. Such partially flat behaviour represents the characteristic of 1-D structures, which produce corresponding two van Hove singularities at the band extrema, as observed in the carbon nanotubes²⁸ and graphene nanoribbons⁷.

Similar to the π electrons of pristine graphene to form the π bands, the extra charges introduced by the dopants also result in the bands near the Fermi level in the system with the linear defects of either B-B or N-N dimers. A portion of the extra charges produces partially flat behaviours at the deeper energy zone while the others are located at the lower energy zone to form the linear dispersion relation. Such extra charges at the low-energy zone can be treated independently from the other charges. Therefore, around the K-point, the electronic energy is linear with respect to $q=k-K$ that can be described as:²⁹

$$E(\pm) = \pm \hbar v_F q + O[(q/k)^2] \quad (1)$$

where v_F is the Fermi velocity. Without taking account of the second and higher order terms associated with q^2 , the v_F of charge carriers of our structures can be calculated with the first derivatives of their linear bands near the K-point.³⁰ The results show that the values of v_F for the Dirac cones along $\pm \hat{y}$ are the same of $\sim 0.70 \times 10^6$ m/s in the system with B-B dimers while they are $\sim 0.82 \times 10^6$ m/s and $\sim 0.81 \times 10^6$ m/s along $\hat{y}$ and $-\hat{y}$ in the system with N-N dimers, respectively. It demonstrates that the v_F is directionless from the Dirac point in k space, thus its cone is isotropy. The values of v_F in these systems are comparable with the pristine graphene ($\sim 0.83 \times 10^6$ m/s). This is because the symmetric behavior of these electronic orbitals in B-B or N-N dimer system is similar to the p_z electrons in some 2-D Dirac carbon allotropes.^{10,11} The conical energy spectra are appeared at the Fermi level in the bands introduced by the B-B or N-N dimers. The charge carriers in these systems, which exhibit the quasi-1-D character, are confined along the dimer line while the charge carriers in the pristine graphene are dispersed two-dimensionally.

Table 1. Fermi velocities (v_F) in 10^6 m/s for the Dirac cones, along the indicated directions.

W	1	2	3	4	5	6	7	8	9	10	11
B	$\hat{y}$	-	-	0.66	0.67	0.69	0.69	0.69	0.70	0.71	0.71
	$-\hat{y}$	-	0.75	0.71	0.70	0.69	0.69	0.69	0.70	0.69	0.69
N	$\hat{y}$	1.00	0.88	0.84	0.83	0.82	0.82	0.82	0.81	0.82	0.83
	$-\hat{y}$	0.63	0.70	0.75	0.77	0.78	0.79	0.80	0.81	0.81	0.81

Moreover, it is very necessary to know whether or how their electronic properties varied as a function of width of primitive cell with W . The band structures with $W=1\sim 11$ are available in Fig. S2. Along k_x direction, the energy range of spectrum is width dependent, and the range decreases with W increasing. When the periodic unit cell of system is extreme narrow (especially for $W=1$), the Dirac cone will be distorted for B-B

dimer case while N-N dimer case still maintains a Dirac cone as shown in Fig. 5. The reason is that the weight of extra charge's distribution is large at B dopants in comparison with that at N dopants. When such strong bounding states resonate with their periodic images, they suppress and destroy the linear dispersion. Additionally, for B-B dimer case with $W=1$, there is another conduction band touching Fermi level at the Γ point. For B-B dimer case with $W=2$, the band show a finite curvature in the $\hat{y}$ direction in Fig. 5b. However, following the notation of Ref.10, if the conduction and valence band meet in a single point at or very close to the Fermi level with zero curvature along at least one direction, a double cone-like feature will be denoted a Dirac cone. The values of v_F along the indicated directions with width of W are listed in Table 1. It is displayed that the v_F of narrow structures depends on the direction from the Dirac point in k space, thus its cone will be anisotropy. The v_F of N-N dimer case is larger than that of B-B dimer case due to different ability of bounding extra charges. It is very interesting to note when the width of W is very narrow, for example $W=1$ or 2 in Fig. 5, also see the 3-D energy spectrum in a reciprocal space and its corresponding electronic orbitals in a real space in Fig. S3, the new 2-D feature appears in which some chains of C six-membered ring are bonded by B-B or N-N dimers.

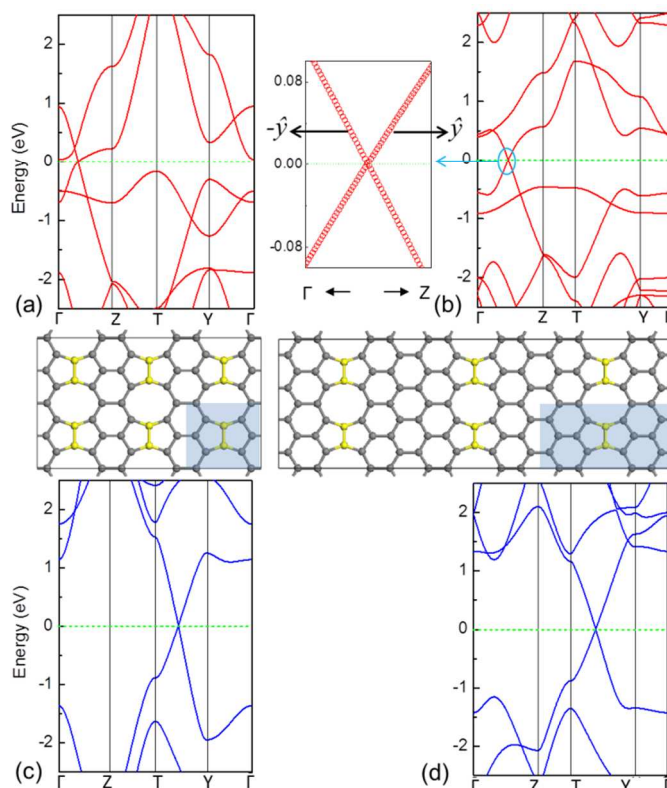


Fig. 5 Band structures of B-B/N-N dimer cases with $W=1$ (a)/(c) and $W=2$ (b)/(d). The spectrum in the left (b) is the magnified image of the band dispersion of the cycled area around the band intersection at the Fermi level in the right panel for B-B dimer case with $W=2$, where one $\hat{y}$ branch is slight curved. The Fermi level of system is set as 0 eV. Inset: Schematic illustration shows the structure of B-B/N-N dimer cases with $W=1$ (left) and $W=2$ (right).

Stability

The geometric structures of B-B/N-N dimer systems with $W=8$ are shown in Fig. 1(d) and (e). In comparison with C-C dimer system [Fig. 1(c)], B-B dimer system stretches along the width while N-N dimer system contracts along the width. The stability of the as-designed dimer lines embedded in graphene is essential for the applications of nanoelectronics. To address this issue, we firstly calculate the cohesive energy E_{coh} per atom of the as-designed systems for evaluating structural stability using following equation:

$$E_{coh} = [E_{tot} - \sum_i n_i E_i] / m \quad (i = C, B, N) \quad (2)$$

where n_i is the number of the constituent i atom and m the total number of atoms in the systems. E_{tot} and E_i are the total energies of the system and individual free atoms within the same cell, respectively. The value of E_{coh} may be not reliable in an isolated environment. Therefore, for comparison, the cohesive energies per atom in the C-C dimer system, BN sheet and the pristine graphene are also calculated. Fig. 6(a) plots the cohesive energies per atom as a function of primitive cell width. The system with the higher negative cohesive energy results in a higher structural stability of the system. It can be seen: increasing the interval distance between the periodical linear defects of dimers increases the stability of the system towards the one of pristine graphene. This is because the proportion of C six-membered ring is high in the system with a large interval distance. In addition, the C-C dimer system is the most stable one among the systems with linear defect dimers. The system with B-B dimers is more structural stable than the system with N-N dimers because B induces charge-transfer-driven extra cohesiveness between the B atoms and their neighbour C atoms.³¹ However, the differences of their cohesive energies per atom are reduced with increasing the interval distance between the periodical linear defects. The stabilities of these dimer-defect systems are between the BN sheet and pristine graphene, showing the possibility of experimental fabrication.

The further consideration should be the thermodynamic stability of the as-designed systems. In this case, the formation energy E_f per atom can be calculated as

$$E_f = [E_{tot} - \sum_i n_i \mu_i] / m \quad (i = C, B, N) \quad (3)$$

where n_i , m , and E_{tot} have the same definitions as described for the eq 2. μ_C , μ_B , and μ_N are the chemical potential of the C, B, and N referred to graphene, a-rhombohedral B, and gaseous N, respectively. Such a zero temperature approach could determine the relative energy cost of B-B/N-N dimer lines embedded in graphene compared to C-C dimer system.³¹ Noticeably, the formation energies of the pristine graphene and BN sheet are equal to zero using this approach. Combined with the C-C dimer system, which has been synthesized experimentally,⁹ thereby it provides us a reference frame for comparison. The system with the slower positive formation energy will be more thermodynamically stable compared to other systems. The formation energies of linear dimer systems are shown in Fig.

6(b). The variation trend of formation energies per atom as a function of primitive cell width is the same as that of cohesive energy. It indicates that the dimer system with a large interval distance will gain the thermodynamic stability arising from the low proportion of interface between 5-5-8 line defect and graphene matrix which minimize interfacial energy. N-N dimer systems have greater extent of E_f compared to the presence of B-B dimer systems. As above discussion of E_{coh} , there is an extra interfacial charge transfer between B and C atoms in B-B dimer system compared to the presence of N-N dimer system, thus inducing an extra energy cost.³¹ Consequently, it indicates that C-C dimer system is the most preferential for forming, and B-B dimer system is the least one. However, for large interval distance, their difference is very small. In fact, the C-C dimer system has been synthesized experimentally.⁹ Similarly, the B-B or N-N dimer system can be expected to be realized experimentally. Alternately, an atom-by-atom substitution technique using a scanning tunneling microscope can also be realized to control nanostructures accurately.³²

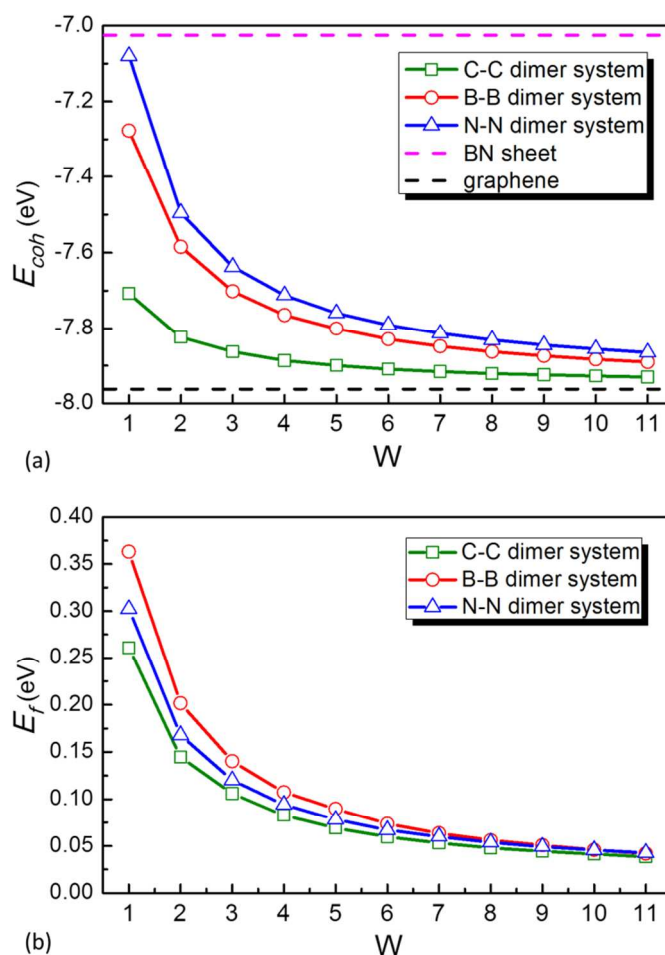


Fig. 6 (a) The calculated cohesive energies (E_{coh}) and (b) formation energies (E_f) per atom of the periodically repeated arrays of linear C-C, B-B or N-N dimers in the graphene as a function of primitive cell width (W).

To study their stability under the room temperature, molecular dynamics simulations for B-B/N-N dimer systems

with $W=1, 8$ have also been performed. The graphene embedded with defect dimer lines is basically stable, and have slight fluctuation after 3ps molecular dynamics simulations (see ESI Fig. S3). Therefore, it is possible that the C-C dimer in graphene would be replaced by B-B or N-N dimer.

Conclusions

We proposed a methodology to engineer a 1-D electron tunnel by manipulating the 2-D structure with the B-B or N-N dimer lines in graphene matrix. It is found that the Dirac cone appears in the bands introduced by the B-B or N-N dimers at the low-energy zone. It results in the transport velocities of the charge carriers to be $\sim 10^6$ m/s, an effective "speed of light", which are comparable with the pristine graphene. Such systems suggest that heteroatoms in graphene can indeed make their contribution to Dirac cone. However, different from the 2-D charge carriers in pristine graphene, the charge carriers introduced by B or N dopants are confined in a very thin nanowire along the B-B or N-N dimer lines in a real space. Therefore, the B-B or N-N dimer lines periodically distributed in graphene can act as a quasi-high conductive nanowire while the graphene matrix possesses the characteristics of semiconductor. Such a structure with the 1-D conductive dimer lines and semiconductor matrix is similar to the current basic structure of the integrated circuit, which the conductive metal nanowires embedded in semiconducting Si-based material matrix. In addition, owing to the ultrahigh carrier mobility and ultra-thin width (less than 0.8 nm) of the B-B or N-N dimer line, the proposed structure would be a promising candidate for the high performance ultra-large-scale integrated circuit. In particular, the type of the carriers can be manipulated by controlling the dopants, such as B or N, to meet the specific requirements of the applications.

Acknowledgements

The authors would like to thank the financial supports from National Natural Science Foundation of China (Grant No. 51372095), the Fundamental Research Funds of Jilin University (Grant No. 201103021), Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT), and the "211" and "985" project of Jilin University, as well as Australian Research Council FT100100956 and DP140104373. Quanguo Jiang and Quan Li are acknowledged for the help of the discussion and calculation.

Notes and references

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Electronic Supplementary Information (ESI) available: [The wide energy bands for B-B/N-N dimer systems with and without relaxing cell lattices. The electronic bands with $W=1-11$ using GGA are exhibited. 3-D energy spectrum and its corresponding electronic orbitals with $W=2$ are available.]. See DOI: 10.1039/b000000x/

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