Dirac cone move and bandgap on/off switching of graphene superlattice

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Using the density functional theory with generalized gradient approximation, we have studied in detail the cooperative effects of degenerate perturbation and uniaxial strain on bandgap opening in graphene. The uniaxial strain could split $\pi$ bands into $\pi_a$ and $\pi_z$ bands with an energy interval $E_s$ to move the Dirac cone. The inversion symmetry preserved antidot would then further split the $\pi_a$ ($\pi_z$) bands into $\pi_{a1}$ ($\pi_{z1}$) and $\pi_{a2}$ ($\pi_{z2}$) bands with an energy interval $E_d$, which accounts for the bandgap opening in a kind of superlattices with Dirac cone being folded to $\Gamma$ point. However, such antidot would not affect the semimetal nature of the other superlattices, showing a novel mechanism for bandstructure engineering as compared to the sublattice-equivalence breaking. For a superlattice with bandgap of $-E_d$ opened at $\Gamma$ point, the $E_s$ could be increased by strengthening strain to close the bandgap, suggesting a reversible switch between the high velocity properties of massless Fermions attributed to the linear dispersion relation around Dirac cone and the high on/off ratio properties associated with the sizable bandgap. Moreover, the gap width actually could be continuously tuned by controlling the strain, showing attractive application potentials.

Graphene consisting of hexagonally arranged carbon atoms has attracted tremendous research interests on both theory and experiment. Attributed to the $p_z$ orbital forming $\pi$ bonding states on both sides of graphene and the sublattice-equivalence confinement, the Dirac cone is formed by the valence band and conduction band crossing at K (K') point. The linear energy dispersion relation around Dirac point brings us many unique and amazing properties, showing fascinating application potentials. The charge carriers, which could be tuned continuously between electrons and holes, have the group velocity as high as $10^6$ m/s being close to that of light. Therefore, the graphene-based nanostructures are believed to be promising materials for next-generation high-performance nanoelectronic devices\textsuperscript{1–4}. However, since the conductivity due to the semimetal nature of graphene cannot be turned off completely, pristine graphene sheet cannot be used as a transistor in optoelectronics, where high on/off ratio is required. Recently, the methodology of quantum confinement by slicing graphene into nanoribbon, the substrate effects, the sublattice equivalence breaking, and the electric field effects are intensively investigated for the bandstructure engineering of graphene-based nanostructures\textsuperscript{5–19}.

In the field of bandstructure engineering of graphene, an issue needs to be addressed. Along with the bandgap opening, the linear energy dispersion relationship around Dirac cone would be usually destroyed, which in turn would obviously reduce the charge carrier mobility. Usually, the wider bandgap opened in graphene to gain higher on/off ratio would lower the carrier mobility much more. Hence, it would be interesting if the bandgap could be switched on/off for a specific graphene-based nanomaterial toward different application demands. Interestingly, the advanced nanotechnologies have been successfully used in fabricating antidot-patterned graphene nanostructures—the graphene nanomeshes. The block copolymer lithography, nanoparticles local catalytic hydrogenation, nanosphere lithography, nanoimprint lithography, etc. have been proved to be efficient for synthesizing graphene nanomeshes\textsuperscript{20}. In 2010, Bai \textit{et al.} reported the nicely patterned graphene nanomesh fabricated by using the block copolymer lithography\textsuperscript{21}. Recently, Wang \textit{et al.} reported the CVD growth of large area smooth-edged graphene

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nanomesh by nanosphere lithography\textsuperscript{22}. A most recent work\textsuperscript{23} on synthesizing large area graphene nanomesh tailored by interferometric lithography was reported by Kazemi \textit{et al.} These progresses in fabricating advanced nanomaterials suggest the possibilities in preparing graphene nanomeshes in experiment with nice precision. In fact, this could be regarded as to pattern graphene into superlattice with carbon vacancies, which would modulate the corresponding Born-von Karman boundary conditions\textsuperscript{24-26}. As shown in the experimental studies\textsuperscript{20-23}, the antidot with circular vacancy hole may be easily realized, which preserves the inversion symmetry. Besides, the two dimensional superlattice may also be obtained through the interaction between sheet material and its supporting substrate, which could be seen in the two dimensional silicene grown on Zrb\textsubscript{2} surface\textsuperscript{27}. The periodic interaction pattern of silicene lattice in matching that of Zrb\textsubscript{2} surface folds the Dirac cone to \( \Gamma \) point. So, to shed light on the experimental studies, we have carried out detailed studies of hexagonal-antidot-patterned graphene superlattice in which the inversion symmetry remains. The novel mechanism differing with the sublattice-equivalence breaking for bandstructure engineering and the effects of uniaxial strain on electronic properties are carefully discussed. Most interesting, for a kind of graphene superlattices whose bandgaps are opened at \( \Gamma \) point, the gap width could be continuously tuned by applying uniaxial strain until it is closed. So, for such superlattices, one could reversibly switch between the massless Fermion properties attributed to the linear dispersion relation around Dirac cone and the high on/off ratio properties associated with the sizable bandgap.

Results and Discussion

Energy band folding and bandgap opening. The studied graphene superlattice is schematically illustrated in Fig. 1. The periodically arranged antidots impose new Born-von Karman boundary conditions to graphene, forming the regularly patterned superlattice. As shown in Fig. 1, we would like to concentrate on studying the superlattice patterned with \( D_{6h} \) high symmetry antidots in this paper for: (1) it could shed light on the circular mesh hole of the synthesized graphene nanomesh, and (2) it preserves the inversion symmetry. This kind of antidots in fact do not break the sublattice equivalence, which however could still open bandgap of some graphene superlattices, showing a novel mechanism for bandstructure engineering.

Firstly, we start the discussion of electronic properties with the energy band-folding analysis. In this paper, the orthogonal superlattice with the \( A \times B \) periodic unit as shown in Fig. 1 has been carefully studied in detail. The \( A \) and \( B \) are along the armchair and zigzag edges, respectively. The smallest rectangle unit cell defined by \( A_1 = a + b \) and \( B_1 = -a + b \) is illustrated in Fig. 2a along with the \( a \times b \) primitive unit cell of graphene. As compared to the graphene studied with primitive unit cell, we would like to hereafter refer the pristine graphene studied with supercell \( A \times B \) as pseudo graphene superlattice (PGS). If a perturbation such as an antidot was introduced in the \( A \times B \) unit cell, the PGS would turn to be a real superlattice. In order to facilitate discussion, we would like to use the notation \((P,Q)\) to account for the lattice \( A \times B \) with \( A = PA_1 \) and \( B = QB_1 \). Therefore, the \((1,1)\) stands for the smallest rectangle lattice \( A_1 \times B_1 \). In Fig. 2b, the hexagonal Brillouin zone (\( h\)-BZ) and the rectangle one (\( r\)-BZ) corresponding to the primitive unit cell and the \((1,1)\) PGS are shown, respectively. One can see that the \( K \) point in \( h\)-BZ would be folded to the \( T_1 \left( \frac{1}{3} \Gamma \frac{2}{3} \right) \) point in \( r\)-BZ. The energy bandstructure of \((1,1)\) PGS is presented in Fig. 2c in which the Dirac cone is located at \( T_1 \) point, confirming the above band-folding analysis. Based on our detailed analysis for the \((P,Q)\) PGSes with different \( P \), we could conclude that the Dirac point would be always folded onto \( \Gamma Y \) axis in the corresponding \( r\)-BZ. Interestingly, the Dirac point could be folded to \( \Gamma \) point when \( Q = 3m \) (\( m \) is an integer). In Fig. 2d-f, the \((1,3)\) PGS is studied. The \((1,3)\) unit cell is schematically shown in Fig. 2d and its corresponding \( r\)-BZ is presented in Fig. 2e. One can see that the \( K \) point in \( h\)-BZ of primitive unit cell is equivalent to the \( \Gamma_3 \) point in \( r\)-BZ of \((1,3)\) lattice. The energy bandstructure shown in Fig. 2f supports the folding of Dirac point to \( \Gamma_3 \).

A bandgap can be opened in the \((P,Q)\) \((Q = 3m)\) PGS by introducing an inversion symmetry preserved defect, such as the \( D_{6h} \) hexagonal antidot, which does not coincide with the sublattice-equivalence breaking mechanism. For illustration, we have studied the electronic properties of \((7,7), (7,8), \) and \((7,9)\) superlattices. According to our energy band folding analysis, the \((7,7), (7,8)\) PGSes should have Dirac points at \( \pm \Gamma Y \) points in corresponding \( r\)-BZs while the \((7,9)\) PGS should have \( \Gamma \) as Dirac point in its \( r\)-BZ. After introducing a \( C_{12} \) hexagonal antidot in

Figure 1. An antidot-patterned orthogonal superlattice defined by \( A \times B \) unit cell is schematically illustrated. The small and big balls are for H and C atoms, respectively.
the unit cell (in order to facilitate discussion, we would like to use the notation $C_n$ to account for the antidot formed by removing a $n$-atom $D_{6h}$ carbon nanoflake from the graphene with the hole edge passivated by hydrogen atoms), their bandstructures are studied and shown in Fig. 2g–i, respectively. Interesting it is the bandgap opening in the (7,9) superlattice while the (7,7) and (7,8) still keep semimetal conducting nature. Besides the orthogonal superlattices, we have also carried out careful studies on the other type superlattices. For a superlattice defined by $A_{\text{any}} \times B_{\text{any}}$, the lattice vectors could be expressed as $A_{\text{any}} = N_{11}a + N_{12}b$ and $B_{\text{any}} = N_{21}a + N_{22}b$ ($a$ and $b$ are the basis vectors of primitive unit cell of graphene). If the coefficients satisfy the conditions of $2N_{11} + N_{12} = 3m$ and

Figure 2. The schematic structure, Brillouin zone $r$-BZ, and energy bandstructure for the smallest orthogonal (1, 1) PGS are shown in (a–c), respectively. Those for the (1, 3) PGS are presented in (d–f), respectively. The Brillouin zone $h$-BZ corresponding to the primitive unit cell of graphene is also shown in (b,e) for comparison. The (g–i) are for the energy bandstructures of the antidot-patterned (7, 7), (7, 8) and (7, 9) graphene superlattices.
2N_{11} + N_{12} = 3m_1 or N_{11} + 2N_{12} = 3m_2 and N_{21} + 2N_{22} = 3m_4 (m_1, m_2, m_3, and m_4 are integers), the Dirac cone would be folded to Γ point and the introduced inversion symmetry preserved defect in the repeated unit cell would then open a bandgap in such superlattice.

Also, we would like to address the case of superlattice patterned with low symmetry antidots, where the inversion symmetry may be broken. The sublattice equivalence breaking would then open a bandgap in such superlattice. In fact, according to our calculated results, the novel bandgap opening mechanism proposed based the studies of inversion symmetry preserved superlattice would still stand, which would combine with the sublattice equivalence breaking mechanism in opening bandgap of the superlattice with Dirac cone being folded to Γ point. As a result, the mass bandgap would be determined by the dominated mechanism which could open a wider gap.

**Splitting between π_1 and π_2 bands.** In the above discussion, the hexagonal antidot acts differently on bandgap engineering of the free-standing graphene superlattice, which strongly depends on the position of the Dirac point. Only for the lattice with Q = 3m, the antidot could open bandgap. Actually, the Dirac cone could be moved away Γ point by some perturbation, such as the uniaxial strain. One may question whether the opened bandgap of antidot-patterned (P,Q) superlattice with Q = 3m could be closed by moving Dirac cone away Γ point? Hence, in this subsection, we would like firstly to concentrate on discussing the effects of uniaxial strain on the Dirac cone move.

In Fig. 3, as to the smallest rectangle (1,1) PGS, we have carefully studied the energy bandstructures after applying uniaxial strain along the armchair (A_lattice) and zigzag (B_lattice) edges, respectively. In our studies, the Dirac cone was found to move along the Γ→Y axis. In the free-standing PGS without strain, the Dirac cone is located at ηΓ→η_Y (marked with T_1 point in Fig. 2). The strain σ_a applied along the armchair edge would move Dirac cone away T_1 point with η > 2/3 while the strain σ_z along the zigzag edge would move it toward Γ point (η < 2/3).

In order to investigate the effects of Dirac cone move on the bandgap opening of the D_{6h}-defect-patterned superlattice, the (3,3) PGS lattice is adopt as a prototype example. As shown in Fig. 4a, the band closing point of (3,3) PGS is folded to Γ point, which corresponds to the Dirac cone shown in Fig. 4b. In our studies, the effects of the strains σ_a and σ_z are investigated in detail. Both of them could shift the Dirac cone away Γ. In Fig. 4c, the effects of the strain σ_z are illustrated. The band closing point at Γ is degenerate in Fig. 4a, which is now split by the strain σ_z, as shown in Fig. 4c. The Fig. 4d shows the three dimensional plotting of Dirac cones, confirming their moves along ΓY and ΓY' respectively. In Fig. 4c, two band crossing points at Γ appear now, which are marked as π_1 and π_2 bands.

![Figure 3. The shifts of Dirac point along ΓY of the reciprocal lattice for the graphene under 5% uniaxial stretching strain applied along armchair (a) and zigzag (b) edges, respectively. The insets show the deviation of Dirac point referred to its position in free-standing graphene as a function of the applied strain. Only π bands those cross to form Dirac point are shown for clarity. The notations of k-points Γ, T_1, and Y_1 are illustrated in Fig. 2b.](image-url)
Figure 4. The band-folded energy bandstructure along $\Gamma-Y$-$Y'$ path in reciprocal space (a) and the three-dimensional plotting of the corresponding Dirac cone (b) for the free-standing (3, 3) PGS. Those for the (3, 3) PGS under 5% $\sigma_z$ strain are shown in (c,d), respectively. The band-decomposed charge densities at isovalue of $\sim 0.03$ e/Å$^3$ for the split $\pi_a$ and $\pi_z$ bands are presented in (e,f), respectively. Both top and side views are shown.
\( \pi_a \) respectively. The charge densities of the \( \pi_a \) and \( \pi_b \) bands are plotted in Fig. 4e,f, respectively. One can see that the \( \pi_a \) band accounts for the orbitals along zigzag edge while the \( \pi_b \) is for the orbitals along armchair edge. This suggests that the Dirac point move could be attributed to the splitting between the energy degenerate bands \( \pi_a \) and \( \pi_b \). Interestingly it is the density distributions of \( \pi_a \) and \( \pi_b \) bands show anisotropic characters. However, due to the fact that they would cross with each other at Fermi level in the neighborhood of \( \Gamma \) point, the anisotropic characters could not be observed in the conducting property studies. But, as to be discussed, the peculiar phenomena may be obtained in the strain engineered defect-patterned superlattice. For the (3,3) PGS without strain, the bond lengths of \( \pi_a \) and \( \pi_b \) bands are exactly the same, which are around 1.425 Å. By applying the 5% \( \sigma_z \) strain along zigzag edge, the \( \pi_a \) bond is elongated by ~3% while the \( \pi_b \) bond remains almost unchanged. The tight binding (TB) method is well known in treating \( \pi \) bands of graphene, which could help to understand the physical origin of the electronic properties of graphene-based nanostructures. By considering only the nearest neighbor atoms, the related energy \( E_{\text{nn}} \) could be obtained through:

\[
E_{\text{nn}} = -2\sum_{j=1}^{3} t_{ij} \cos(k_{ij})
\]

(1)

where, \( t_{ij} \) is the transfer integral, \( k_{ij} \) is the component of wavevector \( k \), \( a_i \) is the corresponding lattice constant, and \( \phi(r) \) is the atomic orbital. According to TB method\(^{28}\), the ~3% elongation of C-C bond length suggests the weakening of the corresponding transfer integral, resulting in the energy band lift of zigzag edge bond in Fig. 4c. The crossings of \( \pi_a \) and \( \pi_b \) orbitals at Fermi level make two separated Dirac points adjacent to \( \Gamma \). In the spirit of the concept of pseudospin, two valleys with different chiralities of the corresponding electrons are located at \( \Gamma \) and \( K \) points in the h-BZ of primitive unit cell of graphene. In the pseudo superlattice (3,3), the valleys are folded onto \( \Gamma \) point in the corresponding r-BZ. The effects of the uniaxial strain are to split the degenerate valleys by shifting them away \( \Gamma \) in opposite directions, which would still keep them equivalent in energy with the apexes of corresponding Dirac cones being located at Fermi level.

**Splitting between \( \pi_{a1} (\pi_{a2}) \) and \( \pi_{a2} (\pi_{a1}) \) bands.** On a hand, due to the linear dispersion relationship around Dirac cone, the charge carriers gain high group velocity, which could also be tuned between the holes and electrons. On the other hand, the semimetal nature of graphene does not favor its usage as for high-performance nano-transistors, which requires high on/off ratio. In order to obtain high on/off ratio, a bandgap needs to be opened for the graphene-based nanostructure. However, along with the bandgap opening, the linear dispersion relation of graphene crystal would be destroyed also, which in turn harms the velocity properties of the charge carriers. So, it would be interesting to explore the possibilities in switching between the high velocity properties of massless Fermions and the high on/off ratio properties. The \( D_{6h} \)-antidot-patterned superlattice studied in this paper may be a potential candidate. In \((P,Q) = (3m)\) PGS, the Dirac point would be folded to \( \Gamma \) point. Then, the high symmetry \( D_{6h} \) antidot can open a bandgap in the corresponding graphene superlattice, which however could not change the semimetal nature of the other superlattices with \( Q \neq 3m \) (the Dirac point is not at \( \Gamma \)). Interestingly, by controlling strain, one can manipulate whether the Dirac point is located at \( \Gamma \) point or not of the \((P,Q) = (3m)\) PGS, which suggests the possibilities in switching on/off bandgap of such superlattice.

As to the (3,3) PGS, in order to facilitate discussion, we would like to first study the effects of a defect in the unit cell by contracting a \( C_6 \) hexagon (see the structural illustration in Fig. 5a). The C-C bonds in this hexagon are shortened by 3% to enhance the corresponding transfer integral\(^{28}\). The atoms of this \( C_6 \) hexagon are fixed while the rest atoms are allowed to relax. For the free-standing (3,3) PGS, the introduced defect could open a bandgap at \( \Gamma \) point according to the discussion of the bandgap opening mechanism. Applying a strain \( \sigma_z \) of ~5%, we have then studied its electronic properties again. The corresponding bandstructure along \( Y'-\Gamma'-Y \) path is shown in Fig. 5b. Now, the bandgap gets closed with the closure Dirac points being around \( \Gamma \), realizing the bandgap switching off.

Compared to the electronic properties shown in Fig. 4c for the (3,3) PGS under 5% \( \sigma_z \) strain, where the strain makes the splitting between \( \pi_a \) and \( \pi_b \) orbitals, the \( D_{6h} \) defect also induce band splitting. As shown in Fig. 5b, the split bands are marked with \( \pi_{a1} \), \( \pi_{a2} \), \( \pi_{a1} \), and \( \pi_{a2} \), respectively, for which the corresponding band-decomposed charge densities are studied in Fig. 5c. It is obvious that the \( D_{6h} \) defect breaks the equivalence among \( \pi_a \) (\( \pi_b \)) orbitals, resulting in different bonding strengths between \( \pi_{a1} \) and \( \pi_{a2} \) bands. As compared to the corresponding C-C bonds of (3,3) PGS studied in Fig. 4c, the contraction of the \( C_6 \) hexagon induces about 0.8% elongation of \( \pi_{a1} \) and 0.6% contraction of \( \pi_{a2} \) bands, respectively. As to the \( \pi_{a1} \) and \( \pi_{a2} \) bands, the corresponding elongation and contraction are about 1.0% and 0.7%, respectively. In the spirit of the TB method\(^{28}\), the shorter the bond is, the higher the transfer integral is, and then the lower the band energy is. Accordingly, as shown in Fig. 5b, the \( \pi_{a2} \) and \( \pi_{a1} \) bands are lower in energy compared to the corresponding \( \pi_{a1} \) and \( \pi_{a2} \) bands, accounting for the splitting of \( \pi_{a} \) and \( \pi_{b} \) bands. Actually, the herein discussed splitting could also be understood by the intervalley scattering. The periodically arranged defects could be approximately treated as introducing a periodic potential \( V(r) \) to the pristine graphene. If the wavevectors of the opposite \( K \) and \( K' \) valleys differ with each other by a reciprocal lattice \( G \), the intervalley scattering would induce band splitting. The energy integral \( E_{\text{g}} \) would be proportional to the integration \( \int_{\text{supercell}} \psi^*(\mathbf{r}) V(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \) with \( \psi^*(\mathbf{r}) \) and \( \psi(\mathbf{r}) \) as the Bloch functions of sublattice \( A \) at \( K \) and \( K' \) points\(^{28}\).

**Reversible on/off switching of bandgap.** Now, one can see that (1) the strain along either armchair or zigzag edges could make the degenerate \( \pi \) bands to split into \( \pi_a \) and \( \pi_b \) bands and (2) the defect could break the...
equivalence among the armchair edge bonds (zigzag edge bonds) inducing the band splitting also. In fact, the competition between the band-split interval $E_s$ induced by the uniaxial strain and the $E_d$ induced by the introduced defect dominates whether the bandgap could be switched on or off. Actually, we have also examined the free-standing defect-patterned (3,3) superlattice. The studied $D_{6h}$ defect also induces the band split $E_d$ between $\pi_{a1}(\pi_{z1})$ and $\pi_{a2}(\pi_{z2})$ orbitals. For there is no strain applied to the lattice, the corresponding $E_s$ equals to zero. So, an obvious bandgap could be opened at $\Gamma$ point. However, for the (3,3) superlattice studied in Fig. 5b, the $E_s$ is larger than the $E_d$, which makes the $\pi_{a1}$ and $\pi_{z1}$ to cross to form new Dirac cone.

In order to benefit experimental studies of patterning graphene nanomesh with circular antidots, we have also studied the bandgap on/off switching of the $D_{6h}$-antidot-patterned graphene superlattice by applying strain. In Fig. 6, the (8,9) PGS is used for discussion. The corresponding band-decomposed charge densities at isovalue of $\approx 0.02 \text{e/Å}^3$ for the split $\pi_{a1}$, $\pi_{a2}$, $\pi_{z1}$, and $\pi_{z2}$ bands are shown in (c).

Figure 5. The $D_{6h}$ defect formed by contracting the C-C bonds by 3% of the black (purple online) hexagon (a) and the corresponding bandstructure along the $Y'\Gamma Y$ path for the (3,3) under 5% $\sigma_z$ strain (b). The corresponding band-decomposed charge densities at isovalue of $\approx 0.02 \text{e/Å}^3$ for the split $\pi_{a1}$, $\pi_{a2}$, $\pi_{z1}$, and $\pi_{z2}$ bands are shown in (c).
increases as the strain $\sigma_z$ enhances from 0% to 5%. As shown in Fig. 6b, the C12 antidot patterned superlattice has been studied. Besides of the experimental fact of the successful fabrication of vacancy hole patterned graphene superlattice, we have performed the molecular dynamics simulations to evaluate the stability of the C12 patterned superlattice. We find that it can withstand the temperature of 1,500 K, implying that this superlattice structure is separated by high-energy barriers from other local minima on the potential energy surface. In this superlattice, the C12 antidot further splits the $\pi_a$ and $\pi_z$ orbitals, which brings the $E_d \approx 0.28$ eV energy interval. For the studied (8,9) superlattice, the $E_d$ remains almost the same as the applied strain increases. For the $\sigma_z = 2\%$ strain, the $E_s$ is smaller than the $E_d$. This still keeps the bandgap opening though the bandgap becomes narrower. An interesting point needs to be addressed. Now, the conduction band minimum (CBM) and the valence band maximum (VBM) consist of only $\pi_a$- and $\pi_z$-type bands, respectively, hinting the possibilities in obtaining anisotropic conducting properties. The electron and hole charge carriers may respectively transport along armchair and zigzag directions. However, for the case of the $\sigma_z = 3\%$ strain, the split energy interval $E_s$ gets larger than the $E_d$. The Dirac cone starts to form. For the condition with $\sigma_z = 5\%$ strain, the formation of the Dirac cone is obvious. So, for the energy interval $E_d$ induced by the defect keeps almost constant, one could then switch on/off the bandgap by manipulating the energy interval $E_s$ through controlling uniaxial strain. This would be interesting for that the high velocity

Figure 6. The calculated energy bandstructures for the graphene-based nanostructures under 2%, 3%, and 5% $\sigma_z$ strains and the ones for the free-standing materials. The (a–c) are for the (8, 9) PGS, C12-patterned superlattice, and (BN)$_6$-patterned superlattice, respectively.
properties of massless Fermions attributed to the linear energy dispersion around Dirac cone and the high on/off ratio properties associated with the sizable bandgap could be switched with each other in the same material. For comparison, the superlattice patterned with (BN)n flake (patching the C12-antidot hole with this nanoflake) has also been studied. For the graphene and BN sheet materials, the atoms are correspondingly hexagonally arranged in a plane to form the honeycomb structures. The calculated lattice constants of graphene and BN sheets are 2.47 and 2.51 Å, respectively. By using (BN)n nanoflake to patch the vacancy hole in graphene, the local strain around the nanoflake should stand due to the lattice mismatch. Considering the fact that the ratio of the area of nanoflake against the one for the graphene is only around 0.04, the local strain would probably be released to some sense at the aid of the structural relaxation of graphene, which would help to stabilize the patched superlattice structure. In order to evaluate the structural stability, we have also carried out the MD simulations of the (BN)n patched (8,9) superlattice, which suggest the stability at temperature of 1,500 K.

In conclusion, the possibilities, for switching between the high velocity properties of massless Fermions attributed to the linear dispersion relation around Dirac cone, and the high on/off ratio properties associated with the sizable bandgap could be switched with each other in the same material. For comparison, the superlattice patterned with (BN)n flake (patching the C12-antidot hole with this nanoflake) has also been studied. For the graphene and BN sheet materials, the atoms are correspondingly hexagonally arranged in a plane to form the honeycomb structures. The calculated lattice constants of graphene and BN sheets are 2.47 and 2.51 Å, respectively. By using (BN)n nanoflake to patch the vacancy hole in graphene, the local strain around the nanoflake should stand due to the lattice mismatch. Considering the fact that the ratio of the area of nanoflake against the one for the graphene is only around 0.04, the local strain would probably be released to some sense at the aid of the structural relaxation of graphene, which would help to stabilize the patched superlattice structure. In order to evaluate the structural stability, we have also carried out the MD simulations of the (BN)n patched (8,9) superlattice, which suggest the stability at temperature of 1,500 K.

In Table 1, we present the calculated average values. Starting from the free-standing C12-antidot-patterned (8,9) superlattice, the opened bandgap would be continuously reduced by enhancing strain, and the corresponding effective mass would be decreased also. According to the simple relationship $\mu = \sigma v / m$ between carrier mobility ($\mu$) and effective mass ($m$) ($\sigma$ is the scattering time of charge carrier)²⁴, the smaller the bandgap is, the higher the charge carrier mobility would be. By using the rough estimation of $10^{-13}$ s for scattering time, we have also estimated the Fermi velocity of $\sim 10^5$ m/s for graphene²⁴. For the semiconducting graphene superlattice, the linear dispersion relation is destroyed, which now could be described by parabola function around the band extremum. Thus, the corresponding effective mass could be obtained by²⁸

$$m = \hbar^2 \frac{d^2 E(k)}{dk^2}^{-1}$$

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(3)

Table 1. The average group velocities of massless Fermions ($v$, in the unit of $10^5$ m/s) or average effective masses of charge carriers ($m$, in the unit of the free electron mass $m_e$) of the (6,6) PGS and the C12 antidot patterned superlattice. The corresponding energy bandstructures are studied in Fig. 6. The stretching uniaxial strain $\sigma_z$ is applied along the zigzag edge.
the latter to elongate. Similar effects are also observed for the \( \pi_z \)-type C-C bonds. The energy interval between \( \pi_{a1} \) and \( \pi_{a2} \) energy bands and the value between \( \pi_{11} \) and \( \pi_{22} \) energy bands are same, which is referred as \( E_\pi \). For the hexagonal-antidot-patterned \((P,Q) (Q = 3m)\) superlattice under uniaxial strain, the competition between \( E_\pi \) and \( E_{\text{Es}} \) dominates whether the bandgap remains open or not. For a given superlattice, the \( E_\pi \) keeps almost unchanged while the \( E_{\text{Es}} \) could be increased by enhancing the strain. Starting from the free-standing \((P,Q) (Q = 3m)\) superlattice, which has a bandgap opened by the energy split between \( \pi_{a1} \) and \( \pi_{a2} \) orbitals, the bandgap decreases along with the increase of the applied uniaxial strain until it closes. Upon this critical point, the energy bands \( \pi_{a1} \) and \( \pi_{a2} \) start to cross to form new Dirac cone. So, the electronic properties of \((P,Q) (Q = 3m)\) superlattice have been switched from the high on/off ratio properties to the high carrier velocity properties. Also, the transformation is reversible along with the strain releasing. Besides, the gap width could be continuously tuned by controlling strain, showing attractive application potentials.

**Methods**

We have carried out spin-polarized first-principles calculations within the framework of density functional theory with a plane wave basis set as implemented in the Vienna \emph{ab initio} simulation package\(^\text{20}\). The projector augmented-wave method was employed\(^\text{11}\). The exchange and correlation energy was calculated by the generalized gradient approximation with the Perdew and Wang (PW91) formulism\(^\text{22}\). The valence electron configurations for B, C, and N were 2s22p2\(^\text{n}\) with \( n = 1\)–3, respectively; for H, the configuration was 1s\(^\text{1}\). The solution of the Khon-Sham equation was calculated by an efficient matrix diagonalization technique based on a sequential band-by-band residual minimization method and a Pulay-type charge density mixing\(^\text{23}\). The graphene superlattice was simulated by applying a supercell with 15 \(\AA\) vacuum to separate the graphene sheet with its periodic images along \(Z\) direction, which was placed in the \(XY\) plane. For the calculation of electronic structure, the cutoff energy of 400 eV was used for the planewave basis set. The \(k\)-point sampling was performed with the Monkhorst-Pack technique\(^\text{24}\). For the studies of the graphene with primitive unit cell and the smallest rectangle graphene superlattice, the integration of electronic structures was calculated by using a \(15 \times 15 \times 1\) \(k\)-mesh. The structural parameters of the primitive unit cell of pristine graphene were firstly optimized, which were then used to construct superlattice. In our studies, the in plane lattices of the hexagonal primitive unit cell were calculated to be 2.466 \(\AA\), which is in good agreement with the previous data\(^\text{5}\). For the studies of large-size orthogonal superlattices, the corresponding unit cells are 12.8 \(\times\) 7.4 \(\times\) 15 \(\AA^3\) and 34.2 \(\times\) 22.2 \(\times\) 15 \(\AA^3\). Thus, the \(k\)-meshes of \(7 \times 9 \times 1\) and \(3 \times 5 \times 1\) were used for studying their electronic properties, respectively. Correspondingly, the charge densities and the local potentials were respectively calculated by using the \(128 \times 72 \times 160\) and \(336 \times 224 \times 160\) grid meshes. The convergence of the electronic properties was set to \(10^{-5}\) eV. In the structural optimization, all the atoms were fully relaxed until the force acting on each atom converged to 0.01 eV/\(\AA\). As to the superlattice, we have also carefully checked the effects of antidot on lattice vectors of the repeated unit. The regularly arranged antidots in fact would not change the angle between lattice vectors, which would only affect the lattice constant. Thus, the symmetry of the superlattice could be preserved, which plays an important role in determining the position of Dirac cone in reciprocal space. For the superlattices simulated in our studies, the lattice constants were carefully optimized. As for testing the accuracy of our method, we also studied the lattice constant of diamond, which was calculated to be 3.571 \(\AA\) in good agreement with the experimental value of 3.567 \(\AA\)\(^\text{21}\). In order to check the thermal stabilities of the defect patterned superlattices, we have carried out first-principles constant energy molecular dynamics (MD) simulations. The MD simulations last for 5 ps with a time step of 0.5 fs. Considering the large unit size of 34.2 \(\times\) 22.2 \(\times\) 10 \(\AA^3\) used for the MD simulations and the purpose to roughly evaluate the structural stabilities, the MD simulations were carried out by using the \(\Gamma\) point. Due to the intensive computing loading, the energy cutoff of 300 eV was adopted for the plane wave basis set. The grid size for numerical integration was chosen to be \(216 \times 140 \times 64\). The stabilities at the temperatures around 1000 and 1500 K were estimated in our studies.

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Author Contributions

G.C. conceived the idea. T.T.J., M.M.Z. and X.Y.F. performed the calculations. The data analyses were performed by T.T.J., M.M.Z., X.Y.F. and G.C. Y.S., S.J.L., H.Y.L. and Y.K. helped discussing. This manuscript was written by G.C. All authors reviewed this manuscript.

Additional Information

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