Stability, defect and electronic properties of graphane-like carbon-halogen compounds*

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We perform first-principles total energy calculations to investigate the stabilities and the electronic structures of graphane-like structures of carbon–halogen compounds, where the hydrogen atoms in the graphane are substituted by halogen atoms. Three halogen elements, fluorine (F), chlorine (Cl) and bromine (Br), are considered, and the graphane-like structures are named as CF, CCl and CBr, respectively. It is found that for the single-atom adsorption, only the F adatom can be chemically adsorbed on the graphene. However, the stable graphane-like structures of CF, CCl and CBr can form due to the interaction between the halogen atoms. The carbon atoms in the stable CF, CCl and CBr compounds are in the sp^3 hybridization, forming a hexagonal network similar to the graphane. The electronic band calculations show that CF and CCl are semiconductors with band gaps of 3.28 eV and 1.66 eV, respectively, while CBr is a metal. Moreover, the molecular dynamics simulation is employed to clarify the stabilities of CF and CCl. Those two compounds are stable at room temperature. A high temperature ($\geq$ 1200 K) is needed to damage CF, while CCl is destroyed at 700 K. Furthermore, the effects of a vacancy on the structure and the electronic property of CF are discussed.

Keywords: graphene, graphane, electronic properties, first-principles

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1. Introduction

Graphene, a monolayer graphite, is the first two-dimensional layer of carbon atoms with a honeycomb lattice and two carbon atoms in each unit cell. Due to the unique electronic properties and the potential applications for carbon-based nanometer-scale electronics,[1−3] graphene has aroused great interest since its discovery.[4−6] The graphene is a zero-gap semiconductor with a point-like Fermi surface and a linear dispersion at the Fermi level. Those characteristics are responsible for the observed anomalous quantum Hall effect, the massless Dirac electrons and the high charge-carrier mobility.[2,4] However, in some device applications, a gap is required between the conduction and the valence bands. One way to create such a gap is to cut a narrow ribbon from a graphene sheet. Another effective way to tune the electronic structure is through doping and adsorbing atoms or molecules on the graphene, thereby producing graphene-based structures.

Many efforts, both experimental and theoretical, have already been devoted to the adatom adsorption on the graphene, which more or less modifies the electronic structure of the graphene.[7−13] Most of these adsorption structures can be manipulated to give rise to interesting new phenomena and even to form new materials. Graphane, which has hydrogen atoms bonded to the carbon atoms on both sides of a graphene layer in an alternating manner, has been successfully synthesized.[14] By bonding with H, graphane changes the hybridization of the carbon atoms from sp^2 to sp^3, thus removing the conducting graphene π bands and opening an energy gap of 3.5 eV at the Γ point.[15] Similar to the H atom, the halogen atom tends to accept an electron to form a closed shell. In addition, it can replace the hydrogen in many hydrocarbons and form carbon–halogen compounds.[16,17] It is possible that the hydrogen atoms in graphane may be substituted by halogen atoms, forming kinds of graphane-like structures, which may affect the electronic structure of the graphene and even brings a possible approach to tuning the width of the band gap. Recently, the synthesis of the graphite fluoride

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(CF) has been realized experimentally,[18] and its electronic structures were discussed,[19−24] while the detailed structural and the detailed electronic characteristics have not been reported systematically. Moreover, other graphene halides may exist, which motivates us to study the graphane-like carbon–halogen compounds.

In this work, the adsorptions of three halogen adatoms (F, Cl and Br) on the graphene and the stabilities of their corresponding graphane-like structures, CF, CCl and CBr, are investigated by using the first-principles method. It is found that for the single-atom adsorption, only the F adatom can be chemically adsorbed on the graphene. However, the stable graphane-like structures of CF, CCl and CBr can form due to the interaction between the halogen atoms. The electronic band calculations reveal that CF and CCl open direct band gaps in the graphene-based structures, providing a way to tune the electronic structure of the graphene. The molecular dynamics (MD) simulations show that the two compounds are thermodynamically stable under the ambient conditions. It is relatively easy to destroy the graphane-like configuration of CCl than that of CF by increasing the temperature. Furthermore, the case of CF containing a vacancy is considered. We find that the graphane-like configuration can be retained and remains stable in the defective CF structure.

2. Method

Our calculations are carried out using the first-principles density-functional theory (DFT) with the CASTEP code.[25] The core electrons are treated with the ultrasoft pseudopotentials,[26] and the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE)[27] is employed for the exchange and correlation function. The calculations are performed with a cutoff energy of 400 eV without the unit cell optimization and 550 eV with the unit cell optimization respectively. The vacuum layer is about 15 Å to make the interaction between the layers negligibly small. The optimizing of the atomic positions and the unit cell is stopped when the change in energy is less than 1×10^{-5} eV/atom, the force on each atom is less than 0.02 eV/Å, and the stress on the cell is less than 0.03 GPa. All the MD simulations are carried out in the canonical ensemble by means of a Nose–Hoover thermostat to control the temperature.

3. Results and discussion

The single-sided adsorption of a single halogen adatom (F, Cl and Br) on the graphene is first considered at three different sites, the hollow site (H) above the centre of the hexagonal ring, the bridge site (B) over the midpoint of the C–C bond and the top site (T) directly above the carbon atom, as shown in Fig. 1(a). The graphene lattice constant is 2.44 Å in our calculations. The adatom–graphene system is modeled using a single halogen adatom on a 4×4 (32 carbon atoms) graphene supercell, which has been used for the study of the metal adatom adsorption on graphene recently.[9,10]

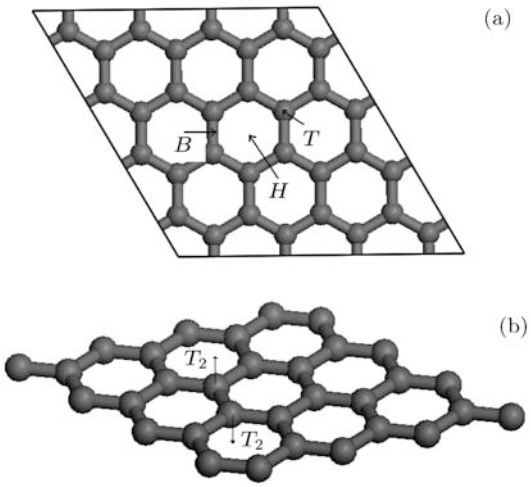


Fig. 1. (a) Three single-sided adsorption sites considered in a periodic 4×4 graphene layer: hollow (H), bridge (B) and top (T). (b) Double-sided adsorption sites (T_2), above and below which two halogen adatoms are adsorbed in a 4×4 periodic graphene layer.

The adsorption energy (E_a) and the adatom height (h) of a halogen adatom on the graphene for the three adsorption sites are summarized in Table 1. The adsorption energy is defined as $E_a = E_{graphene} + E_{adatom} - E_{total}$, where $E_{graphene}$ is the total energy of a clean graphene layer, E_{adatom} is the total energy of an isolated halogen adatom and E_{total} is the total energy of the adatom–graphene system. The adatom height is defined as the difference between the z coordinate of the adatom and the average z coordinate of the nearest carbon atoms in the graphene plane. For the F adatom, the adsorption energy of the T site is 2.273 eV/atom and the adatom height is 1.567 Å, which are the largest adsorption energy and the smallest height among those of the three sites. The distance between F and C, 1.567 Å, suggests a covalent bonding of the two atoms and allows a stronger hybridization

between the adatom and the C atom. Figure 2(a) displays the charge density of the F adatom adsorbed on the T site of the graphene. We can see obviously the electronic overlap between the F and the C atoms. The results indicate that the F adatom forms a covalent bond with the C atom. Such a behaviour has also been obtained in the previous work on impurities in the graphene,[28] which shows that the F adsorbate covalently bonds to the graphene. For the Cl and the Br adatoms on the graphene, the adsorption energies and the adatom heights are similar to each other. The adatom heights are all larger than 3.0 Å, so the interaction between the halogen adatom and the carbon atom is very weak. The charge densities for the Cl and the Br adatoms on the three adsorption sites (not shown here) display little electronic overlap between the adatom and the carbon atoms. These results reveal that a single Cl or a single Br adatom on the graphene belongs to the physisorption, which is different from the chemisorption of the F adatom on the graphene.

Table 1. Values of adsorption energy (E_a) and adatom height (h) of F, Cl and Br adatoms on the graphene layer for hollow (H), bridge (B) and top (T) sites.

Adatom	Site	E_a/eV·atom^{-1}	h/Å
F	H	1.906	2.364
	B	2.046	2.102
	T	2.273	1.567
Cl	H	1.021	3.144
	B	1.024	3.126
	T	1.025	3.136
	T_2	1.199	1.890
Br	H	0.764	3.398
	B	0.767	3.411
	T	0.769	3.412
	T_2	0.762	2.750

Also, we consider the double-sided adsorption of two Cl and two Br adatoms on the graphene respectively. The two halogen adatoms are adsorbed above and below two nearest C atoms in the same 4×4 graphene supercell as shown in Fig. 1(b) and we call those two adsorption sites T_2. We find that the adsorption energy increases to 1.199 eV for Cl on the graphene and the adatom height reduces to 1.890 Å. The charge density shown in Fig. 2(b) indicates that there is also some electronic overlap between the Cl adatom and the C atom. We also find that the Cl adatom has induced an obvious puckering of the graphene, because the C atom needs to accommodate a new hybridization. Accordingly, the double-sided adsorption of two Cl adatoms on the graphene has become the chemisorption, and the interaction of the system has been greatly strengthened. On the contrary, the adsorption energy for Br on the graphene is very similar to that of the single-sided adsorption. Although the adatom height is slightly reduced, it is still close to 3.0 Å. Figure 2(c) shows little electronic overlap between the Br adatom and the C atom, suggesting the physisorption of the Br adatoms on the graphene and the weak Br–graphene interaction. This may be due to the relatively large radius of the Br adatom and the weak electronegativity.

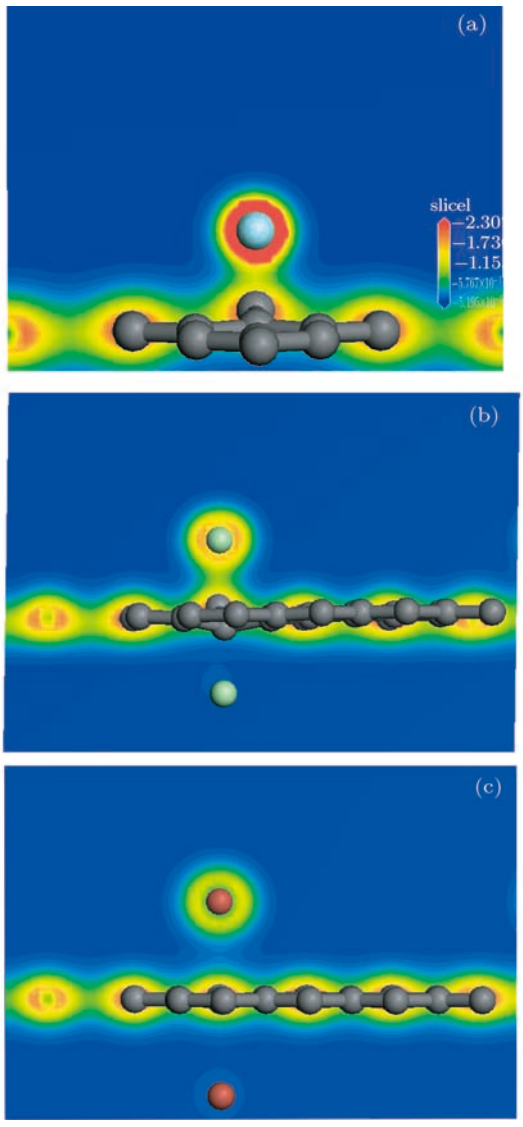


Fig. 2. (colour online) Charge densities of (a) a single F adatom on graphene on the T site for single-sided adsorption, (b) two Cl adatoms on graphene for double-sided adsorption, and (c) two Br adatoms on graphene for double-sided adsorption. The charge density plane includes the upper adatom, but do not include the lower one.

Although the adsorptions of a single atom and two atoms show that the Br adatom has a weak physisorption on the graphene, it does not indicate a similar phenomenon in the graphane-like compounds. Next, we show the structural properties and the binding energies of the graphane-like carbon–halogen compounds, CF, CCl and CBr. Each unit cell of the compounds contains 4 atoms and the ratio of the halogen adatoms to the carbon atoms is 1. Here, the binding energy (E_b) is calculated as the total energy difference between the carbon–halogen compound and the isolated atoms, which has been used for the prediction of the graphane in Ref. [15]. Figure 3 shows the perspective view of the optimized graphane-like structure of CCl. The binding energies and the corresponding structural properties are presented in Table 2. The calculated binding energy of 6.453 eV/atom for CF is close to that for the graphane (6.556 eV/atom). Moreover, the C–C bond length of 1.567 Å and the bond angle of 110.915° are similar to those of the sp^3 configuration, in which the bond length is 1.530 Å and the bond angle is 109.280°. The comparable binding energies and the similar structure properties indicate that this kind of CF is as stable as the graphane. For CCl, the calculated binding energy is 4.926 eV / atom. The C–C bond length of 1.740 Å in CCl is a little larger than that in graphane and the C–Cl bond length of 1.727 Å is close to that (1.760 Å) in the tetrachloromethane (CCl_4). And the bond angle of 111.668° is similar to those of the graphane and CCl_4. It is very clear that the carbon atoms in CCl are sp^3 hybridized, which is the same as those in CCl_4 and the graphane. A similar behaviour of CBr can be seen, although the corresponding bond length and bond angle become larger, and the binding energy is 4.216 eV/atom. A high binding energy is important and required to stabilize the compound. Consequently, the large binding energy provides an evidence that CF, CCl and CBr may be stable under certain conditions. As mentioned above, those three graphane-like structures of the two-dimensional carbon–halogen compounds, CF, CCl and CBr, have shown favourable binding energies and reasonable structures. Therefore, we expect those compounds should be stable and could be observed in experiments.

We compute the electronic structures of those three new graphane-like carbon–halogen compounds. Figure 4 shows the electronic band structure and the corresponding density of states (DOS) for each kind of atom of CF, CCl and CBr. The first two are semiconductors with direct band gaps of 3.28 eV (for CF) and 1.66 eV (for CCl) at the Γ point. While the CBr is a metal. The band gaps of the CF and the CCl structures have been tuned significantly compared with those of the graphene and the graphane. The DOSs of CF and CCl show that for both of them, the top of the valence band and the bottom of the conduction band are attributed to both the carbon atom and the halogen adatom, which is different from those of the

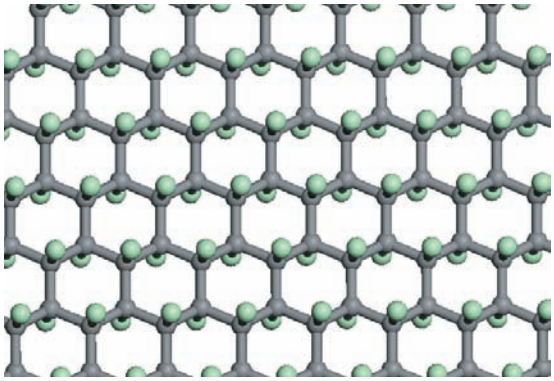


Fig. 3. (colour online) Graphane-like structure of CCl, showing the hexagonal network with carbon in the sp^3 hybridization, where C atoms are shown in gray and Cl adatoms in green.

Table 2. Structural and energetic properties of three optimized graphane-like carbon–halogen compounds. The corresponding properties of graphane and CCl_4 are shown. The carbon–halogen bond length (d_{CH}) and the corresponding C–C bond length (d_{CC}) and bond angle (θ) are given. The lattice parameter a is also presented. The bottom column is the relevant properties of CF with the monovacancy (CF_v), including the maximum C–C bond length (d_{CC}) and the bond angle around the defect. The values cited from Ref. [24] are given in parentheses.

	E_b/eV·atom^{-1}	d_{CH}/Å	d_{CC}/Å	θ/(°)	a/Å	Gap/eV
Graphane	6.556	1.103(1.111)	1.520(1.536)	111.567 (111.51)	2.513(2.540)	3.51(3.53)
CF	6.453	1.372(1.378)	1.567(1.583)	110.915 (110.84)	2.580(2.607)	3.28(3.16)
CCl	4.926	1.727(1.751)	1.740(1.759)	111.668 (111.92)	2.883(2.915)	1.66(1.53)
CBr	4.216	1.898(1.918)	1.837(1.863)	112.740 (112.98)	3.066(3.107)	0.00(0.00)
CCl_4	3.536	1.760	–	109.464	–	–
CF_v	6.304	1.372	1.568	115.916	–	–

graphene, where the top of the valence band and the bottom of the conduction band are π and π^* orbitals, respectively. It indicates that the electronic orbitals of the halogen adatom hybridize with the π orbital of the carbon atom to form a covalent bond and open a band gap. Thus, the transition from the sp^2 to the sp^3 hybridization is the main mechanism for forming those carbon–halogen compounds.

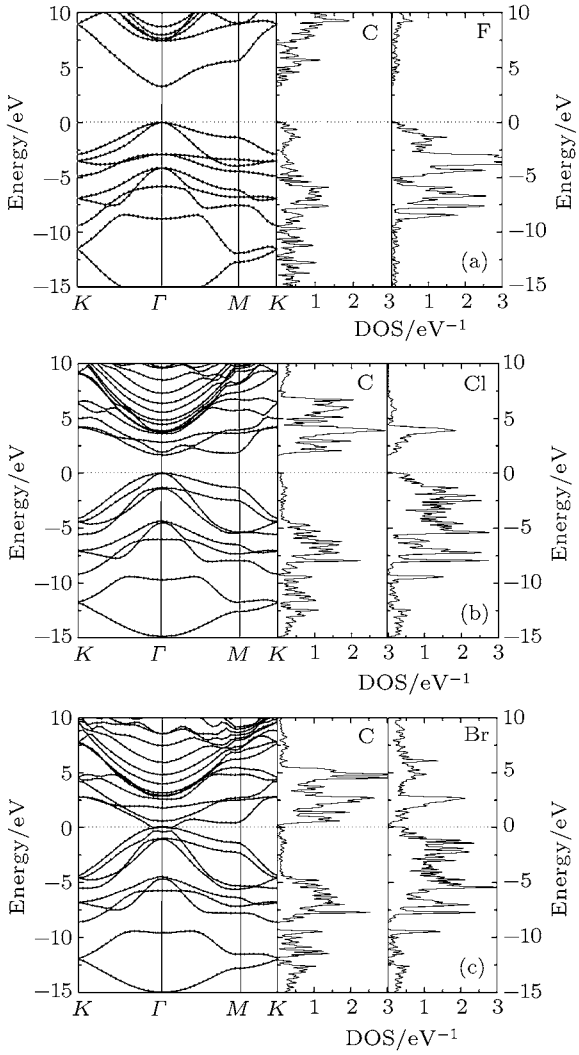


Fig. 4. (a) Band structure (left) and DOSs of C and F for CF (right), (b) band structure (left) and DOSs of C and Cl for CCl (right), and (c) band structure (left) and DOSs of C and Br for CBr (right).

We next compare our results with those obtained by the Vienna ab initio simulation package (VASP) calculations for the same systems. The comparison is presented in Table 2. We can see clearly that for all quantities under consideration, our results are in good agreement with the VASP results[24] with only a small deviation. The deviation is no more than 10% and the largest one is in the band gap. Such deviations may be due to the following reasons. Firstly, the pseudopotential that describes the interaction between the core and the valence electrons is different. The ultrasoft pseudopotential is used in our calculation, while the projector augmented wave one was used in Ref. [24]. Secondly, the lattice parameters including the length and the angle of all atoms in a unit cell are fully optimized in our calculations, while the angle between the lattice vectors was fixed during the relaxation process in Ref. [24]. Despite the small deviation, the overall agreement of the two results can be regarded as being satisfactory. Moreover, one point should be stressed. Our and the VASP results have shown that the halogen atoms can be chemically adsorbed on the graphene with a coverage of 100%. However, this is not true for the single-atom adsorption on the graphene. Our calculations indicate that in the single-atom adsorption, only the F adatom can be chemically adsorbed on the graphene, while the Cl and the Br adatoms are physically adsorbed. Actually, in the single-atom adsorption, the larger atom radii of Cl and Br make the chemical bonding with the graphene difficult. However, in the full coverage, the interaction between the halogen adatoms will favour the bonding of the halogen atom with the graphene, thereby forming a stable adsorption structure as described above.

To better understand the stability of the proposed carbon–halogen compounds, we perform an *ab initio* MD simulation[29−32] in the canonical ensemble by means of a Nose-Hoover thermostat to control the temperature. The simulation configuration contains 64 atoms per supercell. A time step of 1.5 fs is used and the calculations are carried out with a total simulation time of 3 ps.

First, we simulate the system at room temperature (300 K). We do not observe any sign of F and Cl desorption for both the CF and the CCl compounds. No conformational change can be observed from the final simulation configurations of CF and CCl except slight changes in the bond length and the bond angle. Generally speaking, the structure may become unstable with the temperature increasing. Then, a relatively high temperature of 700 K is employed. It is found that many C–C bonds are broken and the graphane-like configuration is destroyed in CCl, while it is retained perfectly in CF. This difference may be attributed to the stronger binding of the F adatom with the graphene, as seen in the comparison of the binding energy described above. Finally, the temperature is increased to 1200 K for the dynamics sim-

ulation of CF. The calculated result indicates that the graphane-like CF can exist stably even at such a high temperature. Therefore, those two graphane-like carbon–halogen compounds can be thermodynamically stable at room temperature, the CCl may be destroyed at a higher temperature, while to damage the stable structure of CF, a temperature higher than 1200 K is needed.

Next, we study the effects of defects on the structural and the electronic properties of the carbon–halogen structure. It has been demonstrated that certain topological defects can be induced by the irradiation of electron beams. In the two-dimensional graphene, topological defects, such as vacancies in the honeycomb carbon lattice, can heavily affect the structural and the electronic properties due to the structural irregularities.[33,34] Therefore, the defect should be considered as an important factor when we study the stability and the electronic structures of those new materials.

We study the stability and the electronic structures of CF (as an example) with a point defect, i.e., monovacancy, which is formed by the removal of one carbon atom. Here, the system is modeled using a 3×3 CF supercell with a monovacancy (17 fluorine adatoms and 17 carbon atoms). The calculated binding energies and the corresponding structural properties are listed in Table 2. For the monovacancy, the binding energy of 6.304 eV/atom is a little smaller than that of the perfect CF. Moreover, the maximum C–C bond length and the bond angle around the monovacancy are calculated to be 1.568 Å and 115.916°, respectively. Besides, the C–F bond length of 1.372 Å remains almost unchanged. It means that CF can overcome the influence of such a defect and keep its graphane-like configuration. In addition, the vacancy has a significant influence on the electronic structure of CF. Figure 5 shows the electronic band structures of the defective graphene and the CF with the monovacancy for comparison. As shown in Fig. 5(a), due to the presence of the vacancy, some bands arise near the Fermi level, while they are not present in the perfect graphene. These bands predominantly result from the atoms located around the vacancy. Similarly, the bands also arise near the Fermi level in the defective CF (Fig. 5(b)) compared with the band structure of the perfect one. Such a semiconductor–metal transition will be of significant importance for future electronic applications.

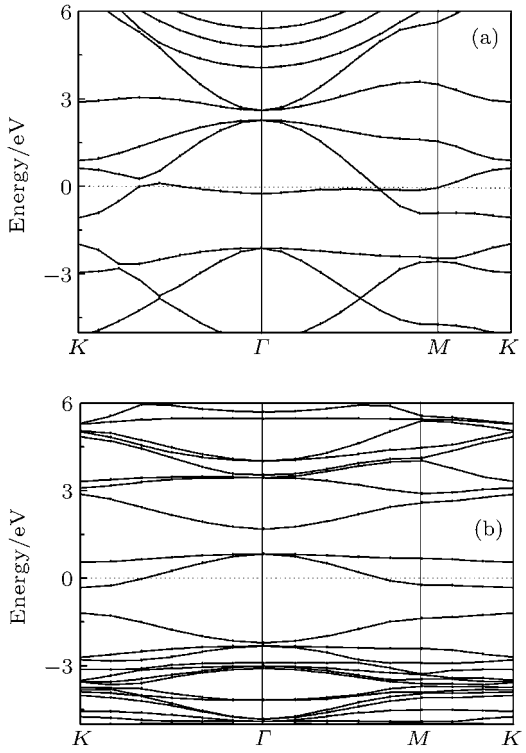


Fig. 5. Band structures of (a) defective graphene and (b) CF with the monovacancy.

4. Conclusion

We perform the first-principles total-energy calculations to predict the stability of the graphane-like structures of two-dimensional carbon–halogen compounds. It is found that the graphane-like structures, CF, CCl and CBr, are energetically stable. However, in the single-atom adsorption, only the F adatom can be chemically adsorbed on the graphene. BOth CF and CCl opens a direct band gap at the Γ point, while CBr is a metal. The electronic band is tuned compared with that of the graphene. The MD simulations reveal that CF and CCl are stable at room temperature, and CCl is destroyed at 700 K, while a temperature higher than 1200 K is needed to damage CF. Furthermore, the graphane-like configuration can be retained in CF even a vacancy is introduced. It is fascinating to find new members of the graphene-based compounds, which open a window into the world of low-dimensional materials.

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