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Double-sided F and Cl adsorptions on graphene at various atomic ratios: Geometric, orientation and electronic structure aspects

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(Zhong-Tao Jiang)
Abstract

Elemental adsorption on graphene offers an effective procedure in fine-tuning electronic and mechanical properties of graphene. The effects of dopants depend on adsorption site, the degree of coverage as well as on the configuration of the deployed supercell. In this contribution, the density functional theory (DFT) calculations were performed to investigate the electronic structures of F and Cl adsorption (double-sided, top site) on graphene in terms of adsorption orientation, atomic ratios, i.e., from C: F/Cl = 18:2 to C:F/Cl = 2:2. Despite being members of the halogens group, F- and Cl- adsorbed on graphene show contrasting trends. F is adsorbed to graphene more strongly than Cl. F favours full and 25% adsorption coverage, while Cl favours half 25% coverage. Both F and Cl cases open band gap (at Fermi energy) at certain atomic concentration coverage, but none creates magnetization.

1. Introduction

Graphene is a magnificent material with unique electronic, mechanical and optical properties applications[1]. Adding impurities to graphene is an effective way to enhance the aforementioned properties. Properties of elemental adsorption on graphene have been calculated in terms of site (bridge, hollow, top), e.g. metal adatoms[2], H – Bi (except noble gases and lanthanides) adatoms[3]. However, graphene with adsorbed O at atomic ratio of O/C of less than 30% was found to have a nonlinear band gap[4]. This band gap nonlinearity appears to be due to the positions of the adatoms relative to one another. This suggests that the electronic structure of elemental adsorption on graphene is affected not only by side of adsorption (single- or double-sided) and site of adsorption (bridge, hollow or top), but also to the relative orientation of the adsorbed sites (zigzag or armchair) (Fig. 1) [5].
Numerous syntheses, progress reports, simulations, experimental and theoretical studies have addressed adsorption of halogens on graphene [6–15]. There are two well-known results for fluorinated graphene. Fully fluorinated graphene (fluorographene/CF) is the most stable configuration for double-sided case, while CF$_{0.250}$ (Fig. 2) is the counterpart for single-sided case. In regards to Fig. 2, two factors appear to play an important role, namely, atomic percent/concentration (at.%) and atomic ratio, e.g. a 25 at.% has multiple C:F atomic ratios (4:1, 8:2, 12:3, 16:4, …). CF$_{0.250}$ cannot be explained using the simplest 4:1 atomic ratio, but rather 8:2 atomic ratio with certain adatom configuration. CF expands the graphene cell lattice constant of $\approx 0.13$ Å and opens a band gap of $\approx 3.00$ eV, while CF$_{0.250}$ opens a band gap of $\approx 2.93$ eV[7]. Liu et al. calculated fluorinated graphene from 3.1 at.% (C:F = 32:1) to 100 at.% (C:F = 2:2) with zigzag graphene cell/supercells [8]. There are some concerns on Liu et al.’s work, in relation to drawing trends on CF$_a$ (a = atomic concentration). Firstly, the cases are mixed between single- and double-sided. Secondly, one-side-adatom-addition/removal might be less stable than two-side-adatom-addition/removal.

Fig. 1. Side, site and orientation in elemental adsorption on graphene.
Fig. 2. Most stable configuration of single-sided fluorinated graphene of 25 at.%, red spheres are F atoms, grey spheres are C atoms [7]. This figure was adopted from Fig. 1 in our previous study [5].

In this contribution, density functional theory (DFT) calculations were applied to perform investigation on the electronic structures of F and Cl adsorption on graphene in terms of adsorption orientation, at various atomic ratios, spanning from very low atomic ratio (C:F/Cl = 18:2) to full adsorption (C:F/Cl = 2:2). The adsorption process is double-sided, to give consistent trends on the results and account for high atomic concentrations. In addition, the site is fixed to top, as it is adequate for the calculations. The most stable site for F is top, while Cl is site-independent, so any site for Cl can be picked. Overall, it is highlighted some prominent effects of orientation aspects on various properties such as binding energy, graphene cell lattice constant expansion, adatom height, band gap, Fermi energy, charge transfer, magnetization and density of states (DOS).

2. Methods

To investigate the most stable configuration, it is necessary to examine all possible positions. Unfortunately, this is not practical, as the number of cases will be infinite. As such, this study is limited to the cases with same number of adatom addition/removal on both sides of graphene supercells. So the calculations for F/Cl-adsorbed to graphene were set to the following atomic ratios (X=F/Cl) : CX_{0.500} (8:4), CX (2:2), and pairs {adatom addition and removal} of \{CX_{0.111} (18:2) and CX_{0.889} (18:16)\}; \{CX_{0.250} (8:2) and CX_{0.750} (8:6)\}; \{CX_{0.333} (6:2) and CX_{0.667} (6:4)\}. Five graphene cells/supercells were used (Figs. 3a – 3e). However, slant 3 × √7 was not used, because the adatoms (F/Cl) are too far to interact with one another. As such, the results for 3 × 3 are expected to be the same as 3 × √7.
All structural optimizations and energy calculations were performed using the plane-wave DFT code of VASP. Calculation methodology consists of spin-polarized PAW-GGA functional [16], HSE06 functional [17], van der Waals correction by Grimme [18] method, and a Gaussian smearing. A pair of particles separated by distance $r$ exhibits a weak short-range Van der Waals force interaction proportional to $r^{-6}$. For our cases, dipole correction to $z$ direction is not needed, as the number of adatoms is the same on both sides of the graphene.

The calculations were conducted in four stages: (1) adatom and pristine graphene energy, (2) geometrical analysis for positioning the adatoms using GGA, (3) graphene-adatom lattice expansion with internal structure optimization using GGA, and (4) adatom-graphene density of states (DOS) calculation using both GGA and HSE06. In the third stage, the calculations were performed using symmetrical lattice expansion (lattice parameters $a$ and $b$ are at constant proportion, $c = 15$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). We set the plane wave cut off energy of 600 500 eV. In all structures, we deployed a tolerance of less than 1 $\mu$eV 0.1 meV for energy and less than 0.02 0.1 eV/Å for forces on each atoms.

The binding energy, lattice constant expansion, adatom height, band gap, Fermi energy, charge transfer, magnetization and DOS were calculated for all the cases. Binding energy $E$ is calculated using equation:

$$E = \frac{(E_{\text{graphene}} + E_{\text{adatoms}} - E_{\text{adatoms-graphene-system}})}{\text{number of adatoms}} \quad (1)$$

$$E = \frac{(E_{\text{graphene}} + E_{\text{upper adatoms}} + E_{\text{lower adatoms}} - E_{\text{adatoms-graphene}})}{\text{number of adatoms}} \quad (1)$$

Fig. 3. Graphene cells/supercells, all are zigzag orientation, except $2 \times \sqrt{3}$ is armchair and $3 \times \sqrt{7}$ is slant.

(a) $1 \times 1$  (b) $\sqrt{3} \times \sqrt{3}$  (c) $2 \times 2$  (d) $2 \times \sqrt{3}$  (e) $3 \times 3$  (f) $3 \times \sqrt{7}$ (not used)
where \( E_{\text{graphene}} \) denotes the energy of the pristine graphene, \( E_{\text{upper adatoms}} \) signifies the energy of the relaxed adatoms above the graphene (without graphene sheet), \( E_{\text{lower adatoms}} \) signifies the energy of the relaxed adatoms below the graphene (without graphene sheet) and \( E_{\text{adatoms-graphene}} \) is the total energy of the adatoms and graphene after the adatom is attached to the graphene. At a lattice constant of e.g. \( a_0 \), all four energy terms were relaxed at \( a_0 \).

Herein, we compute the band gap based on the DOS [19] analysis in which a zero DOS value marks the Fermi energy. Adatom height (Å) signifies the difference in \( z \)-coordinate between adatom’s and the average of \( z \)-coordinates of carbon atoms. Total charge is estimated as the sum of total spin-up and spin-down values whereas magnetization is expressed as the variation between total spin up and total spin down at the Fermi energy level. We calculate charge transfer (as a scalar quantity) based on the Bader’s [20] formalism. A positive value of charge transfer indicates that that charge is shifted from graphene to adsorbates.

### 3. Results and discussion

At high atomic ratio, it is well known that chair structure of CF and CCl [6] is the most stable configuration. At low atomic ratio, Yuan and co-researchers concluded that F atoms tend to form in pairs during fluorination [21]. Whilst at low atomic ratio for Cl case, Şahin and co-researchers stated that single Cl vacancy on one side of the graphene imposes another single Cl vacancy on the other side of the graphene [12]. Armed with these aforementioned findings, we did extensive tests on many geometrical configurations using GGA functional, and Table 1 summarizes the most important test results.
Table 1
Configurations and binding energies for F- and Cl-adsorbed graphene.

<table>
<thead>
<tr>
<th>Configuration(^a)</th>
<th>F case</th>
<th>Cl case</th>
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<tbody>
<tr>
<td></td>
<td>Lattice constant (Å)</td>
<td>Binding energy (eV/adatom)</td>
</tr>
<tr>
<td></td>
<td>7.40</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>7.40</td>
<td>2.55(^b)</td>
</tr>
<tr>
<td></td>
<td>7.40</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>7.40</td>
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<td></td>
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<tr>
<td></td>
<td>7.40</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>7.74</td>
<td>2.18(^c)</td>
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<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>7.74</td>
<td>2.02</td>
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\(^a\) The bigger red circle is the adatom above the graphene while the smaller red circle is the adatom below the graphene.

\(^b\) The most stable configuration (adatom addition).

\(^c\) The most stable configuration (adatom removal).
Based on Table 1, we can verify that for F/Cl-adsorbed graphene (CX, X=F/Cl): (1) at the same atomic concentration, double-sided is more stable than single-sided adsorption; (2) C₂X₂ cluster configuration of Fig. 4a gives stability for both addition and removal; (3) C₂X₂ cluster configuration of Fig. 4b induces less stability. This finding facilitates the positioning of adatoms on both side of the graphene in a more manageable manner. For clarity in the subsequent figures, configuration shown in Fig. 4a is represented using a triangle (Fig. 5). Unfortunately for CX₀.₅₀₀, further simplification for cluster with four adatoms cannot be verified from our cases. As a result, there are more than ten combinations appear for CX₀.₅₀₀. So all possible initial configurations can now be determined as shown in Fig. 6.

**Fig. 4.** Most stable C₂X₂ cluster (X=F/Cl), grey is C, red is F/Cl.

**Fig. 4.** C₂X₂ clusters (X=F/Cl): (a) more stable, (b) less stable, grey is C, red is F/Cl.

**Fig. 5.** Two-adatom adsorbed on graphene, big red circle is adatom at the upper side of graphene, small red circle is adatom at the lower side of graphene (a) is represented using a triangle (b).
Fig. 6. All possible initial configurations for F/Cl-adsorbed graphene based on the used atomic ratios, red triangle is a pair of F/Cl adsorbed on the upper and lower side of the graphene (X=F/Cl).

Figs. 7 - 9 show the calculation results. The most stable orientation for CX$_{0.250}$ and CX$_{0.750}$ is armchair, CF$_{0.500}$ is zigzag and CCl$_{0.500}$ is armchair. This shows that orientation does affect the stability of CX$_X$. Although F and Cl are in the halogen group of the periodic table of elements, their adsorption trends on graphene are very dissimilar (Fig. 8-9). This indicates that having similar electronic configuration ($s^2p^5$ or one unpaired valence electron) does not give similar trends when adsorbed to graphene. Adatom’s size and mass compared to carbon’s size and mass seem to have greater influence. F has comparable atomic radius to C, but Cl is 29% larger than C in radius. F is slightly heavier than C, but Cl is three times heavier than C. Van den Broek and co-researchers [22] showed in their calculations, that fully adsorbed F on silicene (SiF) and germanene (GeF) exhibit some similarities to CF, e.g. most stable at top site with CF-like structure. So, our surmise is within the same group in the periodic table of elements, applying smaller/lighter adsorbate atom (or bigger/heavier adsorbent atom) may
show similarities. On comparing atomic size and mass, F-adsorbed graphene might be analogous to Cl-adsorbed on silicene, but this needs further examinations in future research.

**Fig 7.** Initial configurations that produce the most stable configurations for F/Cl-adsorbed graphene based on the used atomic ratios, red triangle is a pair of identical adatoms adsorbed on upper and lower side of the graphene, from left to right (X=F/Cl) : CX_{0.111} (18:2), CX_{0.250} (8:2), CX_{0.333} (6:2), CX_{0.500} (8:4), CX_{0.667} (6:4), CX_{0.750} (8:6), CX_{0.889} (18:16), CX (2:2).

DOS landscapes (Fig. 8) were created by scaling the original DOS to our largest supercell (zigzag 3 × 3) to give consistent picture across the atomic concentrations. Band gaps (blue areas in Fig. 8) were extracted from the scaled DOS with the threshold of 0.13 state/unit cell. This threshold was selected, because of DOS above 0.13 state/unit cell causes the band gap opening in pure graphene in zigzag 3 × 3 supercell. The numerical result plots on band gaps at Fermi energy are shown in Fig. 9d. With this threshold, our result for CF (≈ 2.63 2.61 eV) is somewhat lower than the experiments (3 eV[23], 3.8 eV[24], 5 eV[25]) or calculations by others (3.1 eV (PBE)[26], 8.3 eV (GW)[27], 3.09 eV (PBE) and 4.88 eV (HSE06)[28], 6.3 eV (GW)[21]). The band gap difference between ours (≈ 2.63 2.61 eV) and other DFT calculations (e.g. 3.1 eV[27]) is mainly because of the DOS threshold selection. Picking up different DOS threshold results different band gap. This lower band gap result is also due to the nature of the pure DFT calculations that underestimate the band gap. However, it’s still valuable to provide the band gap trend against the adsorption orientation. To achieve more accurate results, we have performed calculations based on the GGA optimized structures with HSE06 functional (Figs. 8b, 8d, 9d, 9e and 9f). corrections must be applied (e.g. HSE06 functional, GW approximation), which is in our future consideration.
Fig. 8. DOS (total spin) and Fermi energy (0.0 eV) of (a) CF₄ - GGA, (b) CF₄ - HSE06, (c) CCl₄ - GGA, (d) CCl₄ - HSE06. The blue areas denote zero DOS.
For F cases, binding energies, graphene cell lattice constants and adatom heights are relatively linear at high atomic concentration. Charge transfers are almost linear for all atomic concentrations. However, band gaps and Fermi energy shifts show non-linearity. Binding energies are inversely proportional to adatom heights. Graphene cell lattice constants start increasing significantly when the adsorption is more than 50 at.%.

Fig. 9. Calculated trends for CF₄ and CCl₄. None creates magnetization. The dotted lines are added as guides and do not imply continuity.
Binding energies (normalized to the CF binding energy) are higher for double-sided addition/removal (our results) than single-sided addition/removal results of Liu et al. [8]. This double-sided adsorption results in huge difference on band gaps. This also delays our graphene cell lattice expansion at around 50 at.%. Figures 10a - 10c are plots of the calculated trends for CF\textsubscript{a} compared with results from Liu et al. [8].

Fig. 10. Calculated trends for CF\textsubscript{a} compared to Liu et al.’s work [8]. The dotted lines are added as guides and do not imply continuity.

For Cl cases, at atomic concentration above 50 at.%, the adsorption becomes weak (physisorbed), as indicated by the decreasing binding energies, large adatom heights are approximately 3.50 Å, zero band gaps at Fermi energy and minuscule charge transfers (Fig. 9). Medeiros and co-researchers [11] calculated two different CCl configurations, *i.e.* non-bonding and bonding. Non-bonding configuration has lower total energy. Non-bonding is more likely to occur, because of having greater binding energy and creating more reasonable graphene lattice expansion than the bonding counterpart. On the dynamical side, Although having greater binding lower total energy, Şahin and co-researchers [12] calculated that non-bonding is dynamically unstable, because Cl atom can roam on the graphene surface.
without barrier energy. This is supported by Nakada and Ishii’s calculation [29], which stated that migration energy for Cl-adsorbed graphene is minimal (0.02 eV). Our previous study [5] also supports this and we concluded that non-bonding Cl-adsorbed graphene is basically site-independent. Furthermore, Şahin and co-researchers also reported that bonding configuration is dynamically stable at 0 K and possibly at room temperature, but with graphene lattice expansion of more than 15%. Using the binding energy formula (Eq. 1), our results show that there is competition between bonding and non-bonding configuration, which non-bonding wins at 50% to 75% atomic ratios. At these atomic ratios, the adsorption becomes weak (physisorbed), as indicated by the decreasing binding energies, large adatom heights are approximately 3.50 Å, zero band gaps at Fermi energy and miniscule charge transfers (Fig. 9). As we did not calculate the migration energies, our calculation for CCl is in agreement with the non-bonding calculation of Medeiros and co-researchers.

F is adsorbed to graphene at least two times stronger than Cl (Fig. 9a). CF$_4$ is most stable at full and 25% coverage, while CCl$_4$ is most stable at 25% coverage half coverage or less. Adatom heights for F are inverse proportional to atomic concentrations, but adatom heights exhibit discreteness for Cl (Fig. 9c). For both F and Cl cases, band gap (at Fermi energy) occurs at certain atomic concentration coverage (Fig. 9d). However, magnetization is not created due to the adatom addition/removal that is done in pairs.

4. Conclusions

The electronic structures of F and Cl adsorption (double-sided, top site) on graphene were investigated and analysed geometrically in terms of adsorption orientation, at a wide range of atomic ratios. At the same atomic concentration, double-sided adsorption is more stable than single-sided counterpart. Despite being in the halogens group, F- and Cl-adsorbed graphene cases show contrasting trends. Their electronic structures are affected by the relative orientation of the adsorbed sites (zigzag or armchair) and possibly the relative size/mass of the adatoms and carbon. This calls for careful consideration of the orientation effect in element-graphene systems. F is adsorbed to graphene more strongly than Cl. F favours full and 25% adsorption coverage, while Cl favours half 25% coverage. Finally, taking adsorption orientation into account, both F and Cl cases open a band gap (at Fermi energy) at certain atomic concentration coverage, but none creates magnetization.
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References


**Highlights**

- We examined the orientation (zigzag, armchair) effects of F/Cl-adsorbed graphene
- Both F/Cl-adsorbed graphene systems show contrasting adsorption trends
- F favours full and 25% adsorption coverage while Cl favours 25% adsorption coverage