

Interaction of chlorine adatom with lithium adatom on opposite sides of graphene

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Abstract. Using first principles density functional theory, we study chlorine (Cl) and lithium (Li) adatoms co-adsorption properties on different sides of single-layer graphene sheet. Cl adatom gathers more charge and the adsorption system become more stable. But due to the effects of graphene, the interaction between Li and Cl adatoms is weakened and the lost charge of Li adatom is not all transferred from graphene to Cl adatom.

1. Introduction

Having superior properties, graphene can be used in various carbon based nanodevices [1-3]. The 2s, 2p_x and 2p_y atomic orbitals on each carbon of graphene hybridize to form strong covalent sp² bonds with its three neighbouring carbons and the remaining 2p_z orbital on each carbon overlaps to form a big delocalized π bond. Due to this unique structure, graphene has ultrafast carrier mobility and extremely high electrical conductivity [4]. But the forming of the big π bond reduces the activity of graphene, meaning that pure graphene has inertia in some way. Graphene has other outstanding features such as the wide open double-side surface. Therefore, it can be functionalized by adsorbing atoms to produce novel nanomaterials [5-7].

In our paper, Li and Cl adatoms co-adsorbed on different sides of graphene are studied. And the adsorption geometric structure, electronic properties are reported. The effects of graphene on the interaction between Li and Cl adatoms are discussed.

2. Methods

All calculations have been performed within DFT under the generalized gradient approximation [5]. The kinetic energy cutoff was taken as 550 eV. The reciprocal space was sampled using a 9×9×1 k-point grid during the relaxation process. The standard of convergence during the relaxation process



is that the force on each atom was less than 0.01 eV/Å. The perpendicular distance between the neighbouring graphene layers was taken 25Å.

Figure 1 represents a 5×5 supercell of graphene model with a single adatom adsorbing at three different sites: the T-site, B-site and H-site.

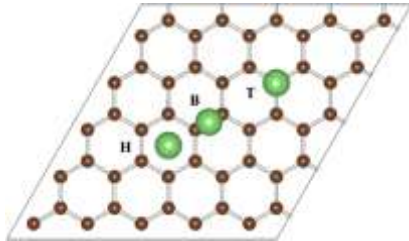


Figure 1. (Color online) Top view of the three adsorption sites.

3. Results

Table 1 lists the adsorption results of a single Li and Cl adatoms.

Table 1. Adsorption results of a single Li and Cl atom adsorbed on graphene.

adatom	site	$\Delta E(\text{eV})$	$h(\text{\AA})$	$\Delta h_c(\text{\AA})$	$\Delta q(\text{e})$
Li	H	-1.52	1.74	0.01	-0.92
	B	-1.22	1.92	0.07	-0.92
	T	-1.19	1.93	0.10	-0.90
Cl	T	-1.12	3.08	0.01	0.51
	B	-1.11	3.10	0.01	0.52
	H	-1.09	3.16	0.01	0.51

The adsorption energy is defined as [5]:

$$\Delta E = E_{\text{total}} - E_G - E_a \quad (1)$$

where ΔE , E_{total} , E_G and E_a are the adsorption energy, the energy of the adsorption system, the energy of pristine graphene, and the energy of the single adatom, respectively [5]. Among the parameters, h represents the adsorption height of adatom. Δh_c is represents the maximum deviation distance of the carbon atoms.

For Li adatom, the adsorption system have the minimum energy at H-site. Li adatom almost transfers its whole outmost valence electron to graphene. These results are consistent with previous reports [5-8]. There is negligible difference among the three sites for Cl adsorbed on the surface of graphene. The adsorption height is in excess of 3Å, far beyond the length of the covalent bond that is forming between single Cl and single carbon atoms. The charge that is transferred from graphene to Cl adatom is relatively less, only about 0.5e. All the results are in agreement with previous reports too [9-10].

Table 2 displays the results of Li/Cl adatoms co-adsorbed on opposite sides of graphene. The adsorption energy is:

$$\Delta E = E_{\text{total}} - E_G - E_{\text{Li}} - E_{\text{Cl}} \quad (2)$$

Table 2. Adsorption properties of Li/Cl co-adsorbed on different sides of graphene.

Adatoms	Site	$\Delta E(\text{eV})$	$h(\text{\AA})$	$\Delta q(\text{e})$	$\Delta h(\text{\AA})$
Li/Cl	H/T	-3.49	1.74/2.81	-0.90/0.69	0.08
	H/B	-3.48	1.75/2.84	-0.90/0.69	0.04
	H/H	-3.44	1.76/2.93	-0.90/0.70	0.01
	B/T	-3.23	1.92/2.83	-0.91/0.68	0.09
	B/B	-3.22	1.95/2.86	-0.91/0.68	0.08
	B/H	-3.15	1.96/2.94	-0.91/0.70	0.06
	T/T	-3.24	1.88/2.80	-0.91/0.65	0.09
	T/B	-3.20	1.93/2.86	-0.91/0.67	0.10
	T/H	-3.12	1.96/2.94	-0.91/0.69	0.10

ΔE , E_{total} , E_G , E_{Li} and E_a are the adsorption energy, energy of adsorption system, total energy of pure graphene, the total energy of a single Li adatom and the total energy of single Cl adatom, respectively. The adsorption system has the minimum and maximum energy when Li/Cl adatoms at the H/T and T/H sites. The adsorption height and the charge loss of the Li adatom change very little compared with the situation that only single Li adatom adsorbed; while Cl adatom receives more charge from graphene, it is about 0.17 e and its adsorption height decreases about 0.2 Å.

Li adatom transfer its outmost valence electron to graphene and then Cl gets charge more easily under the co-adsorbed situation. Therefore, the interaction among the adsorbates and substrate is enhanced. The adsorption energy is larger than the sum of adsorption energy of single Li and Cl adsorption systems (as shown in table 1).

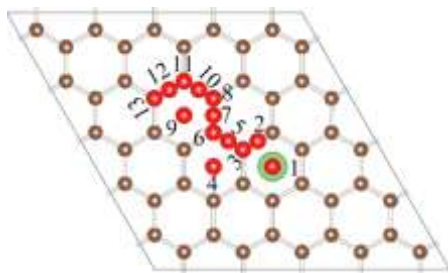
**Figure 2.** Top view of Cl adatom (red balls) adsorbs on different sites on G-Li adsorption system.

Table 3 summarizes the results when Li adsorbs at H-site and Cl adsorbs on another side of graphene at different sites as figure 2 depicts. Among the parameters, d_{xy} represents the distance between Li and Cl adatoms parallel to the surface of graphene. With the increase of the horizontal distance between the two adatoms, the adsorption energy generally shows a slightly decreasing trend. Among the thirteen sites we considered, the largest changing of the adsorption energy is only about 0.15 eV when Cl adatom adsorbed at 3rd and 10th sites respectively. Variations of the adsorption height and the charge transfer of adatoms are very slight too. The insensitive adsorption results with the variation of

the horizontal distance between the adatoms imply that graphene can shield the interaction between the adatoms due to the formation of big π bonds.

Table 3. Adsorption properties of Li/Cl co-adsorbed on different sides of graphene with different horizontal distance.

Adatom	No.	Site	$\Delta E(\text{eV})$	$h(\text{\AA})$	$\Delta q(\text{e})$	$\Delta h_c(\text{\AA})$	$d_{xy}(\text{\AA})$
Li/Cl	3	H/T	-3.49	1.74/2.81	-0.90/0.69	0.08	1.42
	6		-3.43	1.74/2.83	-0.90/0.66	0.05	2.85
	8		-3.39	1.74/2.85	-0.90/0.66	0.04	3.77
	11		-3.35	1.74/2.89	-0.90/0.67	0.03	5.14
	13		-3.35	1.74/2.88	-0.90/0.66	0.04	5.71
	2	H/B	-3.48	1.74/2.84	-0.90/0.69	0.04	1.24
	5		-3.46	1.74/2.84	-0.90/0.69	0.05	2.14
	7		-3.40	1.74/2.87	-0.90/0.68	0.02	3.27
	10		-3.36	1.74/2.89	-0.90/0.68	0.02	4.45
	12		-3.34	1.74/2.91	-0.91/0.67	0.02	5.38
	1	H/H	-3.44	1.76/2.93	-0.90/0.70	0.01	0
	4		-3.40	1.74/2.93	-0.90/0.69	0.02	2.47
	9		-3.33	1.74/2.97	-0.90/0.68	0.02	4.28

4. Conclusion

The characteristic of Li/Cl adatoms co-adsorbed on different sides of graphene are studied. The adsorption system become stronger in the case of co-adsorption. However, Cl adatom does not collect all the charge that Li adatom transferred to graphene. And the adsorption energy insensitive to the variation of the horizontal distance between Li and Cl adatoms. It imply that the Li and Cl adatoms bind with graphene independently. This is due to the formation of the big π bond makes graphene has the obvious inertia and the electrostatic screening effect. Graphene can weaken the interaction and hamper the charge transfer between the two adatoms which co-adsorbed on the opposite sides of graphene.

References

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