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Research paper

First principles study the effects of alkali metal and chorine adatoms on the opposite surface of graphene

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ABSTRACT

Study of the adsorption properties of graphene has great significance for expanding its application. So far, few studies have analyzed the effects of adatoms on opposite sides of graphene. We use density functional theory to report the effects of chlorine and alkali metal adatoms on the other side of graphene. Although there is an obvious charge transfer between the adatom and graphene, the interaction between the adatoms is shielded by the large π bonds of graphene and therefore the effects of the adatom on the other side of graphene are very weak.

1. Introduction

Graphene, which is a common two-dimensional carbon system with outstanding physical and electronic properties, has drawn increased attention for diverse potential applications, ranging from composites to optoelectronics [1–11]. The s, p_x, and p_y atomic orbitals on each carbon of graphene hybridize to form strong covalent sp^2 bonds with three neighboring carbons. The remaining p_z orbital on each carbon overlaps to form a large delocalized π bond [12]. Due to this unique structure, graphene has an ultrafast carrier mobility, which is crucial for its stable existence at room temperature [13,14]. It also has an extremely stable chemical property as the two large π bonds realize a planar distribution of the electron cloud on the graphene surfaces. However, a drawback of graphene is that it does not easily interact with other media. That is, graphene is chemically inert.

Adsorption other atoms or functional groups can increase the surface activity of graphene, realizing new physical and chemical characteristics. Adsorption may expand graphene applications significantly. Therefore, adsorbate decorated graphene nanomaterials have received increased attention. Much effort has been expended to understand the surface properties of graphene [15–20].

Monolayer graphene is the thinnest impermeable film of all atoms and molecules under ambient conditions due to the formation of large π bonds [21–25]. Although many studies have investigated atoms or functional groups adsorption on graphene, studies analyzing the effects of adatoms on opposite sides of graphene are lacking, especially when two different kinds of atoms are simultaneously adsorbed on different sides of graphene.

Alkali metal (AM) atoms and chlorine (Cl) atoms are some of the most active elements. AM atoms easily lose their outmost valence electrons, while the Cl atom always collects electrons [26]. Previous reports have shown that AM or Cl atoms bond ionically with graphene and the effects of the geometric structure of graphene are relatively small [27–33]. The electronegativity of carbon atoms is in between those of AM and Cl atoms, which is beneficial to study the effects of adatoms on the other side of graphene when AM and Cl atoms are adsorbed simultaneously on the opposite sides of graphene.

In this work, we present a detailed analysis of the effects of adatoms on the opposite surfaces of graphene using density functional theory. Our main motivation is to reveal the characteristics of the large π bonds when a single AM atom and a single Cl atom are simultaneously adsorbed on opposite sides of graphene.

2. Theoretical and computational details

All calculations were performed with the Vienna Ab-initio Stimulation Package (VASP) based on first-principles (DFT) with projector augmented wave (PAW) potentials. The exchange correlation functional was approximated by generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerh (PBE) [34–37]. The kinetic energy cutoff was 550 eV. The reciprocal space was sampled using a $9 \times 9 \times 1$ k-point grid for Brillouin zone (BZ) integration during the relaxation process and the total energy calculations, while a $15 \times 15 \times 1$ mesh was adopted for the DOS calculations. The Gaussian smearing method was employed with

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a width of 0.05 eV [31]. In the geometry optimization, all atoms were allowed to relax until the force on each atom was less than 0.01 eV/Å. The primitive graphene lattice constant of 2.46 Å was used in the calculation. The minimum distance perpendicular to the graphene layer was 25 Å to eliminate the interaction between the graphene sheet and its periodic replicas [26]. The Bader method was used in the charge transfer analysis. The supercell dimensions were fixed for all calculations and the polarization was not considered [31].

Fig. 1 represents a 5×5 hexagonal supercell of graphene, which was employed as the graphene model with a single adatom adsorbing at three different sites: the T-site (above a carbon atom), the B-site (above the midpoint of a carbon-carbon bond), and the H-site (above the center of a hexagonal ring of graphene).

The total energy of an isolated adatom was approximated by the calculations with the same supercell dimensions. The $3 \times 3 \times 3$ k-point grid was taken.

3. Results

Table 1 lists the results for single AM and Cl adatoms adsorbed on graphene. The adsorption energy is defined as

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

where ΔE is the adsorption energy, E_{total} is the total energy of the whole system, E_G is the total energy of pristine graphene, and E_a is the total energy of the isolated adatom [31]. The adsorption geometry is obtained from the positions of the atoms after relaxation. The adatom height (h) is defined as the difference in the z-coordinates of the adatom and the average of the z-coordinates of the C atoms in the graphene layer [33]. In the present calculations, the Fermi energy and the work function of pristine graphene are −3.06 eV and 4.26 eV (W_0), which are in agreement with the results of some previous reports [33,38,39]. Of the three adsorption sites, the site with the largest adsorption energy is referred to as the favored site. For the AM and Cl adatoms, the most favored sites are the H-site and the T-site, respectively, but the difference in the adsorption energy is relatively small among the three sites. For the AM adatom on graphene, the Fermi level shifts higher, reflecting a greater occupation of graphene states because the AM adatom almost donates its outmost valence to graphene. Conversely, the Fermi level of graphene drastically decreases as the Cl adatom collects the charge from graphene. All the results agree with previous reports [26–31,33,38]. W_0, W_A, and W_V represent the potential energy of graphene at the vacuum level, the side with the adatom, and the side without the adatom, respectively. There is great difference among the potential energy of the different sites of graphene (Table 1).

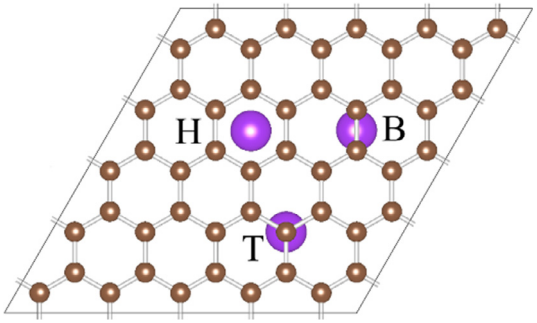

Fig. 1. Top view of the three adsorption sites considered: hollow (H), bridge (B), and top (T).

Table 2 displays the results when a single AM adatom and a single Cl adatom are co-adsorbed on the opposite sides of graphene. The adsorption energy of the co-adsorbed system is about 0.9 eV larger than the sum of the single AM and Cl adsorption systems (Table 1). This indicates that the interaction among the adsorbates and substrate is enhanced. Compared with the AM adatom decorated graphene, the adsorption height and the charge loss of the AM adatom are almost unchanged when the AM and Cl adatoms co-adsorbed on different sides of graphene. Although the Cl adatom receives more charge from the co-adsorbed system, it is about 0.17 e and its adsorption height decreases nearly 0.2 Å. The variation in the adsorption energy is smaller when the AM and Cl adatoms are co-adsorbed on the favored site and the least favored site, respectively (i.e., K/Cl co-adsorbed at H/T and T/H sites).

Fig. 2 depicts the results where a single Cl adatom is adsorbed above the graphene and a single K adatom is adsorbed simultaneously at the H-site below the graphene. As the horizontal distance between the two adatoms increases, the adsorption energy shows a very slightly decreasing trend and the charge transfer of the adatoms changes slightly. Among the thirteen sites considered, the largest difference in the adsorption energy is only about 0.1 eV when the Cl adatom is adsorbed at the third and twelfth sites, respectively. The largest variations in the charge of K and Cl adatoms are only about 0.02 e and 0.03 e. With the variation in the horizontal distance between the K and Cl adatoms, the largest change in the adsorption height and Fermi energy, are 0.04/0.12 Å (h_K/h_{Cl}) and 0.1 eV, respectively. For other AM adatoms on graphene, the adsorption results has similar variational trends. These results indicate that the effects of the adatom on the other side of gra-

Table 1
Energetic and structural properties of AM and Cl adatoms. Properties listed include the adsorbed energy (ΔE), adatom height (h), charge transfer (Δq), Fermi energy (E_F), dipole moment (p), work function (W_0), potential energy of the side with the adatom (W_A), and potential energy of the side without the adatom (W_V).

Adatom	Site	ΔE (eV)	h (Å)	Δh_c (Å)	Δq (e)	E_f (eV)	p (a.u.)	W_0 (eV)	W_A (eV)	W_V (eV)
–	–	–	–		–	−3.06	–	4.27	–	–
Li	H	−1.52	1.74	0.01	−0.92	−1.92	−1.66	3.07	2.63	3.49
	B	−1.22	1.92	0.07	−0.92	−1.83	−1.83	2.97	2.44	3.48
	T	−1.19	1.93	0.10	−0.90	−1.83	−1.95	2.96	2.51	3.49
Na	H	−0.84	2.21	0.01	−0.92	−1.81	−2.19	2.91	2.35	3.47
	B	−0.71	2.32	0.05	−0.86	−1.73	−2.27	2.82	2.20	3.47
	T	−0.70	2.36	0.07	−0.87	−1.74	−2.36	2.84	2.20	3.47
K	H	−1.24	2.56	0.04	−0.92	−1.52	−3.10	2.59	1.88	3.43
	B	−1.17	2.61	0.09	−0.91	−1.46	−3.03	2.56	1.78	3.43
	T	−1.09	2.62	0.11	−0.90	−1.49	−3.14	2.56	1.78	3.43
Cl	T	−1.12	3.08	0.01	0.51	−4.18	2.25	5.56	6.04	4.90
	B	−1.11	3.10	0.01	0.53	−4.18	2.30	5.58	6.03	4.88
	H	−1.09	3.16	0.02	0.51	−4.18	2.42	5.60	6.05	4.89