

Absorption of Na adatom on Cl -Decorated Graphene

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ABSTRACT

The effects of the Na adatom on Cl-decorated graphene are studied using first principles density functional theory. It is calculated the adsorption energy, geometric structure, charge density difference, and density of states. When Na adatom is absorbed on Cl-decorated graphene, the adsorption energy of Na increases by about 1 eV and the adsorption system becomes more stable because graphene can effectively transfer the 3s valence of the Na adatom to the Cl adatom.

Keywords: grapheme, adsorption, first principles

1. INTRODUCTION

Graphene, which is a 2D single layer with an sp^2 -bonded carbon lattice, has many prominent intrinsic chemical and physical features. So it has potential in various applications, including electronics, catalysis, sensors and energy storage . Due to it has exceptionally high specific surface area, which is up to $2675 \text{ m}^2/\text{g}$, graphene can be doped by adsorbing atoms of other elements. Alkalies can form 2D layers on the surface of graphene and have been investigated in a wide range of studies [1-3]. The adsorption energy of Na adatom on graphene is lower than other alkali adatoms, limiting the applications of Na-decorated graphene [4].

Cl atoms have the highest electron affinity and the fourth highest electronegativity of all reactive elements. In this work, the adsorption of Na adatom on Cl-decorated grapheme (G-Cl) is studied using first principles density functional theory (DFT).

2. METHODS

A 5×5 supercell (50 carbon atoms) was used as the graphene model to eliminate the coupling interaction of adjacent adatoms. The calculations used fixed supercell dimensions and a lattice constant of 2.47 \AA , which is

slightly larger than the experimental value of 2.46 \AA . The minimum distance perpendicular to the layer was 25 \AA , making the interactions among the perpendicular cells negligible.

The Vienna Ab-initio Stimulation Package (VASP) [5] was used to perform all calculations under the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerh (PBE). Ion cores were modeled with the projector augmented wave (PAW) potentials. The semicore $2p^63s^1$ states of Na and the $3s^23p^7$ states of Cl were treated explicitly as valence states. Spin polarization is not considered in this work. The cutoff for the plane waves' kinetic energy was 500 eV. All atoms were allowed to relax until the residual forces were less than $0.01\text{eV}/\text{\AA}$ in the optimization. A Gaussian smearing with a width of 0.05 eV was used for the occupation of the electronic levels.

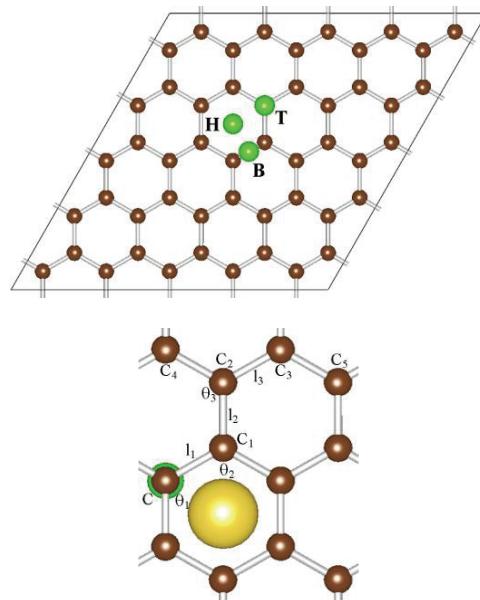


FIG. 1. (Color online) Atomic structure of 5×5 graphene with three different adsorption sites and: hollow (H), bridge (B), and top (T). Na on hollow (H) site of the Cl-decorated graphene.

Figure 1 shows the graphene model with a single Na adatom adsorbing at three different sites on Cl-decorated:

the T-site (directly above a carbon atom), B-site (above the midpoint of a carbon-carbon bond), and H-site (above the center of a hexagonal ring of graphene). Cl were decorated at T-site on opposite.

3 RESULTS AND DISCUSSION

Table I shows the result when a single Na adatom adsorbs above the Cl decorated graphene. We calculated nine combinations of Na and Cl adatoms when they adsorbed on the same hexagonal. The adsorption energy is defined as

$$\Delta E = E_{\text{total}} - E_{G/\text{Cl}} - E_{\text{Na}} \quad (1)$$

where ΔE is the adsorption energy, E_{total} is the total energy of the whole system, $E_{G/\text{Cl}}$ is the total energy of the system when a single Cl adatom adsorbs on graphene, and E_{Na} is the total energy of an isolated Na atom. 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.

TABLE I. energetic and structural properties of Na and Cl adatoms adsorbed simultaneously above and below graphene. Properties listed are the sites of adatoms, adsorbed energy (ΔE), adatom height (h), graphene distortion (Δh_c), charge transfer (Δq), and the distance of the Na and Cl adatoms along z_{axe} ($d_{(\text{Cl-Na})z}$).

Site (Na/Cl)	ΔE (eV)	$h(\text{\AA})$ (Na/Cl)	Δh_c (\AA)	$\Delta q(e)$ (Na/Cl)	$d_{(\text{Cl-Na})z}$ (\AA)
H/	-0.837	2.205	0.009	-0.905	
/T	-1.115	3.077	0.012	0.514	
H/T	-1.758	2.239/2.815	0.084	-0.887/0.680	5.054
B/T	-1.685	2.332/2.827	0.137	-0.878/0.683	5.159
T/T	-1.709	2.311/2.799	0.176	-0.872/0.685	5.110

The Cl adatom binds most strongly to the T-site, the difference in adsorption energies of the three sites is very small (~0.02 eV). For the Na adatom, the most favored site is the H-site, while there is a small difference of adsorption energy between these three sites.

As given in Table I, the adsorption energy of the Na adatom increases about 1 eV and the maximum energy

difference is 0.08 eV among the three combinations, indicating that the migration energy barrier is similar to a single Na adatom adsorbed on graphene. The adsorption energy of the Na adatom is the highest when Na adatom adsorbs above graphene at H-site.

The charge loss and adsorption height are similar for the Na adatom adsorbed on graphene and on the Cl-graphene system (Tables I). However, the Cl adatom receives more charge from the simultaneous adsorption system; it is about 0.18 e and its adsorption height decreases nearly 0.26 \AA.

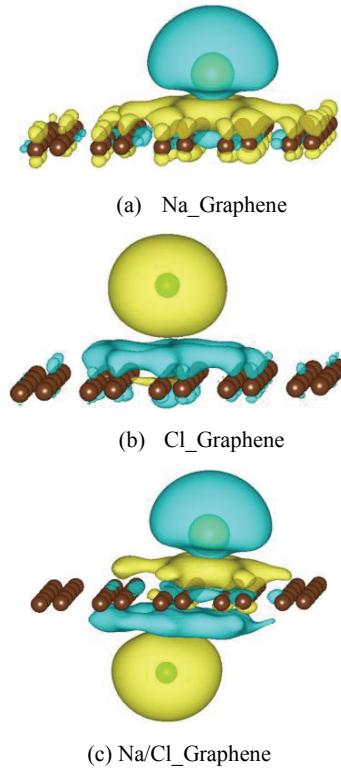


FIG. 2. (Color online) Charge density difference of the adsorbed system. (a) Na adsorbed at the H-site, (b) Cl adsorbed at the T-site, and (c) Na adsorbed at the H-site above the Cl-decorated graphene. Yellow and blue indicate charge accumulation and depletion, respectively. Isosurface boundary is set from -0.008 to 0.008.

Figure 2 shows the charge density difference of the adsorption system, where blue and yellow indicate charge depletion and accumulation, respectively. The charge accumulation on the entire graphene surface suggests that the Na adatom transfers its 3s valence to the big π bond of graphene (Fig. 2(a)). The difference in the adsorption energy of the Na adatom when it adsorbs at the B- or T-site is small

for the big π bond of graphene.

The Cl adatom collects the charge from graphene without obvious charge sharing (Fig. 2(b)) (i.e., a strong covalent bond does not form between the two). Although the charge density of the H-site is less than that of the T- or B-site, the migration energy of the Cl adatom between sites is very small, which may be due to the relatively long distance (about 3 Å) between the Cl adatom and graphene as well as the larger radius of the Cl adatom after adsorption. It also indicates that there has interaction among Cl adatom and several carbon atoms as Fig. 2(b) shows.

Figure 2(c) shows the charge density difference when the Na adatom is adsorbed at H-site of the Cl- decorated graphene. The charge accumulation and depletion are mainly concentrated on the Na and Cl adatoms and a few surrounding C atoms. Although the adsorption distance and charge loss of the Na adatom in the Cl-decorated graphene system is almost the same as the adsorption of the Na adatom alone (Fig. 2(a)). The Cl adatom concentrates the charge, which enhances the interaction between the Na adatom and the graphene. Consequently, the adsorption energy of the Na adatom increases nearly 1 eV. The interaction between Cl adatom and graphene (Fig. 2(c)) is strengthened as well. For the Na adatom, the decreased charge accumulation on graphene will undoubtedly improve the cation ambient.

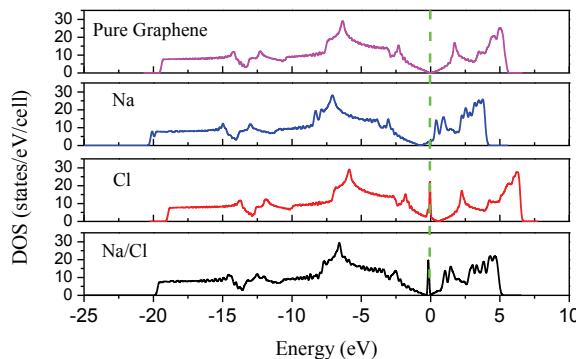


FIG. 3. (Color online) Graphene DOS of the adsorbed system from the top: pure graphene, Na adsorbed at the H-site, Cl adsorbed at the T-site, Na at the H-site of Cl-decorated graphene. Fermi energy is set to zero.

Figure 3 shows the DOS (density of states) of graphene which belong to the system of pure graphene, a single Na adatom adsorbed at the H-site on graphene, a single Cl adatom adsorbed at the T-site on graphene, and a Na adatom adsorbed at the H-site above the Cl-decorated graphene. E_D denotes the energy of the Dirac point. For Na adsorbed alone on graphene, the Fermi level shifts to a higher energy relative to E_D , reflecting a greater occupation of the graphene states because graphene collects the charge. In contrast, for Cl adsorbed on graphene, the Fermi level shifts to a lower energy relative to E_D , indicating that graphene transfers its charge to the Cl adatom. However, when Na are adsorbed on and Cl-decorated graphene, the Fermi level is close to E_D , demonstrating that graphene transfers most of the obtained charge from the Na adatom to the Cl adatom. Under the three adsorption circumstances, the orbit where the Fermi level is occupied indicates that graphene is metalized. Compared to the pure graphene, there is a peak at the Fermi level in the DOS when a Cl adatom is adsorbed on graphene, suggesting hybridization between the Cl adatom and graphene.

4 CONCLUSION

In this paper, the adsorption energy, geometric structure, charge density difference, and density of states are calculated using first principles density functional theory. The Na adatom and graphene form an ionic bond. Although the Cl adatom and graphene mainly form an ionic bond, weaker covalent bond also form between the Cl adatom and the big π bond of graphene. For Na on Cl-decorated graphene, the adsorption energy of the Na adatom is significantly increased.

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