
First-Principles Study of Interaction of Lithium Atoms with H-Adsorbed Graphenes

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Abstract

In this work, we have employed density functional theory (DFT) to investigate the adsorption mechanisms of one lithium atom on the surface of H-adsorbed graphene which have vacancy defects. An understanding of the adsorption is obtained by examining changes of local structures and electronic structures. Our results show that lithium atoms strongly bind to the graphene surface. For the graphene, bonding energy of single lithium atom increase with the number of adsorbed hydrogen atoms. Interestingly, the lithium atom move towards the MVD of the graphene.

Keywords

First-principles calculation, Graphene, Adsorption energy, Vacancy defect, QUANTUM ESPRESSO.

1. Introduction

Graphene [1], a two-dimensional (2D) honeycomb lattice of carbon atoms, is probably the most studied system in recent times [2]. The ease with which graphene can be functionalized with hydrogen [3–5], oxygen [6–8], and metal atoms [9–11] has further added a new dimension to its potential for novel applications. Atomic layer deposition (ALD) is an efficient surface-controlled thin-film growth technique that is often used to deposit metal atoms on graphene [12]. In this technique, maximum benefit is achieved if the metal atoms are homogeneously dispersed on the substrate. However, due to the extended stable π orbitals of graphene and strong affinity of metal atoms toward each other, achieving uniform ALD of metals on graphene has been experimentally difficult. Metals generally tend to disperse inhomogeneously and cluster to form islands on the graphene sheet [13–15].

Carbon nanotubes have potential applications in hydrogen storage [16-17] and rechargeable Li ion batteries [18]. Recently carbon nanotubes have been expected to exhibit superior Li absorption capabilities provided that the Li ions can intercalate both into the channels between the nanotubes, and into the interior of the nanotubes themselves.

Y. Liu et al. [19] have found that the Li absorption energy is larger in the Li absorption outside the nanotube than inside the nanotube as far as the nanotube diameter is small. Z. Zhou et al. [20] have found that B-doping decreases lithium absorption energy dramatically both at inner and outer sites and N-doping will hinder the lithium absorption in SWCNT using first principles calculations. L. Chen et al. [21] have studied molecule with Li-doped carbon nanotube and nanotube based peapod structures. They have found that Binding increases binds to Li-decorated on carbon nanotube surface when H₂ binds to Li-decorated on carbon nanotube surface.

Nanotubes are formed by rolling up hexagonal graphene sheets. Therefore, in order to understand lithium atom and hydrogen atom adsorption on CNTs, it is important to develop an adsorption on

graphene sheets firstly. In this paper, electronic characteristics of pure, vacancy-defected and hydrogen-adsorbed graphene with Li adsorption are investigated by employing density functional theory (DFT) calculations. In the present work, we performed several simulations: one lithium atom adsorbing on one hydrogen atom+graphene sheet, two hydrogen atom+graphene sheet, three hydrogen atom+graphene sheet. The destination of our work is to explore the difference of atomic structures of these systems and to discriminate their electronic structures.

2. Calculation methods

In this investigation we perform calculations based on the density functional theory (DFT) [22]. All calculations were performed using the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) correlation functional [22]. The pseudopotential plane-wave calculations were performed using Rabe-Rappe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotentials [23-24], a 30 Ryd cut-off for plane wave expansion of electron wave functions and a 150 Ryd cut-off for the charge density. The optimization is achieved when the total energy change is less than 0.0027 eV (about $1.0e^{-4}$ a.u.) for ionic minimization and the force components are less than 0.005 eV/Å (about $1.0e^{-5}$ a.u.) for every atom. In the plane-wave-basis calculations, coordinates of all carbon atoms, hydrogen atoms and the adsorbed lithium atom were fully relaxed without any symmetric restrictions. All calculations were performed with an integrated package of computer codes known as Quantum ESPRESSO 5.30 [25].

In our calculations, we adopt a 3×3 graphene. The structure is depicted in Fig. 1(a). For the undefective and defective 3×3 graphene, contain 18 and 17 carbon atoms which are shown in Fig. 1(a). The k-point is set to $6 \times 6 \times 1$ for all slabs. A single layer 3×3 hexagonal supercell with a vacuum width of 12 Å above is constructed, which ensures that the interaction between repeated slabs in the direction perpendicular to the surface is small enough. The variation of energetic results would be within 0.1 eV if the vacuum width is expanded from 12 Å to 15 Å [26]. Defective 3×3 graphene is constructed with one carbon atom missing, to represent one mono-vacancy defect (MVD).

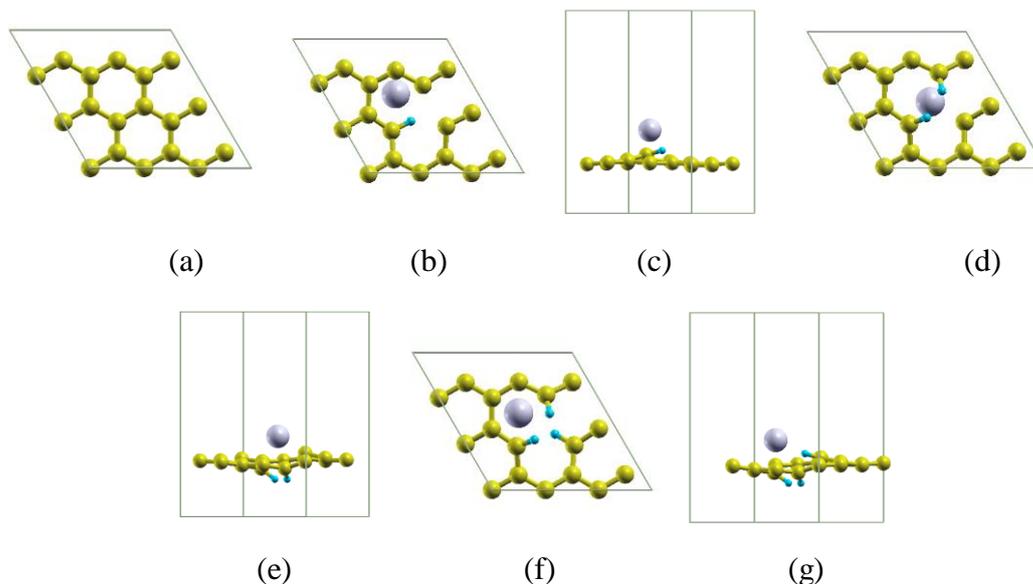


Fig.1 optimized structures for (a) graphene, (b)-(g) top view and side view of one lithium atom adsorbing on the defective graphene with one hydrogen atom, two hydrogen atoms and three hydrogen atoms, respectively.

The Li adsorption energy on the graphene, $E_{\text{adsorption}}$, is defined as the change in the total energy with the Li adsorption, which is used as a measure of the tendency to adsorb hydrogen atoms on the graphene. It is defined as follows

$$E_{\text{adsorption}} = E_{\text{vacancy}}(\text{Substrate@Li}) - n * E_{\text{total}}(\text{Li}) - E_{\text{vacancy}}(\text{Substrate}) \quad (1)$$

Here, $E_{\text{vacancy}}(\text{Substrate@Li})$, $E_{\text{vacancy}}(\text{Substrate})$ and $E_{\text{total}}(\text{Li})$ are the total energies of Li-adsorbed atomic hydrogens+graphene with MVD, atomic hydrogens+graphene with MVD and per isolated lithium atom. Especially, $E_{\text{total}}(\text{Li})$ was obtained by calculating the total energy per lithium atom in a supercell which was large enough (greater than 20Å) to preventing interaction between adjacent atoms. By this definition, $E_{\text{adsorption}} < 0$ in Eq.(1) corresponds to a stable and exothermic chemical adsorption. if $E_{\text{adsorption}} > 0$, it is endothermic, nevertheless, it corresponds to a local minimum. In our calculations, $E_{\text{vacancy}}(\text{Substrate@Li})$, $E_{\text{vacancy}}(\text{Substrate})$ and $E_{\text{indefective}}(\text{Substrate})$ were calculated using the same supercell and calculation parameters for the graphene. All atoms are allowed to fully relax for all energy calculations on the basis of the convergence threshold.

3. Results and discussion

The Li adsorption energy for the lowest-energy position in Fig.1 is -0.0094 eV (Table 1, the value is slightly larger than that was calculated using the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) correlation function [19]). So the adsorption is exothermic and stable, while its value is small.

We have calculated the MVD on the graphene. For graphene, the same single layer 3×3 supercell with a vacuum width of 12 Å [27] above is adopted. The MVD not visibly deforms the structure of the graphene. The vacancy formation energy of the MVD is 7.91 eV. This result is quite close to the previous result of 7.80 eV from local density approximation (LDA) calculations [28]. The Li adsorption energy for the lowest-energy position of Defective graphene is -1.9271 eV (Table 1). The adsorption is exothermic and stable. That is to say, it is chemical adsorption.

Table 1. Lattice parameter along the tube axis and lithium adsorption energy in different graphene systems.

	Adsorption position (to the graphene surface)	lithium adsorption energy
Indefective graphene+1Li	1.69 Å	-0.0941 eV
Defective graphene+1Li	1.88 Å	-1.9271eV
Defective graphene+1H+1Li	1.89 Å	-1.2096 eV
Defective graphene+2H+1Li	1.50 Å	-1.7620 eV
Defective graphene+3H+1Li	1.50 Å	-2.2398 eV

We calculate Li adsorption on the optimized structure of the defective graphene with one hydrogen atom, two hydrogen atoms and three hydrogen atoms respectively. The final optimized structures are shown in Fig. 1(b)-(g).

We investigate one Li atom adsorbing on the defective graphene + 1H system firstly. Evidently, the hydrogen atom can possibly adsorb on various sites in the graphene, for example, top site of carbon atoms, bridge site of C-C bond, and hollow site of carbon hexagon, and so on. Our calculations put an emphasis on the lithium atom adsorbing on the top of carbon atoms around the MVD (by taking positions on the top of a hexagon around the MVD as initial adsorption sites).

From Fig. 1(b)-(c), the structures changes distinctly in positions of atoms around the MVD from the defected graphene. The carbon atom below the lithium atom pops out of the surface by 0.52 Å, forming a C-H bond of length 1.08Å which is obviously in Fig. 1(c). At the same time the C-H bond inclines and the lithium atom approach the MVD. We have observed that the adsorption binding energy of one lithium atom on the graphene with a MVD is -1.9271 eV. It demonstrates that the lithium atom most preferably chemisorbs on the above sites than the sites of undefective graphene. We, after examining the

local structure, have found that the passivation of lithium atom on the graphene results in some change towards sp^3 hybridization in the carbon atom to which bonding occurs.

If the lithium atom adsorbs on the defective graphene + 2H system, the site of adsorption we choose is the adjacent carbon atom of the first carbon atom around the MVD. The adsorption binding energy of the second hydrogen atom on the graphene is -1.7620 eV. The structure of the graphene also changes distinctly (ejustd, of the same) after adsorption. The carbon atom below the hydrogen atom pops out of the surface by 0.35\AA , forming a C-H bond of length 1.07\AA which is obviously in Fig. 1(d)-(e). At the same time the second C-H bonds also inclines and the lithium atom approach the MVD.

Then we calculated the lithium atom adsorbing on the defective graphene + 3H system, we choose the site of adsorption is the last carbon atom around the MVD. The adsorption binding energy of the third hydrogen atom on the graphene is -2.2398 eV. The carbon atom pops out of the surface by 0.31\AA , forming a C-H bond of length 1.06\AA in Fig. 1(f)-(g). At the same time the lithium atom approach the MVD.

So we confirm that lithium atom can chemically adsorb on graphene with the MVD and hydrogen atoms. Further more, the structure of graphene with the MVD will become more stable after the three kinds of adsorption.

The most interesting result, however, is the electronic structure, shown in Fig.2. From discriminate the DOS for indefective graphene and one lithium atom adsorbing on the graphene, we can conclude that the obvious peak at the Fermi level is the contribution of 2s orbital of lithium atom.

We have calculated density of states (DOS) of different types of graphenes. We plot the DOS in Fig. 3. The DOS changes markedly because of the defect and adsorption of the lithium atom, near the Fermi level energy in particular. From Li atom adsorbing on defective graphene + 1H system to defective graphene + 2H system, the DOS value in the Fermi levels increases markedly. The increase enhances the electrical conductivity of the graphene. This result is consistent with the most displacement of the lithium atom during relax. From Figure 1(j) we can see the lithium atom moves from locate right above the hexagon to approaching the MVD. The DOS decreases when Li atom adsorbing on defective graphene + 1H system, defective graphene + 2H system and defective graphene + 3H system. The decrease depresses the electrical conductivity of the graphene.

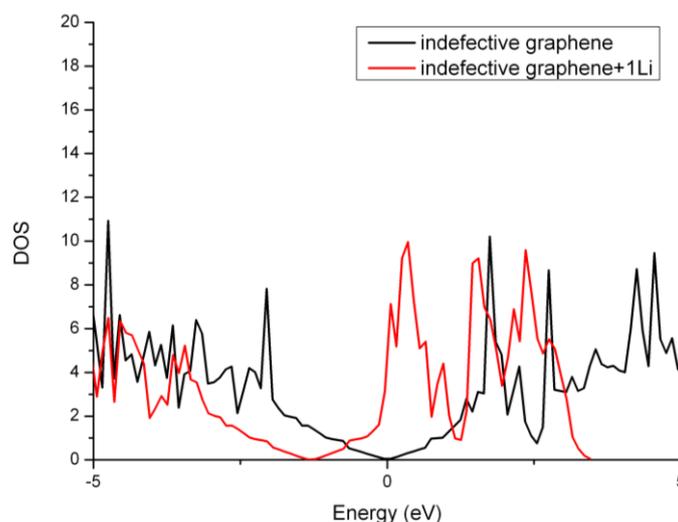


Fig. 2 DOS for indefective graphene and one lithium atom adsorbing on the graphene. The Fermi level energy is set to 0eV .

In order to further investigate the influence of the intercalation of the lithium atom, the electron distribution of the system is also examined. The contour plots for the charge density in the different kinds of graphenes are shown in Fig. 4, which can also clearly describe the changes in the electronic structures due to loss of a carbon atom, gain of hydrogen atoms and a lithium atom.

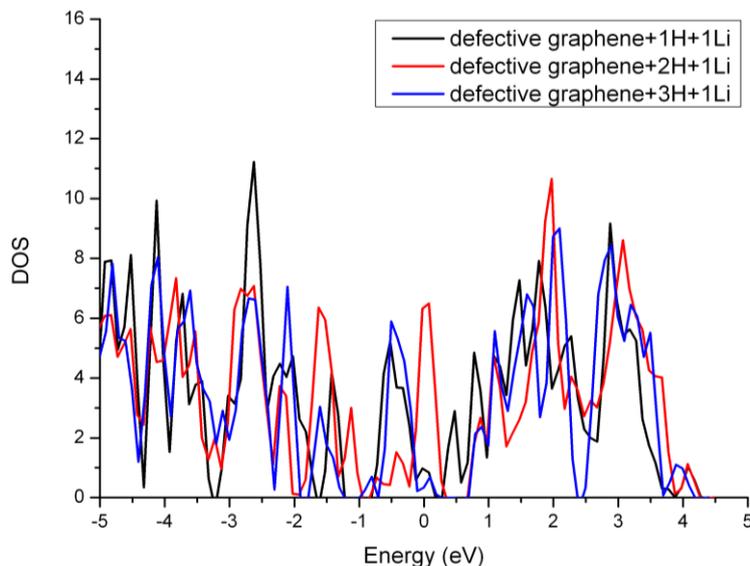


Fig.3 DOS for one Li atom adsorbing on defective graphene + 1H system, defective graphene + 2H system and defective graphene + 3H system. Respectively. The Fermi level energy is set to 0eV.

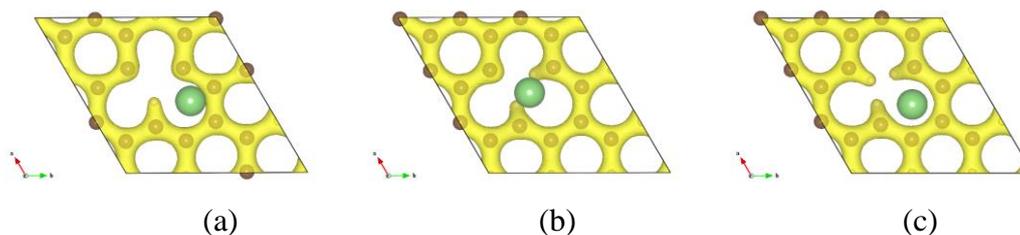


Fig. 4. 3D charge density for one Li atom adsorbing on (a) defective graphene + 1H system, (b) defective graphene + 2H system, (c) defective graphene + 3H system. Respectively.

4. Summary

In summary, we have carried out first-principles density functional calculations based on gradient corrected functional of one lithium atom interaction with indefective graphene + H system, defective graphene + H system.

Our results show that lithium atoms strongly binds to the graphene surface. For the graphene, bonding energy(absolute value) of single lithium atom increase with the number of adsorbed hydrogen atoms. For the defective graphene + 2H system, hydrogen atoms move towards the MVD of the graphene.

Acknowledgments

The authors acknowledge the staff at the laboratory of optics and optoelectronics in Ocean University of China. We also thank XCrySDen, a crystalline and molecular structure visualisation program[29].

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