Density functional theory calculations of atomic hydrogen adsorption on graphenes with vacancy defects

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Abstract

In this paper, we have employed density functional theory (DFT) to investigate the adsorption mechanisms of atomic hydrogens on the graphene which have vacancy defects. All the calculations were performed using the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) correlation functional. Our results show that hydrogen atoms can chemically adsorb on the defective graphene. Bonding energy of per hydrogen atom decreases with the number of adsorbed hydrogen atoms. The hydrogen atoms will enhance the electrical conductivity of the graphene. Besides one hydrogen atom adsorbing on the graphene with a vacancy defect (MVD), hydrogen atoms move towards the MVD of the graphene.

Keywords

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

1. Introduction

The discovery of graphene, the first truly two-dimensional crystal, and its exotic electronic properties (for review, see Refs. 1–3) initiates a huge growth of interest to carbon materials. Most of activity is focused on electronic transport phenomena in graphene, keeping in mind potential applications for carbon-based electronics. However, chemical physics of graphene is also very interesting, in particular, due to opportunity to use graphene for chemical sensors with extraordinary sensitivity [4]. Another interesting direction of investigations is a possible use of graphene for hydrogen storage. One could expect that two-dimensional systems could be very convenient for this aim. In general, carbon-based systems are among the most attractive objects for hydrogen storage. [5] Promising storage properties of single-walled carbon nanotubes (SWCNTs) were first reported in Ref. 6. In the past few years grapheme was used as a model system to study the electronic structure and adsorption properties of the SWCNTs [7-8]. After the discovery of real graphene several works appeared theoretically studying the hydrogen adsorption on graphene, as a special material (see, e.g., Ref. 9). It is commonly accepted now [7–9] that the chemisorption of single hydrogen atom on graphene leads to appearance of magnetic moments in the system.

Prevenient experiments of CNTs in hydrogen background reveal that hydrogen is dissociated and the generated hydrogen atoms spill over to the tubes, leading to C-H bond formation [10]. But many problems remain unresolved notwithstanding current work have build a framework of the effects of vacancies on the electrical characteristics of SWCNTs in the main. For example, atomic hydrogen adsorption on SWCNTs with vacancy defects are not been investigated by density functional theory (DFT) yet. However, atomic hydrogen will form hand over fist when we prepare SWCNTs in Hot Filament Chemical Vapor Deposition (HFCVD) Reactors. It is believed that atomic hydrogen plays important roles in HFCVD Reactors [11-13].

So it is in dire need of understanding the effects of vacancy defect on atomic hydrogen adsorption. In this paper, electronic characteristics of pure, vacancy- defected and hydrogen-adsorbed graphenes are investigated by employing density functional theory (DFT) calculations. The destination of our work is to explore the difference of atomic structures of the three types of carbon nanotubes and to discriminate their electronic structures.

2. Calculation methods

In this investigation we perform calculations based on the density functional theory (DFT) [14]. All the calculations were performed using the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) correlation functional [14]. The pseudopotential plane-wave calculations were performed using Rabe-Rappe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotentials [15-16], a 30 Ryd cut-off for plane wave expansion of electron wave functions and a 150Ryd 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 0.02 eV/Å (about 1.0e-4 a.u.) for every atom. In the plane-wave-basis calculations, the coordinates of all carbon atoms and adsorbed hydrogen atoms were fully relaxed without any symmetric restrictions. All the DFT calculations were performed with an integrated suite (package) of computer codes known as Quantum ESPRESSO 5.30 [17].

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). Defective 3×3 graphene is constructed with one carbon atom missing, to represent one mono-vacancy defect (MVD). The k-point is set to 6×6×1 for all slabs. A single layer 3×3 hexagonal supercell with a vacuum width of 12Å above is constructed, which ensures that the interaction between repeated slabs in a direction normal 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 [18]. All atoms are allowed to relax for all energy calculations.

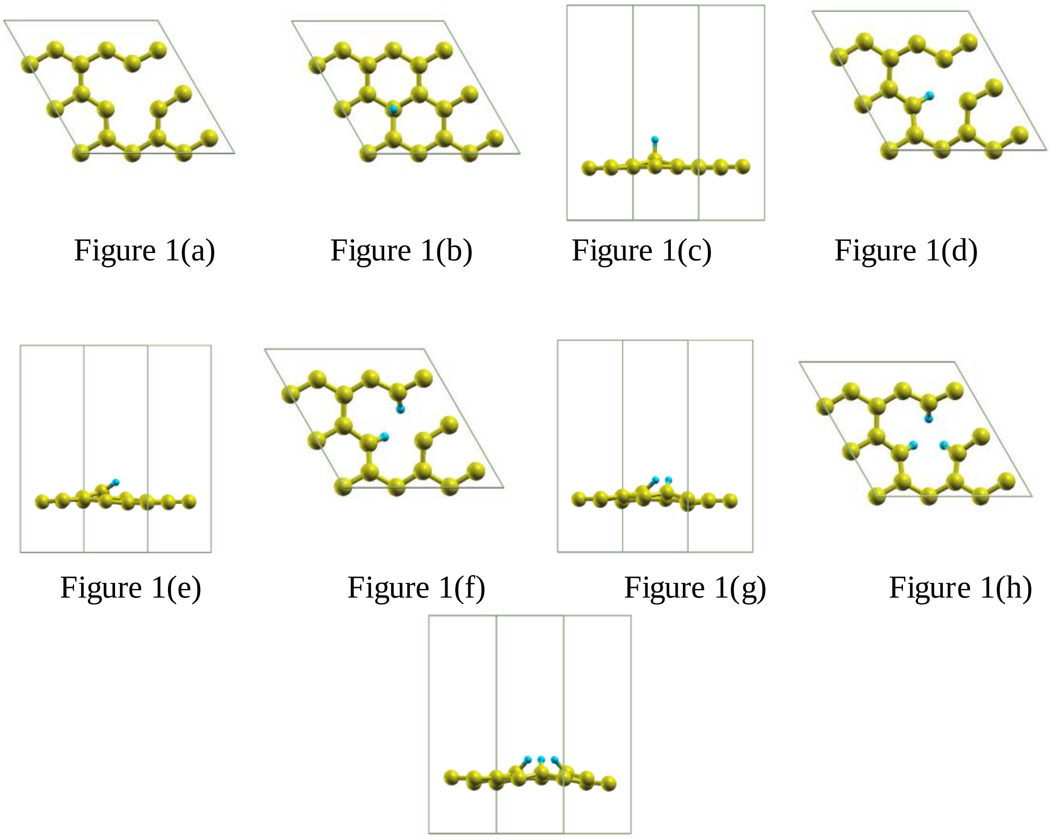


Figure 1(a) Figure 1(b) Figure 1(c) Figure 1(d)

Figure 1(e) Figure 1(f) Figure 1(g) Figure 1(h)

Figure 1(i)

Fig.1 (a) optimized structure for graphene with a MVD, (b) and (c) top view and side view of optimized structures for one hydrogen atom adsorbing on the grapheme, (d), (f), (h) top view of optimized structures for one, two and three hydrogen atoms adsorbing on the graphene with a MVD, respectively. (e), (g), (i) side view of three optimized structures.

The vacancy formation energy of the graphene, $E_{vacancy}$, which was calculated using the total energies of the supercells, is defined as follows

$$E_{\mathrm{f,vacancy}} = E_{\mathrm{vacancy}}(\mathrm{Substrate}) - \frac{n-1}{n} * E_{\mathrm{indefective}}(\mathrm{Substrate}) \qquad (1)$$

Here, E_{vacancy}(Substrate) and $E_{\mathrm{indefective}}$(Substrate) are the total energies of graphene with one MVD and indefective graphene.

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

$$E_{\mathrm{adsorption}} = E_{\mathrm{vacancy}}(\mathrm{Substrate@H}) - n * E_{\mathrm{total}}(\mathrm{H}) - E_{\mathrm{vacancy}}(\mathrm{Substrate}) \qquad (2)$$

Here, E_{vacancy} (Substrate@H), E_{vacancy} (Substrate) and E_{total}(H) are the total energies of H-adsorbed graphene with MVD, graphene with MVD and per isolated hydrogen atom. Especially, E_{total}(H) was obtained by calculating the total energy per hydrogen atom in the same hexagonal supercell which was large enough to preventing interaction between adjacent hydrogen atoms. By this definition, $E_{\mathrm{adsorption}}<0$ in Eq.(1) corresponds to a stable and exothermic chemical adsorption. if $E_{\mathrm{adsorption}}>0$, it is endothermic, nevertheless, it corresponds to a local minimum[21]. In our calculations, E_{vacancy}(Substrate@H), E_{vacancy}(Substrate) and $E_{\mathrm{indefective}}$- (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

After comparison of adsorption energy, the most stable site for adsorption of single hydrogen atom in indefective graphene is on top of the carbon atom. The following calculations are mainly focused on hydrogen atoms adsorbing on top position of the graphene sheet. We start with the geometrics and energetics of the indefective graphene. The optimized structures are shown in Fig. 1(b)-(c) and Fig. 3(b)-(c). It is taken for the samples of our calculations. C-H bond length and hydrogen adsorption energy in different graphene systems are list in Table 1.

A hydrogen atom on top position of the indefective graphene sheet induce approximate sp^3 hybridization of the carbon atom, causing it pop out of the surface of the graphene sheet by 0.35Å, forming C-H bonds with length 1.13 Å that is larger than the bond-length in some molecules (1.090Å in methane [8]; 1.087 Å in C_2H_4 and CH_4 [19]). The hydrogen adsorption energy on the indefective graphene for this adsorption position is -1.79 eV lower than reported result (-1.53 eV which was calculated using GGA with the PBE correlation function with respect to $1/2H_2$) [20-22]. Because the bond energy of the H-H in the hydrogen gas (H_2) is 4.57 eV [19], the dissociation of hydrogen gas (H_2) require theoretically 2.285 eV that is larger than the adsorption energy. So the dissociation of hydrogen gas (H_2) by adsorption on indefective graphene is endothermic or not in favor of the dissociation. This result is consistent with the results by E. J. Duplock et al [8].

Table 1 C-H bond length and hydrogen adsorption energy in different graphene systems.

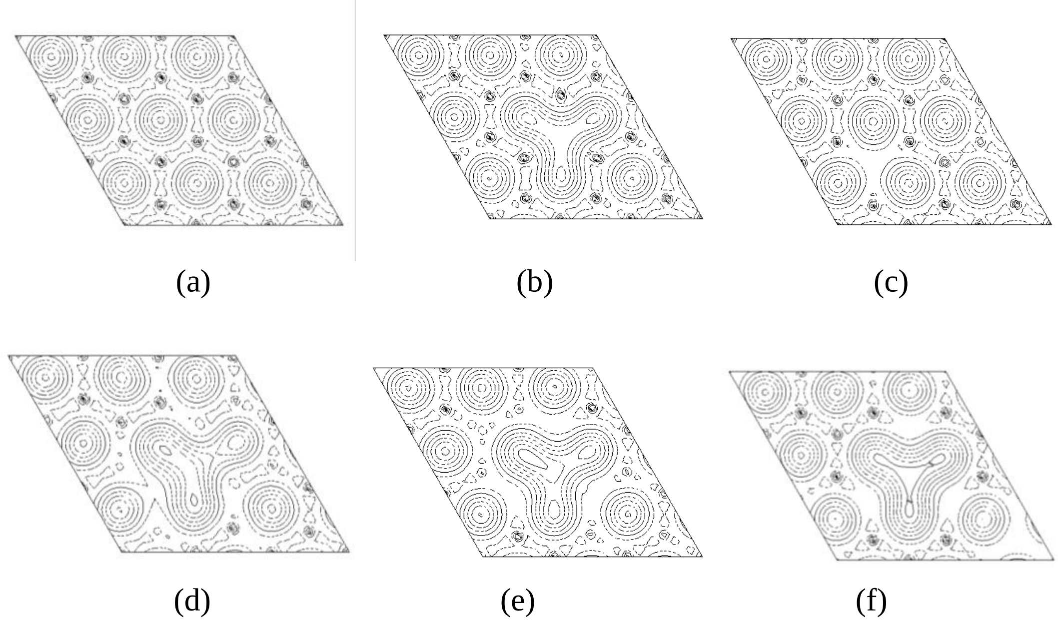
	C-H bond length	hydrogen adsorption energy
Indefective graphene+1H	1.13 Å	-1.79 eV
Defective graphene+1H	1.08 Å	-5.19 eV
Defective graphene+2H	1.07 Å	-4.38 eV
Defective graphene+3H	1.06 Å	-4.07 eV

Because graphenes prepared in labs are not all indefective, we chose the graphene with the MVD to study the role of vacancy defects on hydrogen atoms adsorption on the graphenes. The optimized structures of the graphene with the MVD are shown in Fig 1(a). For the defective graphene, the MVD not visibly deforms the structure of the graphene. There are three dangling bonds in graphene with MVD. The vacancy formation energy of the MVD is 7.91 eV. This result is quite close to the 7.80eV calculated with local density approximation (LDA) [23].

Using structures of the graphene with the MVD optimized above, the calculation is executed for three kinds of hydrogen configurations of adsorption successively: one hydrogen atom, two hydrogen atoms and three hydrogen atoms on the top of carbon atoms around the MVD. The final optimized structures (top view and side view) are shown in Fig. 1(d)-(i).

From Fig. 1(d)-(e) we can find that the structures of the defective graphene changes distinctly in positions of atoms around the MVD after adsorbing one hydrogen atom. Carbon atoms below the hydrogen atom pop out of the surface by 0.52 Å and 0.01 Å, forming a C-H bond with length 1.08 Å and 1.10 Å. The C-H bond of the defective graphene inclines and the hydrogen atom approach the MVD. We have observed that the adsorption binding energy of one hydrogen atom on the defective graphene is -5.19 eV. This energy is far larger than the result of H_2 adsorbing on the grapheme [31]. It demonstrates that the hydrogen atom most preferably chemisorbs on the above sites than the sites of perfect graphene. From the local structure in Fig. 1(d)-(e), we find that the adsorption of the hydrogen atom results in the distance of two carbon atoms around the lost carbon atom increasing to 1.91 Å.

If the second hydrogen atom was located on the defective graphene, as shown in Fig. 1(f)-(g), the structure of the graphene also changes visibly after adsorption. The carbon atom below the hydrogen atom pops out of the surface by 0.35 Å, forming C-H bonds with same length 1.07 Å and which is slightly shorter than C-H bonds of the defective graphene with one hydrogen atom. At the same time all hydrogen atoms approach the MVD of the defective graphene. The adsorption binding energy of the second hydrogen atom on the graphene is -4.38 eV. If the third hydrogen atom have adsorbed on the last carbon atoms around the MVD in the defective graphene, the carbon atom below the hydrogen atom pops out of the surface by 0.31 Å, forming C-H bonds of length 1.06 Å and 1.09 Å as shown in Fig. 2(h)-(i). The adsorption binding energy of the third hydrogen atom is -4.07eV.


(a) (b) (c)

(d) (e) (f)

Fig.2. 2D charge density for (a) indefective graphene. (b) graphene with a MVD. (c) one hydrogen atom adsorbing on the graphene. (d)-(f) one, two and three hydrogen atoms adsorbing on the graphene with a MVD, respectively. The cross section is the plane which the graphene is located.

So we confirm that hydrogen atoms can chemically adsorb on the defective graphene. The adsorption binding energy of each hydrogen atom increases with the number of the hydrogen atoms for the defective graphene. The structure of graphene with the MVD will become more stable after the three kinds of adsorption.

In order to further investigate the influence of the intercalation of the hydrogen atoms, the electron distribution of the system is also examined. The contour plots for the charge density on the different kinds of graphene surface cross section (across original position of the MVD) are shown in Fig. 2, which can also clearly describe the changes in the electronic structures due to loss of a carbon atom or gain of hydrogen atoms.

No approach of the carbon atoms near the lost carbon atom and no formation of the pentagon are not found when a MVD is inserted into the surface of the graphene. Compared the Fig. 2(b) with Fig. 1(a), three dangling bonds are also clearly located around the MVD in the graphene.

The most interesting result, however, is the electronic structure. Fig. 3 shows the calculated density of states of different kinds of graphenes before and after hydrogen adsorption.

In Fig 3, the indefective graphene shows semiconducting character. By identifying the charge density at the Fermi level for the graphene with one hydrogen atom adsorbed in Fig 4, we can conclude that the obvious peak at the Fermi level is mainly from the contribution of 1s obitals of the hydrogen atom and $2p_z$ obitals of carbon atoms around the carbon atom bound the hydrogen atom. The increase of DOS at the Fermi levels will enhance the electrical conductivity of the graphene.

From indefective graphene to defective graphene, the peaks of the DOS in the conduction band decreases distinctly. But the DOS value at the Fermi levels increases. This increase enhances the electrical conductivity which is consistent with the appearance of the MVD. The DOS value at the Fermi level increased after one hydrogen atom adsorbing on the defective graphene. The evident augmentation of DOS value at the Fermi levels also mainly contains the contribution of H 1s orbtals and $2p_z$ obitals of carbon atoms around the carbon atom bound the hydrogen atom. Dissimilarly to the indefective graphene, there also exists the influence of the coupling of the MVD and the π orbitals of the defective graphene. The Fermi levels shift into the previous unoccupied states, and stabilize the tube more strongly. The DOS value at the Fermi levels decreases to zero and become semiconducting after adsorbing two hydrogen atoms. After adsorbing three hydrogen atoms, the value of DOS at the Fermi levels reincreases, but does not exceed the DOS value of one hydrogen atom adsorbing on the defective graphene.

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. The result is consistent with the DOS in Fig.3.

4. Summary

In summary, we have carried out first-principles density functional calculations based on gradient corrected functional of hydrogen atoms interaction with indefective graphenes and defective graphenes.

Our results show that hydrogen atoms strongly bind to the graphene surface. For the graphene, bonding energy (absolute value) of single hydrogen atom decreases with the number of adsorbed hydrogen atoms. Besides one hydrogen atom adsorbing on the graphene with a MVD, hydrogen atoms move towards the MVD of the graphene together.

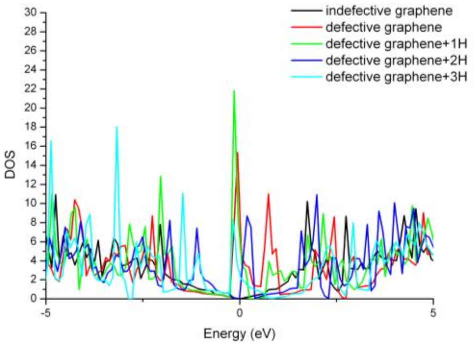


Fig. 3 DOS for (a) indefective graphene and one hydrogen atom adsorbing on the graphene. DOS for an isolated hydrogen atom is also shown in the inset. (b) indefective graphene, graphene with a MVD, one, two and three hydrogen atoms adsorbing on the graphene with a MVD, respectively. The Fermi level energy is set to 0eV.

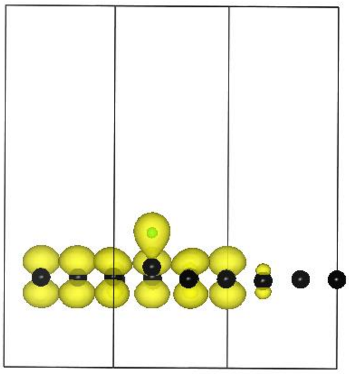


Fig. 4 Charge density at the Fermi level for (a) one hydrogen atom adsorbing on the indefective graphene (side view).

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