Effect of hydrogen on adsorption of hydrocarbon fragments on graphene

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We investigate the effect of hydrogen on adsorption of hydrocarbon molecules on graphene with density functional theory (DFT) calculations. In this study, we calculate the binding energies of hydrogen molecule, carbon atom and other hydrocarbon fragments such as CHx (x=1, 2, 3, 4) on graphene to find the most stable adsorption site. Then, to study the effect of hydrogen, we investigate the adsorption of hydrocarbon fragments in the presence of hydrogen atoms on graphene.

INTRODUCTION

In the chemical vapor deposition (CVD) process for graphene growth, it is known that hydrogen molecules affect the quality of graphene sheet and the hydrogen concentration plays an important role in controlling the number of graphene layers [1,2].

In this study, we calculate the effects of hydrogen molecule on hydrocarbon adsorbed graphene to investigate the hydrogen effects after graphene growth on substrate. Details in the hydrogen effect on graphene growth, we analyze the binding energies which is dependent with hydrogen molecule.

CALCULATION METHODS

In this study, we have performed spin-polarized density functional theory (DFT) calculations within generalized gradient approximation (GGA) for exchange-correlation (*xc*) functional, as implemented in the SIESTA package. For investigation, we use LCAODFTLab simulator in Nanophysics EDISON website [3].

In our calculations, the (3x3) unit cell of graphene is used with a vacuum region of about 20 Å. For the Brillouin-zone integration, a (3x3x1) grid is used in the Monkhost-Pack scheme. To study the effects of hydrogen, hydrogen molecule, carbon atom and other hydrocarbon fragments such as CH_x (x=1, 2, 3, 4) are adsorbed on a graphene sheet.

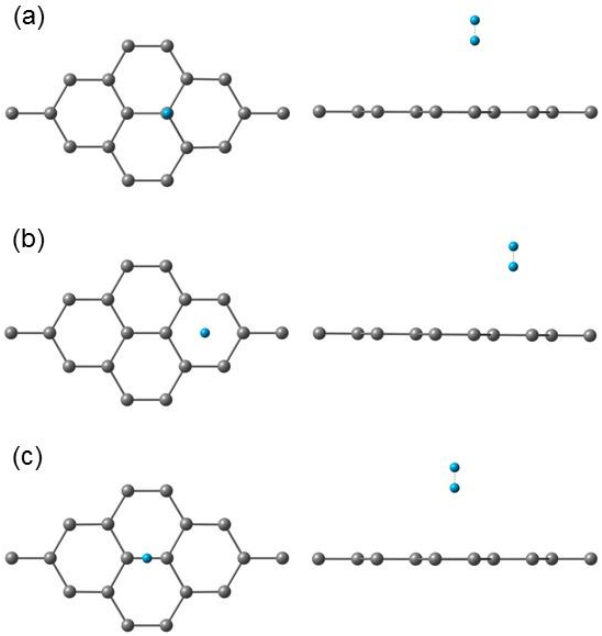

Fig. 1. Optimized structure of hydrogen molecule on (a) top, (b) hollow and (c) bridge sties of graphene. Grey and blue balls represent carbon and hydrogen atoms, respectively.

RESULTS & DISCUSSION

In our study, we investigate hydrogen molecule on adsorption of hydrocarbon molecules on graphene.

First, we investigate adsorption sites of hydrogen molecule on a single layer graphene to find most stable adsorption sites. We consider several adsorption sites including (a) hollow, (b) bridge and (c) top sites as shown in Fig.1. Our calculations show that total energy of hydrogen molecule on graphene is almost same in all

adsorption sites because of weak interaction between graphene and hydrogen molecule. However, we adopt the hollow sites because it represents the lowest energy about 0.006 and 0.007 eV for other adsorption sites in our calculations.

Second, we obtain the atomic structure of hydrocarbon molecule on graphene. In this study, we adsorbed the all carbon atoms, which are include in hydrocarbon molecule, on bridge sites of graphene, because it is known that adsorption of carbon atom on bridge sites is most stable than other sites [4]. Then, we obtain fully optimized structure of (a) carbon atom and hydrocarbon molecule such as (b) CH, (c) CH_2, (d) CH_3 and (e) CH_4 on graphene which is shown in Fig.2. In the case of C, CH, CH_2 and CH_3 adsorption on graphene, there are strong interaction between graphene and molecules, forming the covalent bonds. However, there is weak interaction between graphene and CH_4 molecule, representing the physisorption due to stabilization of CH_4 molecule. Such tendency is also indicated in binding energies which are shown in Table 1, showing the lowest binding energies in the case of CH_4 adsorption on graphene. Binding energies are obtained by equation (1), where E_b is binding energy, E_{total} is total energy of hydrocarbon molecule on graphene, E_G is energy of pristine graphene and $E_{hydrocarbon}$ is energy of hydrocarbon molecule.

$$E_b = E_{total} - (E_G + E_{hydrocarbon}) \qquad (1)$$

C/G	CH/G	CH_2/G	CH_3/G	CH_4/G
-0.80	-1.92	-1.23	-1.19	-0.06

Table.1. Binding energy (eV) of carbon atom and hydrocarbon fragments on graphene.

Third, we calculate the hydrogen molecule on adsorption of hydrocarbon on graphene. In this case, we adsorbed the all carbon atoms in hydrocarbon molecule on bridges sites of graphene. And we also adsorbed the hydrogen molecule on hollow sites of graphene, because these sites are most stable in our calculations as shown above. Then, we obtain fully optimized structure of (a) carbon atom and hydrocarbon molecule such as

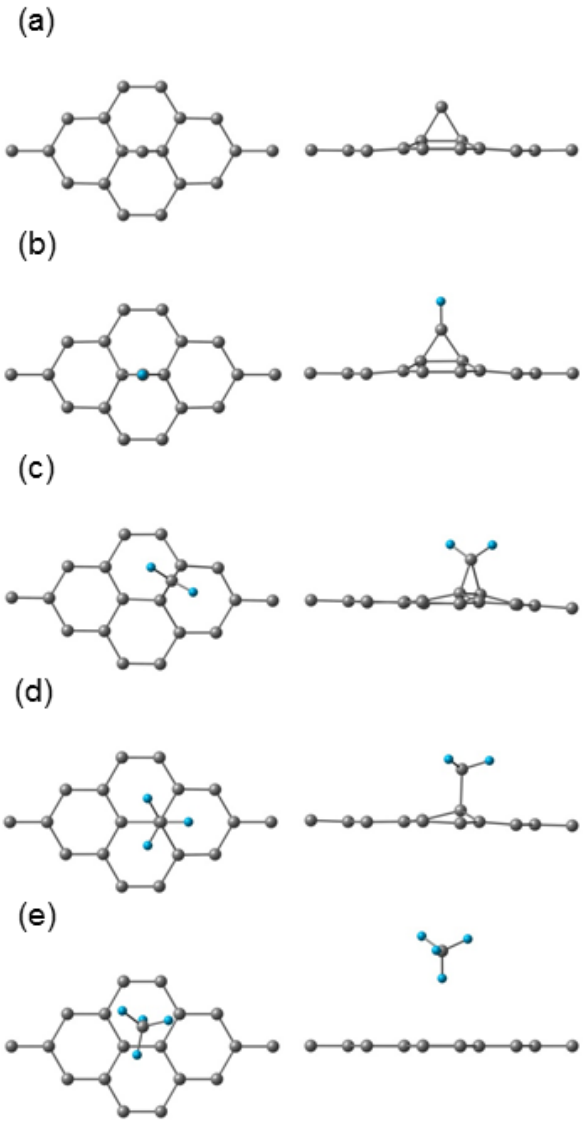

Fig. 2. Optimized structure of hydrocarbon fragments: (a) C atom, (b) CH, (c) CH_2, (d) CH_3 and (e) CH_4 on graphene.

(b) CH (c) CH_2 (d) CH_3 on hydrogen molecule adsorbed graphene which is shown in Fig.3. Here, we did not consider the adsorption of CH_4 molecule on graphene due to weak interaction between graphene and molecule. We also calculate the binding energies of hydrocarbon molecules using equation (2) to identify the effects of hydrogen molecule. In equation (2), E_b^{ref}, E_{total}, $E_{(G+H2)}$ and $E_{hydrocarbon}$ mean binding energy of CH_x, total energy of H_2 and CH_x molecules adsorption on graphene, energy of H_2 molecule on graphene and energy of CH_x molecule, respectively. The

binding energies of hydrocarbon molecule are shown in Table 2.

$$E_b^{ref} = E_{total} - (E_{(G+H2)} + E_{hydrocarbon}) \qquad (2)$$

	C+H_2	CH+H_2	CH_2+H_2	CH_3+H_2
E_b^{ref}	-0.84	-1.38	-1.23	-1.22

Table.2. E_b^{ref} (eV) of hydrogen molecule on adsorption of hydrocarbon molecules on graphene.

To identify the effects of hydrogen atoms, we calculate the relative binding energies, $E_b^{relative}$, using equation (3). Binding energies of hydrocarbon molecule are represented in Table 3. From relative binding energies in Table 3, we could identify that binding energies is generally increased due to presence of hydrogen molecule. As a result, hydrogen molecule can induce more strong interaction between hydrocarbon molecule and graphene sheet. In other words, hydrogen molecule plays very important role after graphene growth. The relative binding energy $E_b^{relative}$ is defined as follows:

$$E_b^{relative} = -(E_b^{ref} - E_b) \qquad (3)$$

	C/G	CH/G	CH_2/G	CH_3/G
$E_b^{relative}$	0.03	-0.54	-1.23	-0.04

Table.3. $E_b^{relative}$ (eV) for carbon atom and hydrocarbon fragments on graphene.

As a result, hydrogen concentration plays on important role in controlling the number of graphene layers in CVD process.

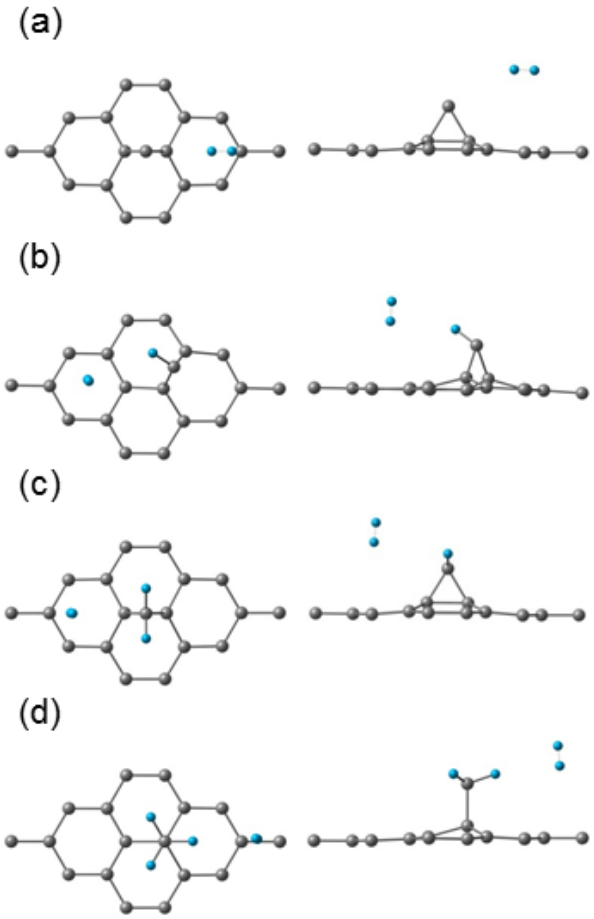

Fig. 3 Optimized structures of (a) C atom, (b) CH, (c) CH_2 and (d) CH_3 on graphene in the presence of hydrogen molecule.

CONCLUSION

We have performed density functional theory calculations to investigate the effect of hydrogen on adsorption of hydrocarbon molecules on graphene. We calculate the binding energies of hydrocarbon fragments on pristine grapheme and that of CH_x in the presence of hydrogen molecules on graphene. We found that the presence of hydrogen molecule changes the adsorption behaviour and binding energies of hydrocarbon molecule on graphene sheet.

ACKNOWLEDGEMENT

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