Effect of Lithium Doping on Hydrogen Adsorption of Defected Graphene: A First-Principles Sudy

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Abstract

Hydrogen storage capacity of defected graphene was studied by first-principles theory based on Density-functional calculations. Adsorption of molecular hydrogen on a defected graphene V_2(5-8-5) and lithium doped defected graphene V_2(5-8-5) was carried out. Hydrogen molecules are physisorbed on defected graphene V_2(5-8-5) with binding energy about 21–48 meV. Whereas the binding energies increase up to 150–152 meV in Li doped defected graphene. Charge-density analysis indicated that the increasing of binding energy is due to the charge transfer from the H_2 molecule to Li . The results explain the enhancement of storage capacity observed in some experimental hydrogen adsorption on defected graphene qualitatively.

Keywords: Hydrogen storage, defected graphene, Density Functional Theory, adsorption.

1. Introduction

Hydrogen is considered to be a promising environmentally friendly fuel for the future as it possesses a very high energy content by mass compared to conventional fuels and can cleanly produce energy with no harmful by-products[1]. Hydrogen contains the highest energy density per unit mass[2,3]. Hydrogen storage medium must meet the requirements of high gravimetric and volumetric density, fast kinetics, and favorable thermodynamics. Therefore, Hydrogen storage is considered to be the biggest challenge in a new hydrogen economy. Classical hydrogen storage methods such as liquid hydrogen, compressed hydrogen, metal hydrides and hydrogen adsorption on activated carbon are not optimal. These methods produce inherent cost, safety, and storage capacity problems. Therefore, designation and application of solid materials is of great importance to provide an alternative choice for hydrogen storage [4]. metal-organic frameworks have been used as options for hydrogen storage[5]. carbon-based nanostructures can also act as effective adsorption media for hydrogen molecules due to their relative low weight and high surface areas. Among these materials, graphene is considered as a one atom thick two dimensional structure gives it the highest

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specific surface area. Hydrogen molecules interact with materials in two ways: physisorb in molecular form or chemisorb in atomic form[6]. In the first case, no charge transfer occurs between the surface and hydrogen molecule, resulting in weak binding. whereas in the second, electron transfer occurs from the surface to anti bonding orbital of H2 resulting in molecular bond cleavage and atomic adsorption leads to strong bonding with the surface. Therefore, there are two groups of materials: one with low hydrogen storage and easy desorption and the other with high hydrogen storage but difficult desorption. An ideal storage system is existing when hydrogen binds molecularly, with the binding energy between the physisorbed and chemisorbed states [4].

It was proven that metal doping can change the properties of adsorbent[7,8]. the use of doped graphene with transition metal can enhance hydrogen capacity[9]. Since metal ions can attract more H_2 molecules by making them polar, transition metals dispersed in graphene are able to bind tightly to H_2 molecules. therefore, such systems filled with transition metal operate in ambient conditions with desired storing capacity. However, transition metal is very heavy, and their binding energy with hydrogen is strong that hydrogen cannot be dissociated from the surface for usage of H_2[10]. Therefore, several alkali and alkaline earth metals have been considered as hydrogen storage materials [11]. Lithium is considered as a suitable doping metal due to the light weight and appropriate binding energy.

It must be considered that the commercially prepared graphene sheets contain topological defects [12]. Therefore, interactions of defects with hydrogen molecules and their modifying role in hydrogen adsorption are important[13].

Moreover, experiment studies revealed that electron damage induced point defects in graphene are effective traps for diffusing atoms and clusters[14]. It was shown that Li doping does not destroy the

structural and stability of the defected graphene while changing their electronic properties[15]. Therefore, we were interested in to investigate the influence of Li doping on hydrogen adsorption of defected graphene.

 This investigation includes of two section . In the first section, H2 molecule adsorption on defected graphene was studied by density functional theory (DFT) calculations . Then hydrogen adsorption of Li doped defected graphene was studied.

2. Computational details

 In this investigation, 585 defected graphene was selected as a model. H atoms were used to cap the ends of this fragment. Li was placed in 12 positions of a finite structure of defected graphene and the structures were optimized. These geometries of adsorbent were implied in the hydrogen adsorption.

 All geometry optimizations of hydrogen adsorption on defected graphene and Li doped defected graphene were performed using Gaussian 03 program package[16]. DFT calculations were performed using a generalized gradient approximation (GGA) in the form of the Perdew, Burke, and Ernzerhof (PBE) functional [17,18]. Natural charge analysis with full NBO calculations have been performed for optimized structures.

3. Results and discussion
3.1.H_2 adsorption on defected graphene

There are several sites of adsorption of H_2 molecule on defected graphene[19,20] and each site has been considered individually. In order to find the best site of adsorption, H_2 molecules are located on various sites(shown in figure 1) with respect to graphene layer[21,22]   and the structures were optimized. H_2 adsorption clearly deforms the graphene sheet and the adjacent atoms push the defect away from the surface and the adsorbed molecule.
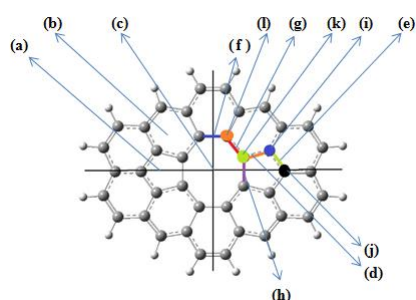
Figure 1. the locations of H_2 in different positions of graphene surface.

The binding energy ,E_b, is given by:

$$E_b = E_{Graphene+H2} - E_{Graphene} - E_{H2} + \delta_{BSSE}$$

where $E_{Graphene+H2}$ is total energy of the optimized configuration of graphene with the adsorbed H2, $E_{Graphene}$ is total energy of single graphene, E_{H2} is total energy of a separated H_2 molecule in its ground state, and δ_{BSSE} is the basis set superposition error (BSSE). The calculated binding energy of the above mentioned complexes are given in Table 1.

Table 1. Binding energies of hydrogen adsorption on different sites of defected graphene

Structure	E_b (eV)
a	0.0218
b	0.0465
c	0.0484
d	0.026
e	0.0466
f	0.0467
g	0.0459
h	0.0463
i	0.046
j	0.0219
k	0.0476
l	0.0463

According to the Table 1, the range of binding energies are from 0.0218 to 0.0484 eV. By Considering the positive adsorption energies, it was concluded practically no adsorption has occurred.

To study the charge transfers throughout the hydrogen adsorption , we utilized the results of natural bond orbital (NBO). The results are included in table 2. According to the results, charge transfer dose not occurred . Therefore positive adsorption energy is confirmed.

Table 2. charge transfer of hydrogen adsorption on   different sites of defected graphene

Structure	interaction	Charge transfer energy (eV)
a	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0022
b	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0023
c	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0052
d	–	–
e	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.00097
f	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.00736
g	$\sigma_{H\text{-}H} \to \pi^*_{C\text{-}C}$	0.003
g	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0169
h	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0082
i	$\sigma_{H\text{-}H} \to \pi^*_{C\text{-}C}$	0.0022
i	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.017
j	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0087
k	–	–
l	$\pi_{C\text{-}C} \to \sigma^*_{H\text{-}H}$	0.0082

3.2. Doping of Li on 585 defected graphene

To find a thermodynamically favored location, Li was located at 5 locations: a, b, c, j and h. After locating Li at the center of six-membered ring (b) and subsequent optimization, carbon-carbon distance in two situations increased from 1.5 to 2.2. Therefore, adsorption of Li on graphene results in deformation and instability of the structure. Consequently, the center of a six-membered ring does not seem to be a suitable place for locating Li and this has been confirmed by the binding energy results.

Table 3. binding energy of Li and defected graphene

Structure	E_b(eV)
585-Li-H-5 (a)	-1.8663
585-Li-H-6 (b)	26.2473
585-Li-H-8 (c)	-1.8665
585-Li-T-5-6 (j)	-0.3957
585-B-5-8-Li (h)	-1.6687

The binding energy of Li adsorption on graphene is defined as follows:

$E_b= E_{Li-Graphene} - E_{Graphene} - E_{Li}$ (2)

where E_{Li} is the energy of an isolated Li atom, $E_{Graphene}$ is the total energy of Graphene in the absence of the adsorbed species, and $E_{Li-Graphene}$ is the energy of the Li doped Graphene.

By definition, $E_b < 0$ in Eq. (2) corresponds to a stable Li doped Graphene. The binding energies were calculated for five binding sites. The results of binding energies were tabulated in Table 3.

As regards in Table 3, binding energy of 585-Li-H-8 is more negative than the other structures. Thus, it is the most stable structure and Li should be place at the center of an eight membered ring.

As it is seen in figure 2, Li doping on the surface of graphene leads to a smaller band gap, and LUMO-HUMO energy levels tend toward positive energy values. Therefore more accessible of binding orbital electrons of Hydrogen to LUMO, results the increment of adsorption.

### 3.3 Hydrogen adsorption on Li doped defected graphene 585

Hydrogen molecule adsorption on the most stable configuration of Li doped defected graphene 585 (center of a eight-membered ring) was investigated.   For Li-Graphene (H2)ₙ complex, adsorption energy is defined as:

$E_b = E_{Li-Graphene(H2)n} - E_{Li-Graphene} - nE_{H2} + \delta_{BSSE}$ (3)

where $E_{Li-Graphene(H2)n}$ is total energy of the optimized configuration of Li-graphene with the adsorbed n^{th} H_2, $E_{Li-Graphene}$ is total energy of single Li doped defected graphene, E_{H2} is total energy of a separated H_2 molecule in its ground state, and δ_{BSSE} is the basis set superposition error (BSSE).
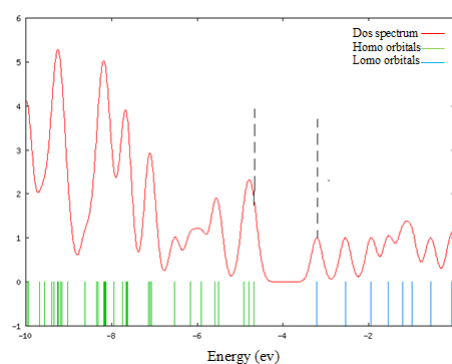
(a)
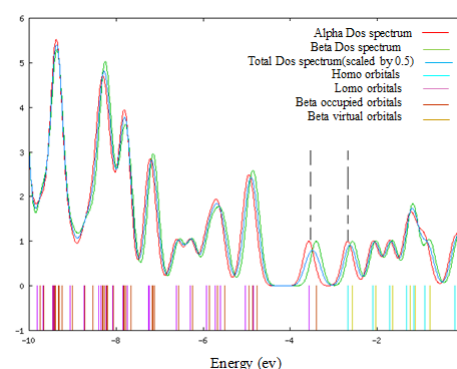
(b)

Figure 2. comparison of DOS diagrams; (a) graphene; (b) Li dopped graphene

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Table 4. Binding energies of the interaction of 1st H_2 molecule and Li doped defected graphene

Structure	E_b (eV)		
	1st H_2	2nd H_2	3rd
a	-0.070245	-0.0048	1.8084
b	-0.151053	0.0368	0.05451
c	-0.151049	0.0369	-
d	-0.15063	0.0112	-
e	-0.150674	0.0112	-
f	-0.150274	0.0589	-
g	-0.15073	0.0589	-
h	-0.150456	-0.0138	-
i	-0.151849	0.0118	-
j	-0.151919	0.0118	0.0529
k	-0.151052	0.0112	-
l	-0.151919	0.0118	0.0457

The binding energies are collected in Table 4. According to the table, the binding energies are between 3.4 to 3.5kcal.mol^{-1} which is compatible with the previous studies [10]. The adsorption of H_2 at the j location has the lowest energy and so it is the most stable structure. j is the most favored adsorption location because of the maximum absolute adsorption energy.

Table 5. charge transfer energy of the interaction of 1st H_2 molecule and Li doped defected graphene

structure	Interaction	Charge transfer energy(eV)
a	-	-
b	$\sigma_{H-H} \rightarrow n_{Li}$	7.2
	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.06
c	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.07
	$\sigma_{H-H} \rightarrow n_{Li}$	7.19
d	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.05
	$\sigma_{H-H} \rightarrow n_{Li}$	7.17
e	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.05
	$\sigma_{H-H} \rightarrow n_{Li}$	7.17
f	$\sigma_{H-H} \rightarrow n_{Li}$	7.84
g	$\sigma_{H-H} \rightarrow n_{Li}$	7.9
h	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.06
	$\sigma_{H-H} \rightarrow n_{Li}$	7.17
i	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.09
	$\sigma_{H-H} \rightarrow n_{Li}$	7.26
j	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.09
	$\sigma_{H-H} \rightarrow n_{Li}$	7.26
k	$\pi_{C-C} \rightarrow \sigma^*_{H-H}$	0.07
	$\sigma_{H-H} \rightarrow n_{Li}$	7.18
l	$n_C \rightarrow \sigma^*_{H-H}$	0.09
	$\sigma_{H-H} \rightarrow n_{Li}$	7.26

NBO results are indicated in table5. According to the table, significant charges transfer are occurred from H_2 to Li. The largest binding energy result the most charge transfer.

The binding energy indicated that hydrogen molecule binds molecularly to Li doped graphene and Li atom provides suitable condition for the adsorption of first hydrogen molecule. Then, second hydrogen molecule adsorption is studied on the optimized Li-graphene(H_2) complex. Since adsorption on j position is the most stable structure with the highest capacity for H2 and occupied with first adsorbed Hydrogen molecule, the second H_2 was placed at different positions. The binding energy of the adsorption of second H2 are also included in Table 4. The results indicated that adsorption of second H2 only occurred on h and a positions. According to the calculated binding energies, adsorption of second H2 on h position forms more stable structure than a.

To confirm the results of adsorption energy, we examined the effect of charge transfer on the adsorption of the second H_2 .The results are indicated in table 6. As it is seen, in both two complexes(adsorption of second H2 on h and a position), significant charge transfers were occurred from H2 to Li. The charge transfer in h position is greater than a, so h position has maximum adsorption capacity and the largest interaction with H2 .

Table 6. charge transfer energy of the interaction of 2nd H_2 molecule and Li doped defected graphene

structure	Interaction	Charge transfer energy (eV)
a	$\pi_{C-C} \rightarrow \sigma^*_{H60-H61}$	0.15
	$\sigma_{H60-H61} \rightarrow n_{Li}$	8.78
h	$\pi_{C-C} \rightarrow \sigma^*_{H60-H61}$	0.17
	$\sigma_{H60-H61} \rightarrow n_{Li}$	8.92

Table 7. charge transfer energy of the interaction 3rd H_2 and Li doped defected graphene

Structure	Interaction	Charge transfer energy (eV)
a	$\pi_{C-C} \rightarrow \sigma^*_{H62-H63}$	0.054
	$\sigma_{H62-H63} \rightarrow \pi^*_{C-C}$	0.124
	$\sigma_{H62-H63} \rightarrow n_{Li}$	0.0883
	$\sigma_{H62-H63} \rightarrow \sigma^*_{H58-H59}$	0.0325
	$\sigma_{C-C} \rightarrow \sigma^*_{H62-H63}$	0.0048
	$\sigma_{H62-H63} \rightarrow \sigma^*_{C-C}$	0.0026
	$\sigma_{H58-H59} \rightarrow \sigma^*_{H62-H63}$	0.011
b	$\pi_{C-C} \rightarrow \sigma^*_{H62-H63}$	0.0091
	$\sigma_{H62-H63} \rightarrow n_{Li}$	0.011
j	$\pi_{C-C} \rightarrow \sigma^*_{H62-H63}$	0.0035
	$\sigma_{H62-H63} \rightarrow n_{Li}$	0.0017
	$\sigma_{H62-H63} \rightarrow \pi^*_{H60-H61}$	0.0013
l	$\pi_{C-C} \rightarrow \sigma^*_{H62-H63}$	0.0039
	$\sigma_{H62-H63} \rightarrow \sigma^*_{C-C}$	0.003
	$\sigma_{H62-H63} \rightarrow n_{Li}$	0.284

According to binding energies of the interaction of third H_2 molecule on Li doped defected graphene (indicated in table 4) the third H_2 molecule will not be adsorbed on the structure. NBO analysis is also used to study the effect of charge transfer on the adsorption of 3rd hydrogen molecule on Li doped defected graphene(Table7). The results indicated that no charges transfer were happen , which confirm positive adsorption energy.

4. Conclusions

  Our results show that Li doped defected graphene is a good candidate for the hydrogen storage material. Since Li doping does not modify structural and stability of the defected graphene while change their electronic properties, new assembled materials based on Li doped defected graphene with novel structural and electronic properties can be developed as compared to other defected graphene. Our results indicated that doping of Li atoms onto defected graphene causes a remarkable enhancement in the hydrogen adsorption capacity, which is found to be better than the defective graphene. Such studies have the potential of showing how the physical properties of graphene are influenced by doping of the metal atoms.

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