A first-principles study of Calcium decorated on the interlayer of bilayer graphene for high capacity hydrogen storage

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Abstract. On the basis of the adsorption of hydrogen on the monolayer graphene, the hydrogen storage properties of the bilayer graphene were studied. The paper makes a simulation analysis of the hydrogen storage capacity of the calcium-decorated bilayer graphene using the first principles based on density functional theory. The layer spacing between the double layers of graphene was regulated by doping CA element. The optimal adsorption model of hydrogen storage of the bilayer graphene was simulated using the vast package. Ultimately, the binding energy of hydrogen meets the U.S. department of energy's range of -0.2eV to -0.6eV. CA can adsorb on the interlayer of bilayer graphene without clustering and have high hydrogen storage capacity. The empty pp. orbital of boron is used as a strong charge receptor, thus improving the adsorption capacity of CA on bilayer graphene. The stability of the modified system and the excellent hydrogen storage performance are obtained through the simulation calculation. The system can adsorb up to 8 hydrogen molecules. The average binding energy of -0.2eV~0.3 eV/H2 is in the range that permits H2 recycling at ambient conditions. Calculation and analysis of the adsorption energy and state density in the adsorption process explained the hydrogen storage mechanism of bilayer graphene.

Keywords. Hydrogen storage, Calcium-decorated, bilayer graphene, interlayer.

1. Introduction
Energy and environmental issues play a vital role in the progress and development of human society. The survival of human beings depends on energy mainly from the burning of fossil fuels. Fossil fuels are dwindling and non-renewable, burning causes serious environmental pollution and global warming[1]. Face energy shortages and harsh environment, human beings must strive to develop new energy sources, such as solar energy, wind energy, nuclear energy, hydrogen energy and ocean energy, etc. Hydrogen as a clean energy is considered to be the most ideal secondary energy. In recent ten years, the scope of using hydrogen fuel is more and more widely, so researchers must solve two problems, one is the research of hydrogen storage amount of hydrogen storage material, the other is a solution to efficiently reversibly storage and release hydrogen at room temperature [2-3]. High security performance is a standard of hydrogen as a fuel. The industry has a big demand for hydrogen use, so it must demand that the cost is low and hydrogen storage quantity is higher. The target value of
the hydrogen storage system as specified by the department of energy (DOE) includes a weight capacity of 10wt. % and volume 4.0vol% by 2017[4-6]. As far as we know, these goals have not been realized. In addition, the adsorption and desorption of hydrogen should be reversible in a certain temperature and pressure range, which requires the optimal hydrogen adsorption energy of -0.2—0.6 eV/ H\textsubscript{2} [7-8]. The range of energy is between physical adsorption and chemical adsorption.

Recently, graphene with high specific surface area have been widely studied for hydrogen storage [9-10]. In recent years, many studies have been devoted to functionalizing the surface of graphene [10–13] to improve hydrogen storage capacity. It is found that CA atom can dispersely adsorbed on graphene and make graphene have high hydrogen storage capacity [14-15]. Due to empty d-orbitals, CA decorated graphene can increase the binding capacity of hydrogen by Kuban type interaction. The interaction between the CA atoms prevents the cluster. The hydrogen storage capacity of CA-decorated C\textsubscript{60} [16], CA-decorated monolayer graphene [17], and CA-decorated B-doped graphene [19] has been studied. These results make us further study the hydrogen storage behavior of CA-decorated bilayer graphene system. In this paper, the most stable adsorption configuration of the modified bilayer graphene and the maximum adsorption amount of the interlayer of the functionalized bilayer graphene are investigated.

2. Calculation details
Our calculations are performed by using the Vienna Abs-initio Simulation Package (VASP) based on the density functional theory [20]. The calculation selects a 3×3 super cell containing 36 carbon atoms. The lattice constants is a=b=7.38Å for a (3×3) cell of bilayer graphene. Considering the computational cost, the energy cut off is chosen to be 450 eV. The Brillion zone is sampled by 5×5×1 mesh points in K space for all system of (3×3) bilayer graphene cell. In order to make the distance between the graphene plane layers large enough to avoid any interaction, the z-direction of the graphene sheet has a height of 15Å. All atoms are allowed to relax in calculation. The structures are completely optimized without any symmetry constraint, geometric optimized structure is obtained by relaxation, until the maximum residual force of each atom is smaller than 0.01 eV/Å. The convergence criterion of energy is selected to be less than 10-7 eV per atom.

3. Results and discussion

3.1. Stable configuration of CA-decorated bilayer graphene
Bilayer graphene has two structures: AA type and AB type. In this paper, AA-type bilayer graphene is used as the basis for the study, as shown in Fig. 3-1. The optimized interlayer distance of pristine AA-type bilayer graphene is 3.55Å. According to calculations, the layer spacing is too small to store hydrogen. According to the study of Y, La, Sir doping single-layer graphene, it is found that metal atoms are easy to form clusters, and B doped graphene can effectively prevent many kinds of atomic clusters. Boron can easily be substituted for graphene’s hexagonal structure, while boron doped graphene can be synthesized experimentally.

Figure 1. AA stacking bilayer graphene
Due to the periodicity, B is substituted for the same position of the upper grapheme and the lower layer grapheme (Fig.3-2). The bond length between two adjacent C atoms of pristine bilayer grapheme is 1.41 Å. The B-C bond length of the B-doped bilayer grapheme is 1.47 Å. The B–C bond length of B-doped bilayer grapheme is much longer compared with C–C bond length of pristine bilayer grapheme. The modified bilayer grapheme structure has not changed. This is similar to the B-doped monolayer grapheme.

Calcium is the first atom to have an empty 3d orbit and has recently become the preferred material for improving the storage capacity of carbon nanostructures. A CA atom is decorated in the interlayer of bilayer grapheme, and the adsorption energy of CA atom (2.48eV) is greater than its internal cohesive energy (1.8eV) calculated. Therefore, the CA atom adsorbed on the bilayer grapheme is not easy to form clusters. Because of the empty p orbital of B atom, there is strong electron acceptability, which makes grapheme short of electronic state. Therefore, the introduction of B atom can improve the adsorption capacity. It is assumed that CA atoms can be uniformly covered on the interlayer of the B-doped bilayer grapheme, and then we study the hydrogen storage capacity of CA-decorated B-doped bilayer graphene. The CA atom is the most stable with the surrounding C atoms in the hollow position (Fig.3-3), and the CA atom will automatically move to the hollow position after completely relaxation at different initial positions. The binding energy is minimum (-5.71eV) indicating the strong interaction between CA atom and B-doped bilayer graphene, while Ca is in the hollow position on the B-doped bilayer grapheme and the interlayer distance is 4.4 Å. So it was decided to use this structure as a basis for hydrogen storage.

Figure 2. The top view and the side view: the stable configuration of the B-doped bilayer grapheme
(The grey represents C, green for B)
3.2. \textit{H2} molecule adopted on the interlayer of the \textit{CA-decorated B-doped bilayer grapheme (CA/B/Grapheme) system}

In order to understand the ability of hydrogen storage of the interlayer the CA/B/Grapheme system, we calculated and analyzed the structure of 1-9 hydrogen molecules adsorbed in this active position after relaxation, and finally obtained the stable configuration as shown in fig.3-4.

\textbf{Figure 3.} the top view and the side view of stable structures of calcium-decorated B-doped bilayer grapheme (The grey represents C, green for B, and blue for Ca.)
Figure 4. The top view(I) and the side view(II) of the atomic structures: (a)-(i) show the optimized structures of 1-8 H2 molecules adsorbed on CA/B/Grapheme respectively(violet represents a hydrogen atom, gray represents a carbon atom, blue represents a calcium atom, green represents a boron atom).

According to figure 3-4, it is found the best adsorption position of hydrogen on the CA/B/Graphene system is in the hollow position. It is consistent with the pristine graphene adsorption [5]. To understand the stability of hydrogen molecule adsorption on the CA-decorated B-doped bilayer graphene system, we calculated the average adsorption energy of hydrogen by equation (2):
And the continuous adsorption energy of H2 molecules on CA/B/Graphene system is defined as:

\[
E_{cd-H_2} = \frac{E_{CaB/G/nH_2} - nE_{H_2}}{n} - E_{CaB/G - nH_2}
\]  (3)

Where \( E_{CaB/G/nH_2} \), \( E_{CaB/G/(n-1)H_2} \), and \( E_{H_2} \) denote the total energy of the CA-decorated B-doped bilayer graphene system with n H2 molecules adsorbed, the total energy of the system with (n-1)H2 molecules adsorbed, the total energy of the CA-decorated B-doped bilayer graphene system and the total energy of free H2 molecule, respectively. The specific data are shown in table 3-1.

Table 1. The average adsorption energies (Ead-H2), the continuous adsorption energies (Ecd-H2) of hydrogen molecules on the single side of Ti-PG system. The H-H bond length and the distance of two B atom

|         | Ead-H2(eV) | Ecd-H2(eV) | dB-H(Å) | dB-B(Å) |
|---------|------------|------------|---------|---------|
| 1H2/Ca/B/G | -0.20891   | -0.20891   | 0.7811  | 4.58372 |
| 2H2/Ca/B/G | -0.21252   | -0.23614   | 0.7808  | 4.65876 |
| 3H2/Ca/B/G | -0.2315    | -0.25242   | 0.7810  | 4.72449 |
| 4H2/Ca/B/G | -0.23672   | -0.26945   | 0.7802  | 4.84620 |
| 5H2/Ca/B/G | -0.24928   | -0.29947   | 0.7800  | 5.02115 |
| 6H2/Ca/B/G | -0.2503    | -0.25544   | 0.7786  | 5.06265 |
| 7H2/Ca/B/G | -0.23531   | -0.14535   | 0.7826  | 5.08128 |
| 8H2/Ca/B/G | -0.22647   | -0.15018   | 0.7823  | 5.10774 |
| 9H2/Ca/B/G | -0.08036   | 1.07407    | ——      | 5.51712 |

The average adsorption energy of H2 molecules is between -0.20eV and -0.25eV, and the continuous adsorption energy of H2 molecule is between -0.20eV and -0.30eV. The H-H bond length is elongated to 0.78Å (that is consist with the report in reference [17]), which indicates the adsorption of H2 on the CA/B/Graphene system is between physisorption and chemisorption and further shows the strong adsorption of H2 molecule on CA/B/Graphene system. We found that as the number of hydrogen molecules increased, the interlayer distance is increased, but the bilayer graphene sheet did not deform significantly. Combined with table 1 and figure 4-5, it can be seen that the CA/B/Graphene system can adsorb up to eight hydrogen molecules. When the ninth hydrogen molecules near the system, the ninth hydrogen molecules into two hydrogen atoms, the CA/B/Graphene system of continuous adsorption can be greater than zero, and the average adsorption is -0.08 eV/H2. The adsorption energy of the ideal hydrogen storage material is -0.2eV/H2 to -0.6eV/H2. So the CA/B/Graphene system is going to adsorb up to eight hydrogen’s.

In order to find the maximum number of hydrogen storage of CA/B/Graphene system, we analyzed the total density of states of nine hydrogen molecules adsorbed by the CA/B/Graphene system and the density of states of the 7th, 8th and 9th hydrogen molecule, as shown in figure 3-5 below. Compared with the density of states of nine hydrogen molecules, the ninth hydrogen has a weak electron state, and the density of states of the 7th and 8th hydrogen molecules has contributed to the total state density. Therefore, it can be seen that the ninth hydrogen molecule cannot be adsorbed,
and it can adsorb up to eight hydrogen molecules. The result is the same as analyzing the adsorption energy.

![Graph](image)

**Figure 5.** The total density of states of nine hydrogen molecules adsorbed by the CA/B/Grapheme system and the density of states of the 7th, 8th and 9th hydrogen molecule

To better understand the mechanism of action among CA, B, H2 and bilayer grapheme, PDOS of the CA/B/G systems with the first adsorbed H2 molecule are analyzed. From Fig. 7, there are many overlaps in the main peaks of H2 1s and CA 3d orbital between 2eV and 6eV, which indicates the strong interaction among H2 and Ca. There are many overlaps in the main peaks of B 1p and C 2p orbital between -6eV and -1eV, which indicates the strong interaction among B and bilayer grapheme. The overlap demonstrates the charge transfer between the CA atom and the H atom and the hybridization of the 3d orbital of CA with the σ orbitals of H2. The filled H2 σ orbital transfers electrons to the empty d orbital of the CA atom, conversely, CA atom back-donates electrons to the H2 σ* orbital. Both can interact through charge transfer, this is a typical Kuban interaction [21, 22].
Figure 6. The total and partial density of states of 1H2/CA/B/Grapheme

In order to better understand how CA atoms change hydrogen storage capacity of bilayer grapheme, we calculated badger charges of the CA/B/Graphene and H2 / CA/B/Graphene, mainly analyzes the charge of CA, H, atoms and the C atoms near the activation center(table.2). In the CA/B/Graphene system, the CA atom carry the positive charge of 0.544e, when the CA/B/Graphene system adsorbs hydrogen molecules, we found that two hydrogen atom of the first H2 molecule carry the positive charge of 0.011e, the CA atomic charge is reduce. It is shown that the charge transfer occurs in the process of hydrogen storage of CA atoms and hydrogen molecules, which is consistent with the result of the density of state.

Table 2. The average charge of a part of the atom in the whole adsorption system

|          | CA   | H    | C19  | C25  | C26  | C32  | C33  |
|----------|------|------|------|------|------|------|------|
| Ca/B/G   | 0.544| —    | 0.692| 0.861| 0.723| 0.064| 0.013|
| 1H2/Ca/B/G| 0.534| 0.011| 0.643| 0.791| 0.606| 0.115| 0.151|
| 2H2/Ca/B/G| 0.535| 0.011| 0.503| 0.617| 0.674| 0.079| 0.010|
| 3H2/Ca/B/G| 0.535| 0.019| 0.470| 0.606| 0.556| 0.227| 0.235|
| 4H2/Ca/B/G| 0.527| 0.010| 0.636| 0.757| 0.699| -0.118| 0.150|
| 5H2/Ca/B/G| 0.534| 0.014| 0.463| 0.480| 0.601| 0.183| 0.003|
| 6H2/Ca/B/G| 0.522| 0.014| 0.474| 0.627| 0.545| 0.109| 0.147|
| 7H2/Ca/B/G| 0.524| 0.011| 0.616| 0.764| 0.708| -0.127| 0.140|
| 8H2/Ca/B/G| 0.522| 0.012| 0.581| 0.597| 0.623| 0.248| 0.228|
4. Conclusion
By using VASP package, we have investigated the structural and electronic properties of CA-decorated B-doped bilayer grapheme system, and the adsorption ability of H2 molecules on CA functionalized bilayer grapheme. A CA atom prefers to adsorb on the center site above the C hexagon, very slight deformation of bilayer grapheme can be observed. To understand the mechanism of hydrogen adsorption, badger charges and density of states of H2 adsorbed on CA/B/Grapheme system are analyzed. The modified bilayer grapheme adsorbed up to eight hydrogen molecules, which indicates the interlayer of CA-decorated B-doped bilayer grapheme could be considered as a potential hydrogen storage medium.

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