The effect of boron dopant on hydrogenated graphene for hydrogen storage application

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Abstract. We investigate the effect of boron dopant on the charge transfer and reaction pathways of hydrogenated graphene based upon density functional theory calculation. We focused on the particularly the charge transfer rate of trimer hydrogen adsorption and its reaction pathways. Firstly, we investigated the effect of B dopant on the pristine graphene which is revealed that B-C bond length prior to hydrogenation is around 1.49 Å resulting the deformed structure of graphene since the size of boron is a bit larger that carbon atom. We have also calculated the charge transfer (CTR) from hydrogen to carbon atom after boron substitution, we found that there is an increasing the CTR with respect to the pristine graphene indicated that the strong bond length between hydrogen and carbon.

1. Introduction

Graphene or well-known as a single layer carbon atom in two-dimensional (2D) honeycomb lattice [1] has been increasingly attached attention since it has fascinating physical properties as well as the unique electronics, thermal [2] and mechanical properties [3,4]. Those unique properties are gain a big promising for future application in such a many technology such that nanocomposite, sensors, biomedical and hydrogen storage application [5]. It is well known that hydrogen-based energy has been taking part in the scientist life. Hydrogen storage was one of the key technologies in the application as the future energy carrier. The reason is when the hydrogenated graphene in the form of graphene was demonstrated by Elias et al. [6] and shows that the process of hydrogenation is reversible, making the hydrogenated graphene a potential candidate for hydrogen storage material. The advantage of graphene hydrogenation as a means for storing hydrogen. However, it is fact that many of H storage has a problem with the low storage capacity.

In recent years, carbon-based materials especially graphene have been developed among the scientist in order to increase the capacity of H storage. One of plausible way to modify the graphene surface is by creating a single vacancy, which is good for hydrogen storage application [7,8]. Other facile way to modify the graphene surface to meet the need of diverse applications is chemical doping.

There are two popular chemical doping that commonly used such that B- or N- substitution in graphene materials [9] using Density Functional Theory (DFT) in order to calculate the stability, adsorption and desorption energy. Zhou et al. [9] shows that B- doping forms an electron-deficient six-
membered ring structure and decreases the H atomic adsorption energy. Meanwhile, the N-doping has electron-rich six-membered ring structure and increase the H atomic adsorption energy. In addition, the size of boron and nitrogen are almost the same with the carbon atoms, so that, it is might be possible to do the B and N-doping in the graphene. However, the study of the B and N-doping on H adsorption is controversial since the study in this field is still rarely.

One important parameter to identify the interaction between hydrogen and graphene is charge transfer rate (CTR) since the CTR mediated the local bonding between carbon and hydrogen (C-H bonding). Gagus et al. have been observe the CTR rule from hydrogen to graphene surface [10]. However, based on our best knowledge, the CTR from hydrogen on doped graphene especially boron-doped graphene still not explore yet. Thus, in this study, we would like to study the CTR from hydrogen to graphene with and without boron doping.

2. Method

All the calculation including the structural and electronic structure optimization were performed using density functional theory (DFT) calculation[11], as implemented using the quantum espresso (QE) code [12]. We used the ultra-soft pseudopotential and projector-augmented- wave method [13]. Then we adopt the Perdew-Zunger parameterization [14] using local density approximation. The parameters for hydrogenated graphene with and without boron doping in a super cell were the energy cut off of 40 Ry for the plane wave expansion of the wave function and 400 Ry for the expansion of the augmented charge. The convergence criterion for the structural optimization was that the total absolute value of the inter-atomic force vector became less than 10-4 Ry/au.

The distance between graphene planes was separated by 10 Å in orders to avoid interaction between layers. Distribution of k-points on a mesh of 12x12x1 was selected via Monkhrost-Pack scheme [15]. The structure models used for simulation are graphene sheets consisting of 48 carbon atoms in rectangular super cells. We used lowdin charge analysis to calculate the charge transfer rates from hydrogen to graphene and boron-doped graphene [16] and NEB method to calculate the reaction pathways of the hydrogen adsorption on graphene with and without boron doping [8].

3. Result and Discussion

3.1 Charge Transfer rate

We investigated the trimer hydrogen adsorption on graphene with and without boron doping and calculated its charge transfer rates (CTR).

| Table 1. Value of CTR from hydrogen to pristine graphene and B-doped graphene. |
|-----------------|-----------------|-----------------|-----------------|
| Pristine Graphene | CTR [e] | B-doped Graphene | CTR [e] |
| 48C+3H | 0.2035 | 47C+B+3H | 0.2366 |
| 72C+3H | 0.2041 | 71C+B+3H | 0.2386 |
| 96C+3H | 0.2041 | 95C+B+3H | 0.2388 |

Table 1 shows that B doped increasing the CTR from hydrogen to graphene from 0.20e to 0.24e. CTR enhances by boron doping and suggests higher reactivity in a sense. In addition, enhanced CTR also might contribute stronger bonding between a hydrogen atom and a carbon atom. Since the size of boron is a little bigger than the size of carbon atom, thus there is a little bit distortion in the optimized of hydrogenated graphene with boron doping. The distortion effect could affect the CTR from hydrogen to graphene.
3.2 Deformed Structure
We found the reason why the CTR is increasing in hydrogenated B-doped graphene. Figure 1 shows the structure of hydrogenated graphene with and without boron doping.

![Figure 1](image1.png)

Figure 1. The optimized structure of hydrogenated pristine graphene (a & b), the optimized structure of hydrogenated B-doped graphene (c & d). The yellow, blue and purple atoms denote carbon, hydrogen and boron, respectively.

We found that the location of boron and hydrogenated carbon around boron atom is a bit shifted upward around 0.42 Å and 0.52 Å respectively. This is the reason why the CTR is increase on graphene with boron doping.

3.3 Potential Energy Surface
We investigated the influence of boron doping on the hydrogenation of graphene sheet by investigated the reaction pathways of trimer hydrogen adsorption on pristine graphene and boron-doped graphene.

As seen in Figure 2 (a) and (b) show the reaction of trimer hydrogen adsorption on pristine graphene and boron-doped graphene are exothermic, which indicated that the reaction is plausible in the nature.

The potential energy of the final state of trimer hydrogen adsorption on pristine graphene is around -4.5 eV, while the potential energy of the final state of trimer hydrogen adsorption on boron-doped graphene is around -2.4 eV. It means that in the boron-doped graphene the structure a little bit unstable if we compare with the pristine one. Since this is a bit unstable, thus the structure a bit distorts due to the presence of boron doped graphene. Thus, the results of deformed structure combining with the reaction pathway profile show clearly the reason of increasing the CTR from hydrogen to boron-doped graphene.
Figure 2. Minimum energy pathway of trimer hydrogen adsorption on pristine graphene (a) and trimer hydrogen adsorption on boron-doped graphene (b).

4. Conclusion
We have investigated the effect of boron dopant on the charge transfer rate (CTR) of trimer hydrogen adsorption on graphene using density functional theory calculation. We found the deformed structure of boron-doped graphene increasing the CTR. It was indicated that the CTR mostly affected by deformed structure due to the presence of boron doping.

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