A DFT Study of Hydrogen Adsorption on h-BN: Boron Doping Effects

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In the paper, we have theoretically studied the adsorption of a hydrogen molecule on hexagonal boron nitride (h-BN), boron-rich h-BN, and the h-BN/graphene heterostructure by using standard GGA PBE as well as dispersion-corrected PBE-D3 and B3LYP-D3 density functionals. The coronen molecule (C8H3) has been adopted as a graphene model system. As the h-BN structure we use B3N2H12 model. As the boron rich models, we involve B12N3H16, B24N2H24, and B24N3H24. For the h-BN/graphene heterostructure we use the C8BN12H16 model. It has been found that the dispersion interactions make an important contribution to the hydrogen adsorption energy (\(E_a\)). For h-BN, the step-by-step substitution of nitrogen with boron atoms modifies \(E_a\) values. However, these changes are rather moderate. All three methods used predict the considerable increase in \(E_a\) for the h-BN/graphene heterostructure, especially when the horizontal configuration is considered. The results of this work indicate that the introduction of the small amount of atoms with different electronegativities in one adsorbent structure may substantially increase \(E_a\), but the increment is strongly dependent on the configuration of the interacting species. We believe that some of the considerations, derived in our work, will contribute to a deeper insight into hydrogen adsorption phenomena and development of new materials for hydrogen storage.

Keywords: h-BN, Boron, Hydrogen, DFT, Adsorption.

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1. INTRODUCTION

Nowadays, there are a lot of negative consequences of fossil fuel consumption: air pollution, acid rains, and the greenhouse effect. Indeed, the need for new energy sources is widely understood and shared by scientific community; however, the implications and issues that must be resolved require concerted efforts. Molecular hydrogen has the potential to be a powerful energy source, as it offers a clean, sustainable, and flexible energetics [1]. Many problems, however, exist that slow down the ultimate conversion to hydrogen-based fuels: the mass hydrogen production, purification, storage and delivery.

One- (1D) and two-dimensional (2D) carbon materials such as carbon nanotubes (CNTs) [2] and graphene [3] are generally adopted as the potential hydrogen storage systems. To increase the quantity of hydrogen uptake by these materials, different experimental techniques are used.

It is supposed that there is a possibility to enhance the hydrogen adsorption on graphene by an elemental substitution. Thus, for example, the recent works include the introduction of alkali metal atoms (Li, Na) [4], 3d transition metal atoms (Fe, Co, Ni, and Cu) [5], and gas atoms (N) [6].

On the other hand, different 2D materials, such as hexagonal boron nitride (h-BN), silicene, and graphene oxide provide a novel unique platform as hydrogen storage media. Among them, h-BN material, a planar graphene counterpart, consisting of boron and nitrogen atoms bonded in an alternate manner is selected. Various electronegativities of B and N atoms lead to a creation of small dipoles, which can promote the H2/adsorbent interaction.

Also, heteroatom doping of h-BN has been thoroughly studied in earlier papers. It is supposed that such a technique can significantly increase hydrogen \(E_a\). At the same time, boron doping has received little attention. For example, Choi et al. theoretically studied CO2 capture by boron-rich BNNT [7]. Rahmani et al. showed that boron doping improves the reactivity of single-walled CNTs [8]. Very recent studies of Shokuh Rad et al. have shown that B doping also enhances the ozone adsorption by graphene [9]. The comprehensive work of Wang and Guo has shown that boron-rich doping of BNNTs significantly enhances adsorption of the noble gases [10]. Therefore, in this paper we will study the boron doping effects on hydrogen adsorption.

Besides this, controversial results on hydrogen adsorption energies (\(E_a\)) for graphene and h-BN (CNTs and boron nitride nanotubes (BNNTs)) can be found in the literature. For example, some studies indicate that the adsorption energy of H2 on BNNTs is larger than on CNTs possibly due to their heteropolar binding [11]. On the other hand, the work of Zhou et al. shows that both chemi- and physisorption of hydrogen on CNTs is more energetically favorable than on BNNTs [12]. Thus, it is worth comparing H2 adsorption on both graphene and h-BN.

In view of our continuing interest in studying non-covalent interactions between hydrogen and various types of adsorbents [13, 14], in this paper, we focus on the density functional theory (DFT) study of the adsorption of H2 on h-BN, boron-rich h-BN, and h-BN/graphene heterostructure.

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2. COMPUTATIONAL METHODS

All calculations were carried out using Orca 4.0.1 program package [15]. For the DFT calculations, the pure GGA method, PBE, and dispersion-corrected (as proposed by Grimme) GGA PBE-D3 and hybrid B3LYP-D3 functionals together with the SVP basis set were employed. It has been demonstrated that these functionals are reliable and commonly used in the studies of hydrogen adsorption phenomena [13, 14].

The coronene molecule \((C_{24}H_{12})\) is widely adopted as a graphene model system [16, 17]. To obtain the employed models, we substitute carbon atoms in coronene with nitrogen and boron atoms. Thus, for example, for h-BN model (Fig. 1a) we substitute all carbon atoms in coronene with B and N in an alternate manner. For boron-rich models (Fig. 1b-d), we substitute one (4B h-BN), two (5B h-BN) or three (6B h-BN) nitrogen atoms with additional boron atoms in h-BN. For heterostructure, we substitute C atoms with B and N in the central ring of coronene only. It is worth noticing that it is not a focus of this paper to discuss the stability of the involved structures, but to analyze the substitution effects on \(E_a\) values of H. First, pristine h-BN, B-rich h-BN, as well as a heterostructure molecule, were fully optimized at the respective level of theory. The geometries of these structures were then frozen. Second, we fixed perpendicular orientation of a hydrogen molecule relative to the involved systems and studied the “hollow” (vertical hollow, VH) adsorption site (Fig. 1f). Third, we fixed parallel orientation of hydrogen with respect to the studied models and then investigated the same adsorption site (horizontal hollow, HH) (Fig. 1o). We selected the hollow adsorption site, as it was earlier shown [18, 19], that the hollow positions are the most favorable for hydrogen adsorption. The distance between H and studied models is defined as the length of a perpendicular line dropped from the hydrogen center-of-mass to the plane of graphene. Finally, we varied the distance from 5.5 to 2 Å and calculated the single-point adsorption energies \((E_n)\), \(n = 1-7\), using the following equation (1):

\[
E_n = E(\text{adsorbent/H}_2) - E(\text{adsorbent}) - E(H_2),
\]

where \(E(\text{adsorbent/H}_2)\) denotes energy of the physically adsorbed adsorbent/H\(_2\) system, \(E(H_2)\) is the total energy of \(H_2\), and \(E(\text{adsorbent})\) is the total energy of the corresponding adsorbent model.

Final \(E_n\) for each adsorbent is the minimum of the respective potential curve (Fig. 2).

![Fig. 1](image1.png)  
**Fig. 1** – All models involved in this study (a–e), as well as vertical (VH) and horizontal (HH) configurations (f) of hydrogen adsorption on h-BN (as an example). Color code: light blue – hydrogen, blue – nitrogen, magenta – boron, yellow – carbon

3. RESULTS AND DISCUSSION

Fig. 2 shows the graphs of \(E_n\) vs. the distance (R) between the h-BN/graphene heterostructure and the hydrogen molecule, which is oriented horizontally (HH) relative to the adsorbent plane and located on the hollow position. All three calculation methods used (PBE, PBE-D3, and B3LYP-D3) exhibit binding between hydrogen and graphene. For studied models, adsorption energies as well as equilibrium distances are summarized in Table 1. The pure GGA method, PBE, as known, poorly predicts adsorption energies. It yields only a fraction of the whole energy value. Indeed, the shape of the potential curve (Fig. 2, ▲, green) and obtained data (Table 1) show very small \(E_n\) values in the case of PBE calculations.

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For PBE, equilibrium distance between the plane of h-BN and hydrogen (3.3 Å) is overestimated considerably in comparison with the results of calculations with PBE-D3 (~ 3.1 Å) or B3LYP-D3 (3.1 Å). In general, our results also confirm the inadequacy of standard DFT in describing the van der Waals interaction, as it was cited earlier [18, 20]. In turn, B3LYP-D3 and PBE-D3 functionals show much better performance. Potential curves obtained using these density functionals exhibit clear minima at the distances of ~ 3.1 Å. The absolute $E_a$ values are larger in the case of the PBE-D3 functional (~ 6.2 kJ/mol), and B3LYP-D3 shows slightly smaller values (~ 5.8 kJ/mol).

We now compare the results of $H_2$ adsorption on graphene, which we obtained earlier [13] with those on h-BN. As a whole, we may notice that the results are quite close. It may explain the scattering in outcomes of the previous works, which predict opposite results. $E_a$ values are larger in the case of the PBE-D3 functional (~ 6.2 kJ/mol), and B3LYP-D3 shows slightly smaller values (~ 5.8 kJ/mol).

In summary, we have studied $H_2$ adsorption onto h-BN, boron-rich h-BN, and the h-BN/graphene heterostructure using standard PBE, as well as dispersion-corrected PBE-D3 and B3LYP-D3 density functionals. Our results show that PBE-predicted energies are strongly underestimated owing to the well-known shortcomings of the pure DFT functionals. At the same time, dispersion-corrected methods indicate strong bonding of the molecular hydrogen.

The boron doping does not lead to the increase in $E_a$ in comparison with pristine h-BN for hydrogen adsorption. However, all three methods used predict the considerable increase in $E_a$ values for the h-BN/graphene heterostructure. PBE-D3 predicts that $E_a$(h-BN/graphene heterostructure) > $E_a$ (pristine h-BN) on 0.8 kJ/mol (14%). In turn, B3LYP-D3 yields the following: $E_a$(h-BN/graphene heterostructure) > $E_a$ (pristine h-BN) on 3.2 kJ/mol (62%). Such an increase we ascribe to larger dipole moments of the central ring of the heterostructure model, and thus enhanced interaction between permanent dipole (heterostructure) and induced dipole (hydrogen). Larger $E_a$ values for HH configurations are explained by the enhanced interaction.

**4. CONCLUSIONS**

In summary, we have studied $H_2$ adsorption on h-BN, boron-rich h-BN, and the h-BN/graphene heterostructure using standard PBE, as well as dispersion-corrected PBE-D3 and B3LYP-D3 density functionals. Our results show that PBE-predicted energies are strongly underestimated owing to the well-known shortcomings of the pure DFT functionals. At the same time, dispersion-corrected methods indicate strong bonding of the molecular hydrogen.

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between the hydrogen molecule aligned horizontally and the adsorb as both atoms of H$_2$ are involved in this interaction in such a case. An effect of B and N doping of graphene, leading to the increased $E_a$ values, should have potential applications for engineering of novel hydrogen storage media.

### REFERENCES


**ACKNOWLEDGEMENTS**

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**4B**

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**5B**

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**6B**

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**h-BN/graphene heterostructure**

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Дослідження адсорбції водню на h-BN за допомогою функціональної теорії шільнісіті: ефекти домішки бору

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У роботі теоретично досліджене адсорбцію молекул водню на гексагональному нітриді бору (h-BN), на h-BN збагаченому бором та гетероструктурі h-BN/графен з використанням стандартного узагальненого градієнтного наближення GGA PBE, а також функціоналів шільнісіті PBE-D3 або B3LYP-D3 з корегованою дисперсією. Молекула коронену (C_{24}H_{12}) була взята як модель графенової системи. Як структура h-BN, використовувалась модель B_{12}N_{12}H_{12}. Ми залучили B_{13}N_{11}H_{12}, B_{14}N_{10}H_{12} та B_{15}N_{9}H_{12} як моделі збагачені бором. Для гетероструктур h-BN/графен ми використали модель C_{18}B_{3}N_{3}H_{12}. Встановлено, що дисперсійні взаємодії вносять важливий внесок у енергію адсорбції водню (E_a). Для h-BN покрокове заміщення азоту атомами бору змінює значення E_a. Однак ці зміни є досить помірними. Всі три використані методи прогнозують значне збільшення E_a для гетероструктур h-BN/графен, особливо при розгляді горизонтальної конфігурації. Результати цієї роботи показують, що введення невеликої кількості атомів з різними електронегативностями в одну структуру адсорбенту може істотно збільшити E_a, але приріст сильно залежить від конфігурації взаємодіючих видів. Ми вважаємо, що дані з міркувань, отриманих у роботі, сприятимуть більш глибокому розумінню явищ адсорбції водню та розробці нових матеріалів для зберігання водню.

Ключові слова: h-BN, Бор, Водень, DFT, Адсорбція.