JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **11** No 2, 02024(5pp) (2019)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **11** № 2, 02024(5cc) (2019)

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

I.K. Petrushenko*

Irkutsk National Research Technical University, 83, Lermontov St., 664074, Irkutsk, Russia

(Received 10 January 2019; revised manuscript received 05 April 2019; published online 15 April 2019)

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 coronene molecule ($C_{24}H_{12}$) has been adopted as a graphene model system. As the h-BN structure we use $B_{12}N_{12}H_{12}$ model. As the boron rich models, we involve $B_{13}N_{11}H_{12}$, $B_{14}N_{10}H_{12}$, and $B_{15}N_{9}H_{12}$. For the h-BN/graphene heterostructure we use the $C_{18}B_{3}N_{3}H_{12}$ model. It has been founded 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.

DOI: 10.21272/jnep.11(2).02024 PACS numbers: 31.15.E –, 61.48.De, 68.43. – h, 68.43.Bc

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 slowdown 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 H_2/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 CO_2 capture by boron-rich BNNT [7], Rahmanifar et al. showed that boron doping improves the reactivity of single-walled CNTs [8]. Very recent studies of Shokuhi 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 H_2 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 H_2 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 H_2 on h-BN, boron-rich h-BN, and h-BN/graphene heterostructure.

---

* igor.petrushenko@istu.edu

2. COMPUTATIONAL METHODS

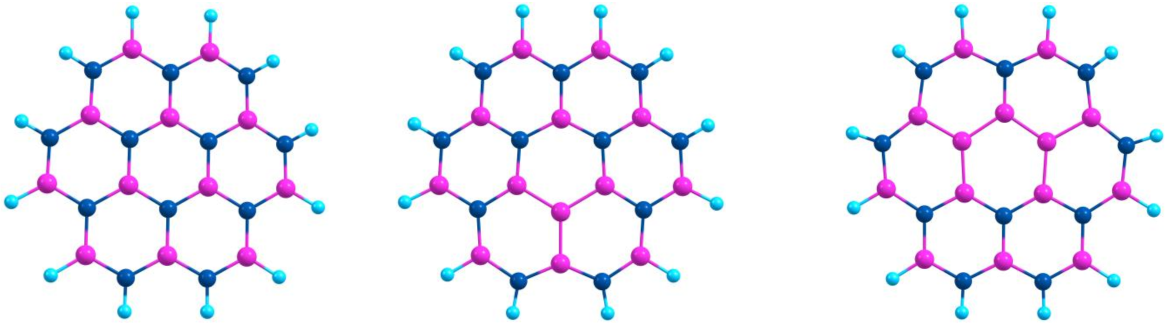
All calculations were carried out using Orca 4.0.1 program package [15]. For the DFT calculations, the pure GGA method, PBE, and dispersion-corrected (as proposed by Grimme) GGA PBE-D3 and hybrid B3LYP-D3 functionals together with the SVP basis set were employed. It has been demonstrated that these functionals 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_2. First, pristine h-BN, B-rich h-BN, as well as a heterostucture 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. 1f). 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_2 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_{an}), n = 1-7, using the following equation (1):

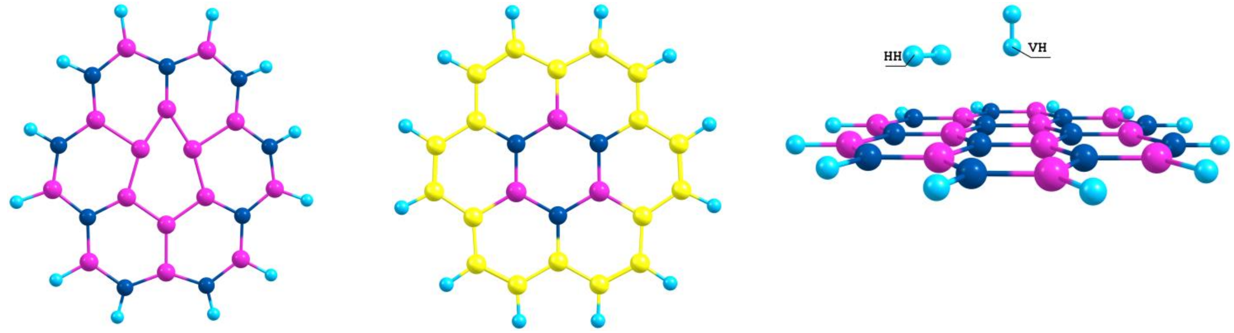
$$E_{an} = E(\text{adsorbent}/H_2) - E(\text{adsorbent}) - E(H_2), \quad (1)$$

where E(adsorbent/H_2) denotes energy of the physisorbed adsorbent/H_2 system, $E(H_2)$ is the total energy of H_2, and E(adsorbent) is the total energy of the corresponding adsorbent model.

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



(a) Pristine h-BN (b) 4B h-BN (c) 5B h-BN



(d) 6B h-BN (e) Heterostructure h-BN/graphene (f) VH and HH configurations on h-BN

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_{an} *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_a values in the case of PBE calculations.

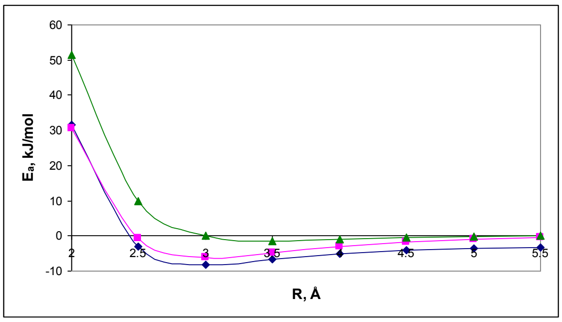


Fig. 2 – Potential energy curves for the hydrogen h-BN/graphene heterostructure interaction (HH (horizontal) configuration) calculated by using PBE (▲, green), PBE-D3 (■, magenta),and B3LYP-D3 (♦, blue) methods

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 (h-BN) > E_a (graphene) [11] and E_a (graphene) > E_a (h-BN) [12]. For pristine models, the data for both HH and VH configurations show that E_a (graphene) > E_a (h-BN) slightly. Only PBE method, which poorly predicts E_a, yields approximately equal values for graphene and h-BN (Table 1). Besides this, we can note that boron-rich h-BN exhibits smaller E_a values in comparison with both graphene and pristine h-BN (Table 1).

Next, we turn to h-BN and boron-rich h-BN. For VH configurations, the PBE functional yields the smallest E_a values and predicts the very weak binding of hydrogen to h-BN (Table 1). Moreover, the E_a value of – 1.4 kJ/mol (H_2 adsorption on pristine h-BN) is the largest among studied boron-rich models. Boron doping does not lead to the increase in E_a. It should be noted, however, that one should use results of PBE with care. For HH configurations, all three methods used predict the same trend in E_a changes on going from pristine to 6B h-BN (Table 1). In general, the E_a values for HH are smaller than E_a for VH configurations. The equilibrium distances between H_2 and graphene also converge to larger values. We ascribe the nearly double decrease in E_a for the PBE calculations to the poor van der Waals interactions treatment, therefore, further we mainly focus on the results of dispersion-corrected functionals. PBE-D3 and B3LYP-D3 also show E_a decrease.

Opposite to the previous report on the noble gas adsorption on pristine and boron-rich BNNTs [15], we cannot say that such a doping increases E_a for hydrogen. Although in our case, E_a are favorable, but, in general, the doping diminishes non-covalent interactions between H_2 and boron-rich graphene. We can ascribe such behavior to the different polarization of a hydrogen molecule and noble gas atoms (He, Ne, Ar, Kr), and, therefore, the different effects of doping.

We then directly compare the E_a values for both HH and VH configurations. The larger E_a absolute value can be explained in terms of the shape of the electronic cloud of hydrogen. For the vertical configuration, the cloud of a hydrogen molecule is ellipsoid-shaped, therefore, at the equilibrium distance of 3.1 Å, H_2 can approach closer to the adsorbent sheet compared with the horizontally aligned molecule. E_a values of – 5.8 and – 5.2 kJ/mol (h-BN, B3LYP-D3 method) corresponding to the VH and HH configurations, respectively, reflect the fact that the hydrogen adsorption at a distance of 3.1 Å is slightly stronger at VH configuration than at HH one. This scenario holds when one studies hydrogen adsorption on pristine graphene [13], h-BN, and boron-rich h-BN. However, when one introduces different atoms with non-equal electronegativities into adsorbent (for our case, they are C, B, and N), the local dipole moments in various domains of the heterostructure increase. Such an increase leads to the considerable enhancement in the adsorption energy of H_2. Indeed, for the h-BN/graphene heterostructure (Table 1), B3LYP-D3 calculations predict E_a of – 8.4 kJ/mol; it much larger than E_a for pristine h-BN (– 5.2 kJ/mol, ~ 60%), graphene (– 5.5 kJ/mol, ~ 50 %), and B-rich h-BN (varies from – 2.0 to – 5.1 kJ/mol, from ~ 300 % to 50 %). All of these indicate that the BN/graphene heterostructure is expected to be applied to H_2 adsorbents.

As a whole, graphene doping by B and N atoms or *vice versa* can promote the hydrogen uptake and thus improve storage abilities of modern hydrogen storage systems. It is expected that our predictions will provide a useful guide to develop high-capacity H_2 storage materials for practical usage.

4. CONCLUSIONS

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 binding 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

Table 1 – Hydrogen adsorption energies (E_a) and separations (R) between H_2 molecule and h-BN for vertical (VH) and horizontal configurations (HH)

h-BN	HH, kJ/mol	R, Å	VH, kJ/mol	R, Å
B3LYP-D3	– 5.2	3.1	– 5.8	3.1
PBE-D3	– 5.7	3.1	– 6.2	3.2
PBE	– 1.3	3.3	– 1.4	3.3
4B				
B3LYP-D3	– 4.6	3.1	– 5.3	3.1
PBE-D3	– 5.1	3.2	– 6.0	3.2
PBE	– 1.1	3.5	– 1.5	3.5
5B				
B3LYP-D3	– 5.1	3.1	– 5.8	3.1
PBE-D3	– 4.1	3.2	– 5.5	3.3
PBE	– 0.7	3.7	– 1.7	3.6
6B				
B3LYP-D3	– 2.0	3.6	– 3.8	3.5
PBE-D3	– 3.1	3.6	– 4.7	3.5
PBE	– 0.5	4.0	– 1.6	3.7
h-BN/graphene heterostructure				
B3LYP-D3	– 8.4	3.1	– 8.1	3.1
PBE-D3	– 6.5	3.1	– 5.8	3.1
PBE	– 1.7	3.4	– 1.8	3.5
Graphene [20]				
B3LYP-D3	– 5.5	3.1	– 5.9	3.1
PBE-D3	– 6.5	3.1	– 6.7.	3.1
PBE	– 1.2	3.2	– 1.4	3.2

between the hydrogen molecule aligned horizontally and the adsorbent 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 has potential applications for engineering of novel hydrogen storage media.

ACKNOWLEDGEMENTS

This work was partially supported by the base part of the Government Assignment for Scientific Research from the Ministry of Education and Science of Russia (project code: 13.7232.2017/8.9) and Mikhail Lomonosov grant of the Government Assignment for Scientific Research from the Ministry of Education and Science of Russia (project code: 4.13413.2019/13.2).

REFERENCES

1. G.W. Crabtree, M.S. Dresselhaus, M.V. Buchanan, *Phys. Today* **57** (12), 39 (2004).
2. S. Iijima, *Nature* **354**, 56 (1991).
3. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Science* **306**, 666 (2004).
4. S.-M. Choi, S.-H. Jhi, *Appl. Phys. Lett.* **94**, 153108 (2009).
5. Y. Zheng, W. Xiao, M. Cho, K. Cho, *Chem. Phys. Lett.* **586**, 104 (2013).
6. M. Fan, Z.-Q. Feng, C. Zhu, X. Chen, C. Chen, J. Yang, D. Sun, *J. Mater. Sci.* **51**, 10323 (2016).
7. H. Choi, Y.C. Park, Y.H. Kim, Y.S. Lee, *J. Am. Chem. Soc.* **133**, 2084 (2011).
8. E. Rahmanifar, M. Yoosefian, H. Karimi-Maleh, *Synth. Met.* **221**, 242 (2016).
9. A. Shokuhi Rad, S. Sadeghi Shabestari, S. Mohseni, S. Alijantabar Aghouzi, *J. Solid State Chem.* **237**, 204 (2016).
10. C. Wang, C. Guo, *Superlattice Microst* **107**, 97 (2017).
11. S.H. Jhi, *Phys. Rev. B* **74**, 155424 (2006).
12. Z. Zhou, J. Zha, Z. Chen, X. Gao, T. Yan, B. Wen, P.V.R. Schleyer, *J. Phys. Chem. B* **110**, 13363 (2006).
13. I.K. Petrushenko, *J. Nano- Electron. Phys.* **9**, 03018 (2017).
14. I.K. Petrushenko, K.B. Petrushenko, *Int. J. Hydrogen Energ.* **43** (2), 801 (2018).
15. F. Neese, *WIREs Comput. Mol. Sci.* **8**, e1327 (2018).
16. M. Pykal, P. Jurecka, F. Karlicky, M. Otyepka, *Phys. Chem. Chem. Phys.* **18**, 6351 (2016).
17. P. Lazar, F. Karlicky, P. Jurecka, M. Kocman, E. Otyepkova, K. Safarova, M. Otyepka, *J. Am. Chem. Soc.* **135**, 6372 (2013).
18. D. Henwood, J.D. Carey, *Phys. Rev. B* **75**, 245413 (2007).
19. S. Krishnan, R. Vadapoo, K.E. Riley, J.P. Velev, *Phys. Rev. B* **84**, 165408 (2011).
20. M. Rubes, O. Bludsky, *Chemphyschem.* **10**, 1868 (2009).

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

І.К. Петрушенко

Іркутський національний науково-технічний університет, вул. Лермонтова, 83, 664074, Росія

У роботі теоретично досліджено адсорбцію молекули 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 щільності PBE-D3 and B3LYP-D3 з корегованою дисперсією. Молекула коронену ($C_{24}H_{12}$) була узята як модель графенової системи. Як структура h-BN, використовувалася модель $B_{12}N_{12}H_{12}$. Ми залучили $B_{13}N_{11}H_{12}$, $B_{14}N_{10}H_{12}$ та $B_{15}N_9H_{12}$ як моделі збагачені бором. Для гетероструктури h-BN/графен ми використали модель $C_{18}B_3N_3H_{12}$. 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 гетероструктури 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 деякі 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.