

A DFT Study of Hydrogen Adsorption onto Graphene: Effect of Nitrogen Doping

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Using standard GGA PBE as well as dispersion-corrected PBE-D3 and B3LYP-D3 functionals we have theoretically studied the adsorption of a hydrogen molecule onto pristine and N-doped graphene. We have found that the van der Waals interactions make an important contribution to adsorption energy (E_a) of H_2 . In graphene, the step-by-step substitution of carbon atoms with nitrogen modifies E_a values. All three methods used predict the considerable increase in E_a for N-doped graphene, when the horizontal configuration is considered. The results of the present study indicate that the introduction of the small number of nitrogen atoms may increase the adsorption energy in graphene, but the increment, seemingly, is dependent on the configuration of the interacting species.

Keywords: Graphene, Nitrogen, Hydrogen, DFT, Adsorption

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1. INTRODUCTION

The negative consequences of fossil fuels consumption on the environment (air pollution, acid rains, oil spills, and the greenhouse effect) will accelerate the transition to the renewable energy sources. Molecular hydrogen is generally recognized as one of the best candidates for 'green' energetics [1 – 3]. There are a lot of problems, however, that decelerate 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) [4] and graphene [5] have been extensively studied as the potential hydrogen storage systems. In order to increase the quantity of hydrogen uptake by these materials, different experimental techniques and various levels of computations have also been involved to study carbon nanostructures and their functionalized counterparts. The experimentally obtained results are still controversial due to lack of reproducibility. Besides this, pristine graphene does not provide sufficient binding for hydrogen, namely less than 9.6 kJ/mol, compared with the ideal binding range 15.3 – 38.6 kJ/mol at ambient conditions [6]. It is believed that there is a possibility to enhance the hydrogen adsorption onto graphene by an elemental substitution. Thus, for example, the recent works include the introduction of alkali metal atoms (Li, Na) [7], 3d transition metals (Fe, Co, Ni, and Cu) [8], and gas atoms (N) [9, 10]. Several experimental efforts have been done to ascertain whether it is possible to effectively substitute carbon atoms with nitrogen, and thus advance the hydrogen storage. Jeong et al. and Li et al. have synthesized N-doped graphene and discussed the nitrogen influence on its main properties [11, 12]. Nitrogen atoms have sizes similar to those of carbon, and also they have the lone pair of electrons. These facts are a motif of a nitrogen selection as a dopant to increase the electron density of

graphene, and, therefore, enhance the non-covalent H_2 /N-doped graphene interactions.

In view of our continuing interest in studying various physical and chemical properties of carbon nanostructures [13 – 16], in this paper, we focus on the density functional theory (DFT) investigation of the interaction between hydrogen molecules and nitrogen-doped graphene, and the clarification of the role of step-by-step nitrogen doping in hydrogen adsorption.

2. COMPUTATIONAL METHODS

All calculations were carried out using Orca 3.0.3 program package [17]. For the DFT calculations, the pure GGA method, PBE, and dispersion-corrected (as proposed by Grimme) GGA PBE-D3 and hybrid B3LYP-D3 functionals [18 – 21] together with the SVP basis set [22] were employed. These functionals has been demonstrated to be reliable and commonly used in the studies of adsorption phenomena [23, 24].

The coronene molecule ($C_{24}H_{12}$) is adopted as a graphene model system (Fig. 1). It was predicted that coronene is the smallest molecule that resembles properties of graphene [25, 26]. To obtain N-doped models, we substitute carbon atoms in the central ring of coronene with nitrogen atoms (Fig. 1). It is worth noticing that it is not a focus of this paper to discuss the stability of the involved N-doped structures but to analyze the substitution effects on E_a values of H_2 . Firstly, pristine graphene, N-doped graphene as well as a hydrogen molecule were fully optimized at the respective level of theory. The geometries of these structures was then frozen. Secondly, we fixed perpendicular orientation of a hydrogen molecule relatively studied systems and studied the "hollow" (vertical hollow, VH) adsorption site (Fig. 1, b). Thirdly, we fixed parallel orientation of hydrogen molecule relatively studied models and then investigated the same adsorption site (horizontal hollow, HH) (Fig. 1, a). We selected the hollow adsorption site as it

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had shown earlier that the hollow positions are the most favorable for hydrogen adsorption [27, 28]. 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 angstroms and calculated single-point adsorption energies (E_a) using equation 1:

$$E_a = E_t(\text{graphene}/H_2) - E_t(\text{graphene}) - E_t(H_2), \quad (1)$$

where $E_t(\text{graphene}/H_2)$ denotes energy of the physisorbed graphene/ H_2 system, $E_t(H_2)$ is the total energy of H_2 , and $E_t(\text{graphene})$ is the total energy of a graphene model.

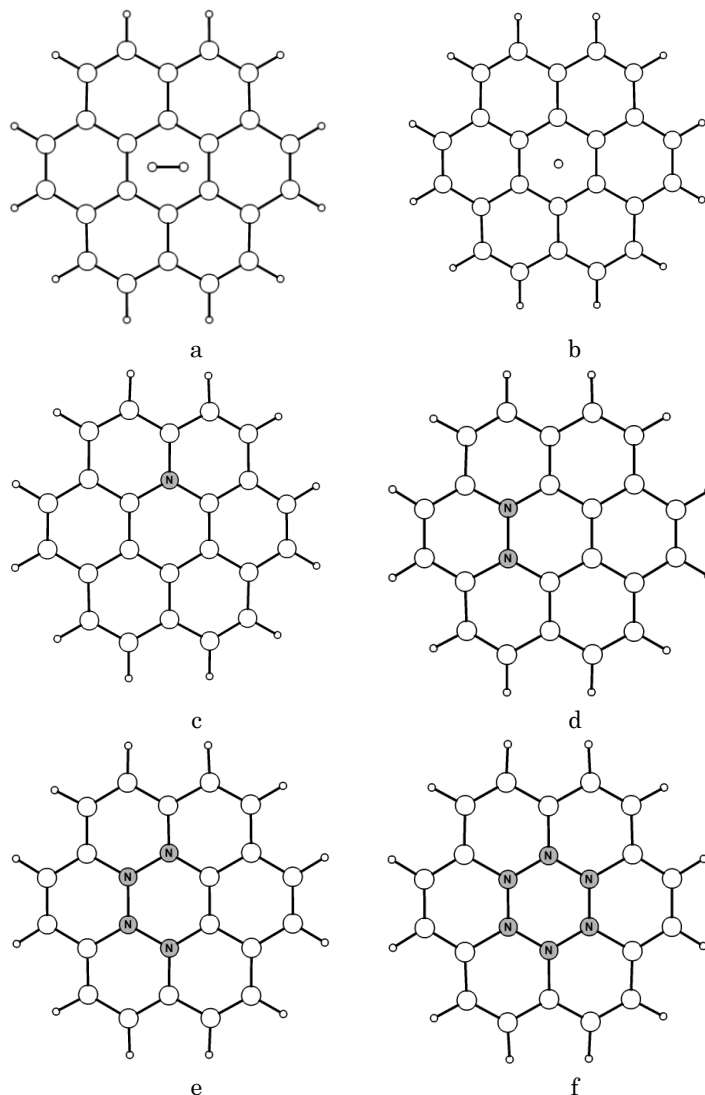


Fig. 1 – a – Horizontal configuration (HH) of hydrogen adsorption onto pristine graphene; b – Vertical configuration (VH) of hydrogen adsorption onto pristine graphene; c – 1N-doped graphene; d – 2N-doped graphene; e – 4N-doped graphene; f – 6N-doped graphene. Small balls are hydrogen, large balls are carbon. Nitrogen atoms are labeled as “N”

3. RESULTS AND DISCUSSIONS

Fig. 2 shows the graphs of E_a vs. the distance between graphene and the hydrogen molecule, which is oriented vertically (VH) or horizontally (HH) relatively the graphene plane and located on the hollow position. All three calculation methods 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 is known poorly predicts adsorption energies. It yields only a fraction of the whole energy value. Indeed, Fig. 2 and Table 1 show very small E_a values in the case of

PBE calculations. Equilibrium distance between the plane of graphene and hydrogen, seemingly, is overestimated (3.2 Å). Thus, our results also confirm the inadequacy of standard DFT in describing the van der Waals interaction, as cited in [24, 27]. As for B3LYP-D3 and PBE-D3, they show much better performance. The potential curves exhibit clear minima at the distances of ~ 3.1 Å. The absolute adsorption energy values are larger in the case of the PBE-D3 functional larger in the case of the PBE-D3 functional (- 6.7 kJ/mol), and B3LYP-D3 shows slightly smaller values (- 5.9 kJ/mol). Table 1 summarizes hydrogen

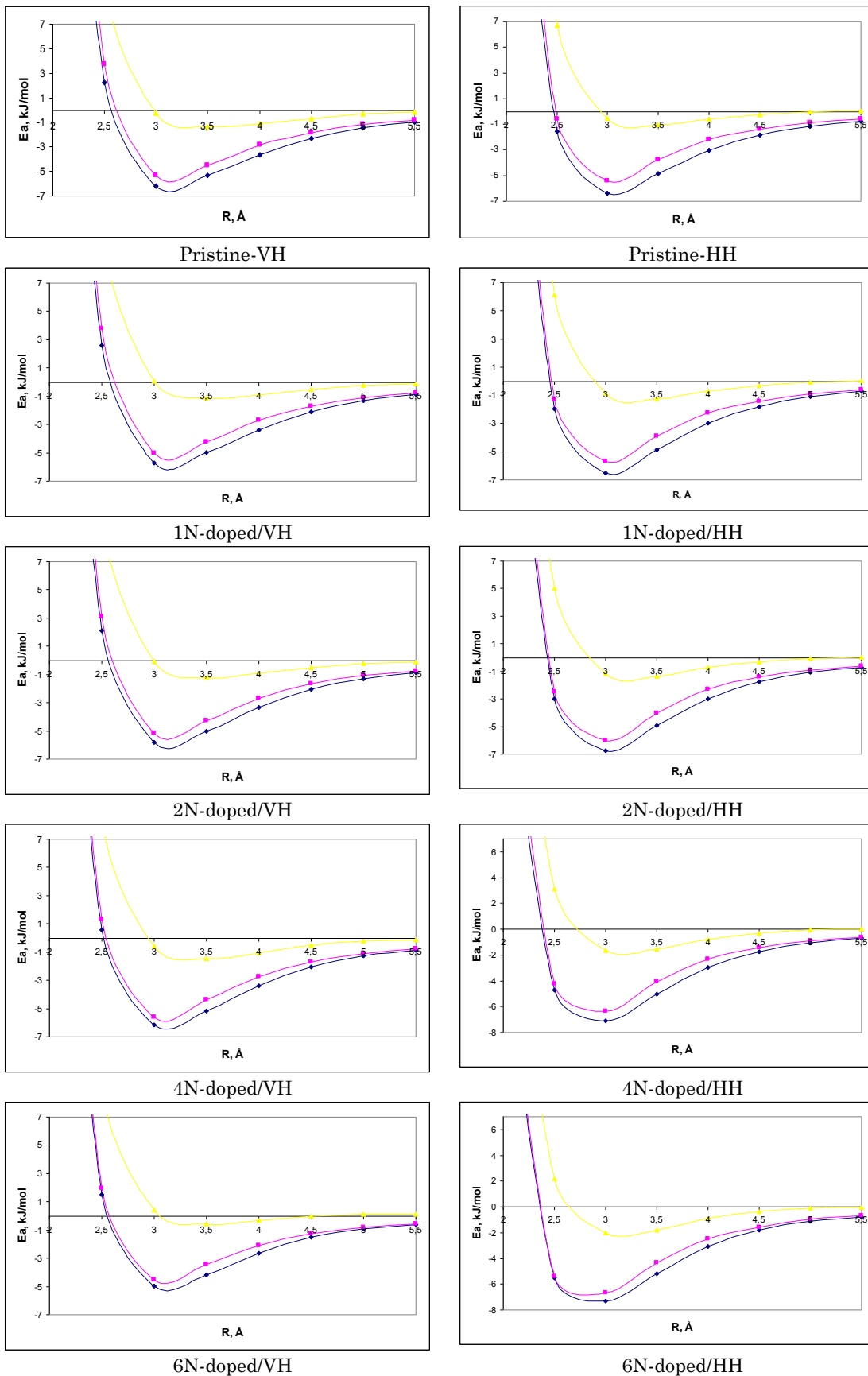


Fig. 2 – Potential energy curves of H₂/graphene interaction (VH denotes vertical configuration, HH – horizontal configuration) calculated by using PBE (▲, yellow), PBE-D3 (◆, blue), and B3LYP-D3 (■, magenta) methods

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

Method	Model	VH		HH	
		E_a , kJ/mol	R , Å	E_a , kJ/mol	R , Å
PBE	Pristine	-1.4	3.2	-1.2	3.2
	1N- doped	-1.2	3.2	-1.4	3.2
	2N- doped	-1.2	3.2	-1.5	3.2
	4N- doped	-1.4	3.2	-1.9	3.2
	6N- doped	-0.6	3.2	-2.2	3.1
PBE-D3	Pristine	-6.7	3.1	-6.5	3.1
	1N- doped	-6.1	3.1	-6.6	3.1
	2N- doped	-6.2	3.1	-6.8	3.0
	4N- doped	-6.4	3.1	-7.1	3.0
	6N- doped	-5.3	3.1	-7.3	3.0
B3LYP-D3	Pristine	-5.9	3.1	-5.5	3.1
	1N- doped	-5.4	3.1	-5.8	3.1
	2N- doped	-5.6	3.1	-6.1	3.0
	4N- doped	-5.9	3.1	-6.3	3.0
	6N- doped	-4.8	3.1	-6.7	3.0

adsorption energies and equilibrium distances between a H_2 molecule and graphene. First, we study the VH configuration. The PBE functional yields the smallest E_a values and predicts very weak binding of hydrogen onto graphene (Table 1). Moreover, the E_a value of -1.4 kJ/mol (H_2 adsorption on pristine graphene) is the largest among studied. Nitrogen doping does not lead to the increase in E_a . Only one E_a value for 4N-doped graphene (-1.4 kJ/mol) is equal to that of pristine graphene. It should be noted, however, that we should use results of PBE calculations with care as this method improperly treats the long-range interactions. PBE-D3 and B3LYP-D3 exhibit the similar trend: the adsorption to pristine graphene is energetically favorable. The E_a value of -6.7 kJ/mol (-5.9 kJ/mol) is the maximum among studied for the PBE-D3 (B3LYP-D3) method (Table 1). The graphene doping with nitrogen diminishes adsorption on energies, and thus makes the adsorption process unfavorable. Dispersion corrected functionals yield equilibrium distances of 3.1 Å, whereas the pure GGA functional show $R = 3.2$ Å. The values are consistent with those of the previously published works [24, 27, 28], the latter results are larger than those of PBE-D3 and B3LYP-D3 calculations. PBE-D3 exhibits the larger absolute values among methods used herein, and B3LYP-D3 results fall between PBE-D3 and PBE predictions. As a whole, one can see that for the VH configuration, the nitrogen doping decreases the adsorption energies.

Next, we turn to the HH configuration. All three methods used predict considerable increase in E_a on H_2 adsorption on going from pristine to 6N-doped graphene (Table 1). Indeed, even the pure GGA functional shows stronger binding between graphene models and hydrogen. The data of Table 1 show large absolute increase in E_a from -1.2 (pristine graphene) to -2.2 (6N-doped graphene) kJ/mol. The equilibrium distances between H_2 and graphene also converge to a more reliable value of 3.1 Å. The overall double increase in E_a is rather unrealistic as is was mentioned above, pure PBE does not treat the van der Waals interactions properly,

therefore, further we mainly focus on the results of dispersion-corrected functionals.

PBE-D3 results as in the case of VH studies are the largest, PBE results are the smallest. B3LYP-D3 shows intermediate values (Table 1). PBE-D3 predicts stronger binding of a H_2 molecule on N -doped graphene sheets. The gradual increase in E_a values can be easily seen from Table 1. E_a (6N-doped graphene) is larger than E_a (pristine graphene) on 0.8 kJ/mol (12 per cent) (Table 1). R values are in a close connection with B3LYP-D3 calculations as well as results of literature data. In the case of B3LYP-D3, E_a (6N-doped graphene) $> E_a$ (pristine graphene) on 1.2 kJ/mol (22 per cent) (Table 1). It speaks for an interesting effect of considerable enhancement of E_a when N -doping is done.

We then directly compare the E_a values of both HH and VH configurations. The larger E_a absolute value can be explained in terms of electronic structures of hydrogen. For the vertical configuration, the electronic cloud of a hydrogen molecule is ellipsoid-shaped, therefore, at the equilibrium distance of 3.1 Å it can approach closer to the graphene plane than the horizontally aligned molecule. E_a values of -6.7 and -6.5 kJ/mol corresponding to the VH and HH configurations, respectively, reflect the fact that hydrogen adsorption at a distance of 3.1 Å is slightly stronger at VH configuration than at HH one.

When one introduces more electronegative nitrogen atoms into graphene, we increase the dipole moment of a certain domains in a graphene sheet and thus increase the induction interaction between a H_2 molecule (an induced dipole) and graphene (a permanent dipole). For the HH configurations, the two hydrogen atoms are in at the same distance above the graphene plane and both contribute to the same interaction. On the contrary, for the VH configurations, only one hydrogen atom makes an input to the interaction. It is very possible that nitrogen atoms, displacing the electron cloud of the hydrogen molecule, stabilize it in the case of the HH configuration as the nitrogen atoms interact simultaneously with two hydrogen atoms

(Table 1). Alternatively, in the case of VH configuration, the nitrogen atoms interact mainly with only one lower hydrogen atom, and slightly destabilize the hydrogen molecule, which leads to smaller adsorption energies. We should also discuss the interesting behavior of H₂ adsorption (VH configuration) on 6N-doped model. Table 1 clearly shows that E_a values of -0.6 (PBE), -5.3 (PBE-D3), -4.8 kJ/mol (B3LYP-D3) are distinctly smaller than E_a for both pristine and other N-doped models. However, it is worth noticing that in this case adsorption occurs on the six-membered nitrogen cycle rather than the six-membered carbon cycle which constitute graphene. It is the main reason of the difference of the above-mentioned results.

All in all, gradual N-doping can promote the hydrogen uptake and thus improve storage abilities of carbon-based hydrogen storage systems. Our predictions can pave the way for the employment of high-capacity H₂ storage materials for practical usage.

4. CONCLUSION

In summary, we have studied hydrogen adsorption onto pristine and N-doped graphene using standard PBE and dispersion-corrected PBE-D3 and B3LYP-D3 DFT methods. 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. All three

methods used predict the considerable increase in E_a values for N-doped graphene, when the HH configuration is considered. PBE-D3 predicts that E_a (6N-doped graphene) $> E_a$ (pristine graphene) on 0.8 kJ/mol (12 percent). In turn, B3LYP-D3 yields the following: E_a (6N-doped graphene) $> E_a$ (pristine graphene) on 1.2 kJ/mol (22 per cent). Such an increase we ascribe to larger dipole moments of N-doped graphene and thus enhanced interaction between permanent dipole (N-doped graphene) and induced dipole (hydrogen). Larger E_a values for HH configurations are explained by larger interaction between the hydrogen molecule aligned horizontally and graphene as both atoms of H₂ are involved into this interaction in such case. An effect of N-doping leading to the increased E_a values should have potential applications for engineering of novel hydrogen storage media.

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Исследование методом функционала плотности адсорбции водорода на графене: эффект допирования азотом

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Используя стандартный функционал GGA PBE, а также функционалы с дисперсионной коррекцией PBE-D3 и B3LYP-D3, мы теоретически изучили адсорбцию молекулярного водорода на чистый, и допированный азотом графен. Мы обнаружили, что взаимодействия Ван-дер-Ваальса вносят важный вклад в энергии адсорбции (E_a) водорода. Пошаговое замещение атомов углерода азотом в графене изменяет значения E_a . Все три метода предсказывают значительное увеличение E_a для допированного азотом графена при изучении горизонтальной конфигурации. Результаты данного исследования показывают, что введение небольшого количества атомов азота может увеличить энергию адсорбции в графене, но приращение, по-видимому, значительно зависит от конфигурации взаимодействующих частиц.

Ключевые слова: Графен, Азот, Водород, DFT, Адсорбция

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