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Stability of hydrogenated graphene: a first-principles study

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In order to explain the disagreement between present theoretical and experimental investigations on the stability of hydrogenated graphene, we have systematically studied hydrogenated graphene with different configurations from the consideration of single-side and double-side adsorption using first-principles calculations. Both binding energy and formation energy are calculated to characterize the stability of the system. It is found that single-side hydrogenation of graphene is always unstable. However, for double-side hydrogenation, some configurations are stable due to the increased carbon-carbon sp^3 hybridization compared to the single-side hydrogenation. Furthermore, it is found that the system is energetically favorable when an equal number of hydrogen atoms are adsorbed on each side of graphene.

1 Introduction

Since the experimental discovery of graphene in 2004,¹ this one-atom-thick material has attracted considerable attention due to its remarkable electronic and structural characteristics.² Researchers have fruitfully investigated graphene to optimize its chemical and physical properties. For example, to open a sizable band gap in graphene for use in electronic and spintronic devices, several methods have been proposed, such as fabricating graphene nanoribbons,³ utilizing bilayer structures,^{4, 5} and chemical modification.^{6, 7} Among them chemical adsorption of non-carbon atoms on graphene is a good way to open a band gap. When such atoms are adsorbed on a graphene surface, they form covalent bonds with the carbon (C) atoms. These C atoms change their hybridization from sp^2 to sp^3 , which dramatically alters the electronic structure of graphene. In recent years, adsorbing hydrogen (H) atoms on graphene surface has received the most

consideration.^{8, 9} On the one hand hydrogenation is the simplest adsorption, which is easily controlled and studied, whereas on the other hand hydrogenation is related to hydrogen storage,¹⁰⁻¹³ which is promising for application of graphene in energy storage. Since the adsorption of H atoms on graphene is so important, a systematic investigation of its stability is highly desirable.

However, present investigations show that there is a disagreement about the stability of hydrogenated graphene. Some theoretical works predict that hydrogenated graphene is very stable.¹⁴⁻¹⁶ The calculated formation energy of hydrogenated graphene is negative and the absolute value is much higher than the heat that the room temperature can provide. For example, a widely studied fully hydrogenated graphene with C:H=1:1, which is also called graphane, has a negative formation energy lower than that of benzene.¹⁴ Its binding energy appears to be rather similar to fluorinated graphene,¹⁵ which has been demonstrated to be stable both in theory¹⁵ and experiment^{6, 17}. Nevertheless, experimental investigations have shown that hydrogenation of graphene is unstable, which rapidly loses H atoms at moderate temperature.¹⁸⁻²¹

In experiments, graphene membranes are often set on a substrate, such as SiO₂.^{18, 19} In this situation, only one side of graphene is accessible for H adsorption, because the diffusion of atomic H along the graphene-SiO₂ interface is negligible.^{19, 22} In contrast, for free-standing graphene membranes, both sides can adsorb. Therefore, to answer the stability question of hydrogenation of graphene, we have to consider single-side as well as double-side adsorption.

In this paper, using first-principles calculations we systematically study the stability of single-side and double-side hydrogenated graphene. Both the binding energy and the formation energy are calculated to characterize the stability of the system. The remainder of the paper is organized as follows. The model and methods are described next; the results and discussion section is presented subsequently. Finally, the main conclusions are given.

2 Model and Methods

The purple rhombus as sketched in Fig. 1 is used as the supercell, which is composed of 8 C atoms marked as 1-8. For hydrogenated graphene, the number of adsorbed H atoms and the adsorbing positions result in a large number of configurations. In this work, we focus on a limited

number of typical configurations.

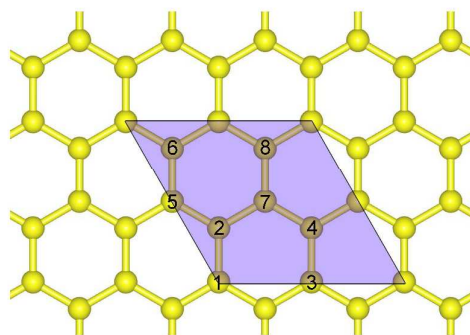


Fig. 1. Top view structure of pristine graphene. The purple rhombus area is chosen as the supercell containing 8 C atoms marked as 1-8. The yellow balls represent C atoms.

Both the binding energy E_B and the formation energy E_F are introduced to characterize the stability of hydrogenated graphene. We adopt the definition of E_B (E_F) as the difference of the hydrogenated graphene with respect to pristine graphene per H atom for the corresponding atomic H (diatomic molecules H_2).^{14, 15} The corresponding expressions are given by:

$$E_B = [E_{HG} - (E_{PG} + nE_H)] / n$$

$$E_F = [E_{HG} - (E_{PG} + nE_{H_2} / 2)] / n$$

where E_{HG} and E_{PG} represent the total energy of hydrogenated graphene and pristine graphene, respectively, E_H and E_{H_2} are the total energy of the free H atom and H_2 molecule, n denotes the number of adsorbed H atoms. The binding energy represents the average strength of each C-H covalent bond, and in this definition, the larger the absolute value, the stronger the C-H covalent bond. The formation energy can be regarded as a measure of the stability against molecular desorption from the graphene surface. In this definition, positive (negative) value means the process is endothermic (exothermic). That is to say, the state of hydrogenated graphene has a higher (lower) energy than the state of pristine graphene and H_2 molecules. If we get a positive (negative) formation energy, the system of hydrogenated graphene is unstable (stable). Therefore, binding energy and formation energy reflect the stability of hydrogenated graphene from different perspectives.

The first-principles calculations are performed using density functional theory (DFT) method


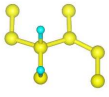
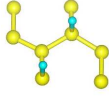

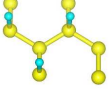
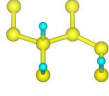
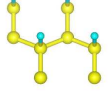
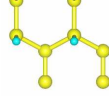
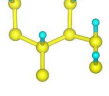
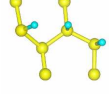
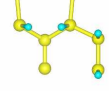

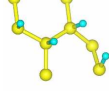
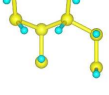
implemented with SIESTA code,²³ which was successfully applied previously to describe adsorption on graphene.²⁴ The exchange-correlation potential is approximated by generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) functional,²⁵ which is usually invoked for electronic structure calculations of C-H systems. The double- ζ plus polarization function (DZP) basis set is used, together with a mesh cutoff of 400 Ry and the Brillouin zone is sampled by $20 \times 20 \times 1$ k points. Since periodic boundary conditions are applied in all three dimensions, a vacuum layer of more than 20 Å is included to minimize the interaction between adjacent layers. All the atoms in the supercell are fully relaxed to fulfill the energy and force convergence of 10^{-5} eV and 10^{-3} eV·Å⁻¹, respectively. As hydrogenation may change the bond length and bond angle of graphene, both the size and the shape of supercell are allowed to relax in our calculations.

3 Results and Discussion

First, we consider the single-side hydrogenation of graphene. Typical configurations of 1-7 H atoms adsorbing on the supercell of 8 C atoms are considered. As the fully single-side hydrogenated graphene (8 H atoms) has a flat structure and the lengths of C-C covalent bonds are much longer than the standard sp^3 C-C bond length of 1.54 Å, this configuration is not considered.²⁶

Table I shows all the configurations we chose for single-side adsorption in our calculations. For 1H or 7H adsorption, there is only one configuration, because every adsorbing site or vacant site is equivalent; for 2H and 6H adsorption, there are three configurations [ortho (o) meta (m) and para (p)] in all; for 4H adsorption, we only chose two typical configurations [chair (c) and boat (b)] that are widely studied;^{14, 27} for 3H or 5H adsorption, we also chose two configurations which are obtained by subtracting or adding one equivalent atom from 4H configurations.

Table I. All the configurations for single-side hydrogenation of graphene in our calculations. All the structures are obtained after relaxation. Each configuration is given a label to distinguish it from others. The yellow balls are C atoms and the cyan ones are H atoms.

n=1	 1H		
n=2	 2H-o	 2H-m	 2H-p
n=3	 3H-c	 3H-b	
n=4	 4H-c	 4H-b	
n=5	 5H-c	 5H-b	
n=6	 6H-o	 6H-m	 6H-p
n=7	 7H		

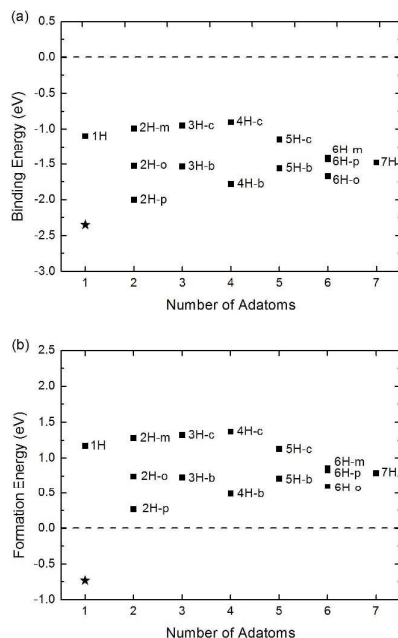


Fig. 2. (a) Binding energy and (b) formation energy of single-side hydrogenation of graphene with different number of adatoms. The corresponding energy of each configuration is marked using its label. The dashed lines represent zero energy. The star points in (a) and (b) denote the binding energy and formation energy of one fluorine atom adsorbing onto graphene under the same condition, respectively.

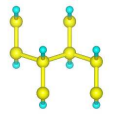
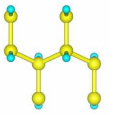


Fig. 2(a) shows the binding energy of single-side hydrogenation of graphene with different number of adatoms. The star point indicates the binding energy of one fluorine (F) atom adsorbing onto graphene as a reference. For the binding energy, it is found that all the values are negative, and have a similar order of magnitude as that of F adsorption. However, as shown in Fig. 2(b), the formation energies of hydrogenated graphene are always positive, which is quite different from the negative value of fluorinated graphene. The positive formation energy indicates that H atoms are easy to dissociate from the surface of graphene and form H_2 molecules. It is also obtained that among all the configurations of single-side hydrogenation, 2H-p is the most stable one (C:H=4:1), instead of the most widely studied 4H-c configuration (C:H=2:1),^{28,29} which happens to be the most unstable one in our calculations.

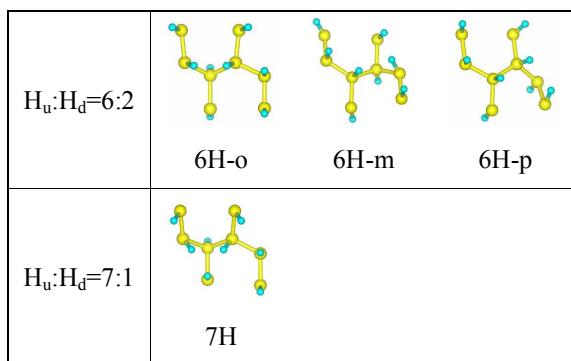
The processes of H atoms dissociating from graphene and forming H_2 molecules have a barrier to overcome (breaking the C-H bond), and if two H atoms form a free H_2 molecule far

away from the graphene surface, the value of the barrier is related to the binding energy. However, if two adsorbed H atoms form a confined H₂ molecule near the graphene surface, the barrier may be much lower than the calculated binding energy. The low barrier of H migration from one C atom to another can be used as an indirect evidence.³⁰ The exothermic process of H₂ formation also indicates the possibility, whereas desorption of F atoms is impossible, because the process is endothermic. Therefore, at moderate temperature, H atoms are easy to dissociate from graphene, when the adsorption only takes place on one side.

Next, we consider the double-side hydrogenation of graphene. On the basis of single-side hydrogenation we investigated, we adsorb H atoms on all the vacant sites at the other side of graphene, forming double-side adsorption. The number of H atoms adsorbed on each side is denoted as H_u and H_d, respectively. The ratio H_u:H_d is used to distinguish between different configurations. For example, for configuration 7H of single-side adsorption, the vacant site is position 2 as marked in Fig. 1, and one H atom is adsorbed on this site at the other side of graphene to form double-side adsorption. All the configurations we calculated for double-side hydrogenation are listed in Table II. Because of the symmetry, some of the configurations are equivalent, such as 1:7 and 7:1. For convenience, the same labels are used as in single-side hydrogenation.

Table II. All the configurations for double-side hydrogenation of graphene in our calculations. Each configuration is given the same label as its counterpart of single-side hydrogenation, as well as the same view angle.

H _u :H _d =4:4		
H _u :H _d =5:3		



Comparing the corresponding configurations with the same labels in Table I and Table II, we find that adding H atoms changes the C backbone a little. The structures of double-side adsorption are similar to their counterparts, so the comparison of corresponding configurations makes sense, which can reveal the changes when more H atoms are adsorbed on the other side of graphene. Of course, double-side adsorption of $H_u:H_d=1:7$ has similar structure to single-side adsorption with 7 H atoms (but not to the 1 H atom).

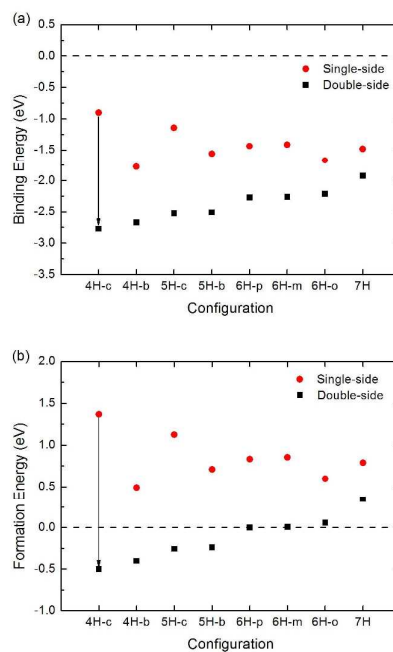


Fig. 3. (a) Binding energy and (b) formation energy of single-side and double-side hydrogenation of graphene with different configurations. The dashed lines represent zero energy.

The binding energy and formation energy of double-side hydrogenation are shown in Fig. 3, including corresponding data of single-side hydrogenation for comparison. It is found that both the

binding energies and the formation energies of the double-side adsorption are lower than those of the single-side adsorption, which means that the system becomes more stable when hydrogen atoms are adsorbed on graphene from both sides. Much more important is the formation energy; as shown in Fig. 3(b), with the increasing ratio of $H_u:H_d$, the formation energies change from negative to a positive value. As indicated above, a negative (positive) formation energy indicates the system of hydrogenated graphene is stable (unstable). Therefore, our calculation shows that 4H and 5H adsorption are stable, but 7H adsorption is still unstable. Comparing to the normal room temperature (~ 25 meV), the calculated formation energies of 4H and 5H adsorption are an order of magnitude higher, so these configurations are still stable. This phenomenon indicates that adding H atoms on the other side strengthens the binding of C and H atoms.

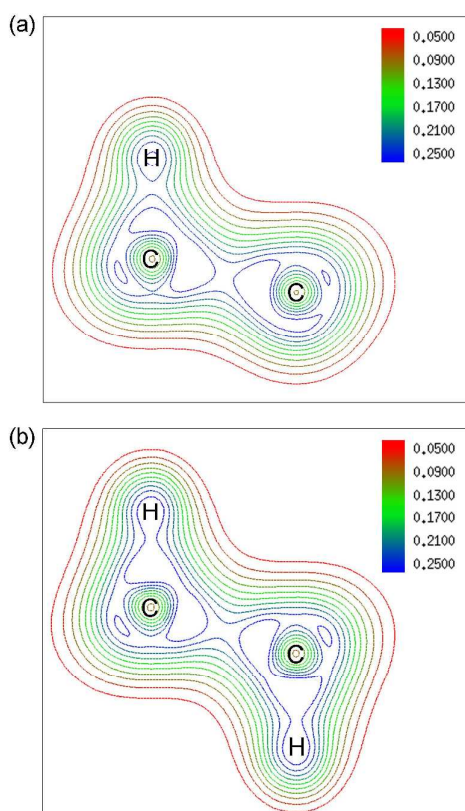


Fig. 4. Contour plots based on electron density of 4H-c for (a) single-side and (b) double-side adsorption. The plane which contains two C atoms (position 1 and 2 marked in Fig. 1) and their adsorbed H atoms is selected. Contours of the valence electron density are plotted from 0.05 a.u. to 0.25 a.u. with colors changing from red to blue.

The configurations of 4H-c for two kinds of adsorption have the most obvious change as shown in Fig. 3, and they also have been given the most consideration among hydrogenated graphene studies, for example, in the works of Wang and Ding *et al.*, where foreign atoms are doped in the two configurations and half-metallic behavior is obtained.^{31,32} Therefore, we select the two configurations for further analysis of their electronic structure. Fig. 4 shows the contour plots based on electron density of the two configurations. For single-side adsorption, more electrons distribute around their own atoms as shown in Fig. 4(a), while for the double-side case, more electrons distribute between C and H atoms and become shared electrons, corresponding to stronger C-H covalent bonds.

Table III. C-C bond lengths and C-C-C bond angles for the different configurations of single-side and double-side hydrogenated graphene. Distances are given in Å and angles in degrees. All the data are averaged over the supercell of Fig. 1.

		4H-c	4H-b	5H-c	5H-b	6H-p	6H-m	6H-o	7H
\bar{d}_{CC}	Single-side	1.505	1.524	1.520	1.536	1.548	1.549	1.550	1.567
	Double-side	1.539	1.548	1.551	1.554	1.562	1.562	1.564	1.573
$\bar{\theta}_{CCC}$	Single-side	115.1	116.5	117.7	117.7	118.6	118.6	118.9	119.2
	Double-side	111.4	111.8	113.3	113.3	114.5	114.9	115.7	116.7

Considering the influence on the geometric structures by adding H atoms on the other side, we provide a comparison of C-C bond lengths and C-C-C bond angles for all the configurations in Table III. As is well known, adsorption on graphene is a process of breaking π bonds and producing additional σ bonds, and transforming C-C sp^2 hybridization to sp^3 . Compared to single-side adsorption, the calculated C-C-C bond angles of double-side are closer to 109.5° , which is the bond angle in diamond and results in enhanced system stability. The configuration of 4H-c of double-side adsorption has the most standard sp^3 hybridization, where both the C-C bond length and the C-C-C bond angle are closest to those in diamond, leading to the most stable hydrogenated graphene. Furthermore, from left to right in Table III, the C-C bond length and C-C-C bond angle of double-side hydrogenation increase gradually, and the same tendency is

found in Fig. 3. In the work of adsorption of H_2 molecules on graphene studied by Zhou *et al.*,¹³ it was found that higher the symmetry, the stronger the binding energy, which is consistent with our findings. In summary, when the ratio of adsorbing H atom of the two sides tends to 1:1, the hybridization of C-C bond is close to sp^3 and the C-H covalent bonds are strengthened. From our calculations, it is found that not all the configurations of double-side hydrogenated graphene are stable. Previous theoretical studies focused on the configurations with the same number of H atoms on each side and obtained stable results. However, in experiment, even though the graphene membranes can be set as free-standing and both sides are accessible to atomic H, the randomness of adsorption and a higher probability of adsorption on upper surface quite likely lead to a metastable state, and even the uncorrelated H frustrated domains would prevent the formation of configurations with $H_u:H_d=4:4$.^{9, 16} Therefore, double-side hydrogenation of graphene in experiments may lead to unstable states.

4 Conclusions

In summary, we have systematically studied the stability of hydrogenated graphene considering different number of adatoms and positions, and provided a reasonable explanation for the disagreement between present theoretical and experimental investigations on the stability of hydrogenated graphene. When adsorption takes place only on one side of graphene, the system is unstable, even though the binding energy of C-H bond has the same order of magnitude as that of C-F bond. However, double-side hydrogenation of graphene is more stable, as the C-C sp^3 hybridization is enhanced, leading to the stronger combination of C and H atoms. Therefore, if we intend to get more stable hydrogenated graphene in experiments, double-side adsorption seems necessary, and a better control of the number of H atoms adsorbing on the two sides of the graphene membrane.

Acknowledgments

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