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Dynamic nano-pulling effect of the boron-functionalized graphene monovacancy for molecule dissociation

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Abstract

We investigate the molecule dissociation and separation roles of graphene membranes with different functionalized monovacancies using first-principles density functional theory calculations. We have found that the boron-functionalized graphene vacancy can effectively dissociate one H₂ molecular into two hydrogen atoms through a novel nano-pulling effect; at the same time it can separate the two hydrogen atoms on different sides of the graphene monolayer, with about 0.21 eV net adsorption energy. The boron-functionalized monovacancy acts like a pair of nanoscissors in this process. The binding energies of the two separated hydrogen atoms with the boron-functionalized monovacancy are 2.82 eV and 1.54 eV, respectively, in the two releasing steps. The boron-functionalized graphene monovacancy as a molecular dissociator can remarkably decrease the potential barrier of H₂ dissociation compared to that of 4.58 eV for free H₂ molecules. This method may open up new avenues for the development of safe hydrogen storage and biomimic photosynthesizers.

(Some figures may appear in colour only in the online journal)

1. Introduction

In the biological field, such as the chloroplast membrane in the photosynthesis process, it is very common that a biofilm can reduce the activation barrier and transport certain reaction products through the channel of a membrane to realize the separation of the products, which can make the reaction easier and prevent a back reaction. However, for artificial systems, it is very challenging to reduce the reaction barrier of molecular bond dissociation and effectively separate the products spatially. As far as we know, little progress has been made on achieving this difficult goal. Herein, we will offer significant progress towards this ambitious goal; we achieve

it through a special molecule-dissociator based on defected graphene.

Taking up the aforementioned bionic challenge, we thought that finding a suitable material with the dual properties of bond dissociating and product separating might be the key to success. Various available materials could meet the needs for molecular bond dissociation and activation; however, the requirement for the stable separation of the dissociated products (atoms or ions) might need an impermeable membrane with a special transportation channel. In addition, temporary stabilization of the separated atoms or ions would be highly desirable to ensure no back reaction. Graphene with a chemically stable two-dimensional structure

can be created with a large area; the perfect graphene membrane is impermeable to molecules as small as He [1, 2]. On perfect graphene, some studies have been done around hydrogen molecule dissociation [3, 4]; but in these products, the dissociated hydrogen atoms are located on the same side of the graphene membrane. Very recently, Wang *et al* [5] demonstrated experimentally that high-energy atom/ion bombardment on free-standing graphene can create nanopores with different sizes and forms, such as the monovacancy, bivacancy and trivacancy. Here, a monovacancy means that one carbon is removed from perfect graphene to create a single vacancy. We attempt to find out whether or not such a graphene monovacancy structure can dissociate a H₂ molecule on one side of the graphene membrane and then transfer one H atom to the other side through the monovacancy, which would work like a biofilm. So far, very little work has been done on understanding molecule dissociation and the separation role of the graphene membrane with different functionalized vacancies. For example, the role of the vacancy in the molecule dissociation process is not understood, even though such a process could be vital to the eventual application of the vacancy for the dissociation and separation of molecules.

The system of a H₂ molecule and a functionalized monovacancy in graphene is unique for molecular bond dissociation research, because the H₂ molecule is the smallest and simplest diatomic molecule and the graphene sheet is the thinnest membrane, one-atom thick [6], which can thus be viewed as the sharpest scissors for cutting molecules. Also, the functionalized monovacancy is the smallest vacancy in graphene. These unique properties of the system can help to reveal the fundamental physical mechanism of the dissociating and separating process of molecules and to eliminate the potential interference coming from a more complex system.

In this work, using a first-principles density functional theory, we carry out a comprehensive study on the dissociation and separation role of different functionalized monovacancies in a graphene membrane on the H₂ molecule dissociation, obtaining the reaction barriers, adsorption binding energies, relaxed atomic and electronic structures of the H₂ molecule and the functionalized monovacancy in the graphene membranes. The results indicate that the functionalized monovacancy in graphene can remarkably decrease the dissociation potential barrier of the H₂ molecule and at the same time separate the H atoms on different sides of the graphene membrane.

2. Computational methodology

The calculations are performed using the VASP code, which is based on Perdew–Wang’s generalized gradient approximation [7] and the projector augmented wave representation [8, 9], including spin polarization and dipole moment corrections [10, 11]. The plane-wave cutoff energy of 600 eV is used for all the elements in the calculations. The first Brillouin zone is sampled using the $8 \times 8 \times 1$ Monkhorst–Pack k -point mesh; Gaussian smearing with a width of $\sigma = 0.05$ eV is used in all calculations. In the energy minimization, we allow all atoms in the slab to fully relax. Energy convergence is reached when the forces on the relaxed atoms are less than 0.02 eV Å⁻¹. The

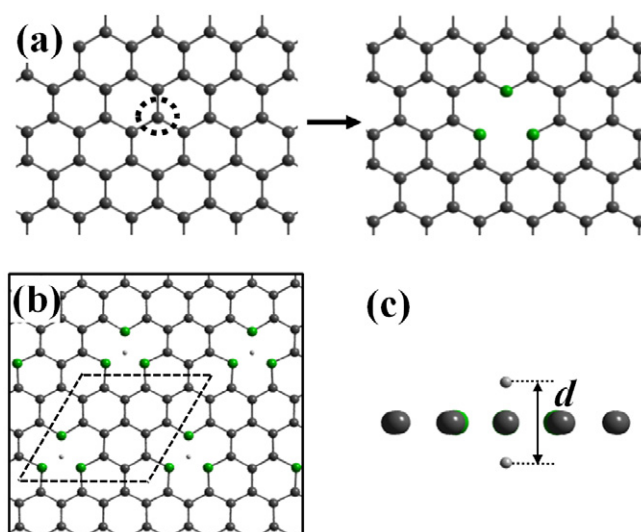


Figure 1. (a) Creation of a functionalized monovacancy in a graphene membrane. The carbon atom in the dashed circle is removed and the three nearest carbon atoms either remain or are replaced by X atoms ($X = \text{B}$ or N) respectively. (b) Top view of the porous graphene membrane with a H₂ molecule in the middle of the vacancy. The dashed lines indicate a unit cell. Carbon, X and hydrogen atoms are denoted with grey, green and white balls. (c) Side view of the same systems in (b). $d = 1.92$ Å, 1.44 Å and 1.14 Å, which are the distances between the upper and lower hydrogen atoms for the CB.mH₂, CC.mH₂ and CN.mH₂ systems, respectively.

supercell dimension along the vertical axis is kept fixed in order to keep the vacuum region stable, while the other two dimensions are not fixed. With these calculation settings, the hexagonal lattice constant of perfect graphene obtained from our calculation is 2.463 Å, which is in good agreement with the experimental value of 2.461 Å and the theoretical value of 2.467 Å [12]. After introducing the monovacancy into the 3×3 parallelogram graphene supercell, the periodic length of the relaxed supercell is 7.372 Å, which is slightly smaller than the triple lattice constant of perfect graphene by 0.017 Å. The transition state (TS) diffusion pathway was determined by way of the ‘climbing image nudged elastic band’ method [13], whereafter spline interpolation was applied to determine the kinetic energy barrier.

In order to explore the potential energy surface and the dynamics of hydrogen arriving to and dissociating at the functionalized monovacancy created in a graphene membrane, the H₂ and functionalized monovacancy graphene system is modelled by having one H₂ molecule with a 3×3 parallelogram graphene supercell with periodic boundary conditions as shown in figure 1(b). The distance between the centre of the adjacent monovacancy is 7.4 Å, which is enough to avoid an interaction between the adjacent H₂ molecules. The graphene membrane is separated by a 16 Å vacuum region in the z direction of the supercell.

3. Results and discussion

Figure 1(a) illustrates the creation of a functionalized monovacancy. Firstly, we removed one carbon atom from

each 3×3 graphene supercell, while other carbon atoms remain at their original sites with the 2.463 Å lattice constant. This graphene membrane with the monovacancy is named the CC membrane. Secondly, the three carbon atoms around the monovacancy were substituted with three boron or nitrogen atoms, which are named the CB membrane and the CN membrane, respectively. When one H_2 molecule sits at the middle of the graphene vacancy of the CB, CC or CN membranes, such systems are named CX_mH_2 ($X = B, C$ and N ; m means the middle of the vacancy), respectively. We use the relaxed structure of the CB_mH_2 system to illustrate the top and side view of the CX_mH_2 systems, as shown in figures 1(b) and (c), respectively. The H_2 with a length 0.75 Å in the initial structure is perpendicular to the porous graphene surface, so that the vacancy in graphene can easily have the chance to break the H_2 bond. This is different from the parallel configuration of the H_2 molecule [14], where the H_2 bond cannot be broken by the graphene vacancy. All three systems, i.e. CB_mH_2 , CC_mH_2 and CN_mH_2 , are fully relaxed. In the relaxed structures, the two hydrogen atoms symmetrically locate on the two sides of the graphene vacancy. The final structures of the three systems are almost same, except that the distances, d , in figure 1(c) are different, which is defined as the distance between the upper and lower hydrogen atoms in the relaxed system. The distances, d , are 1.92 Å, 1.44 Å and 1.14 Å for CB_mH_2 , CC_mH_2 and CN_mH_2 , respectively, while all of them are much larger than that of the free H_2 molecule. It is worth mentioning that the d for CB_mH_2 is the largest one among the three systems, despite B being the smallest atom among the three. The results suggest that the monovacancy of the CB membrane can more effectively break the bond of the H_2 molecule, because the two hydrogen atoms are separated on the two sides of the CB membrane further than that of the CC and CN membranes. Therefore, the CB membrane with a monovacancy is a better candidate for the bond dissociation of the H_2 molecule than the CC and CN membranes.

The bonding charge distributions ($\Delta\rho(\vec{r})$), which can help one to visualize the bonding characteristics and the electron transfer between the H and the CX membranes, is defined as $\Delta\rho(\vec{r}) = \rho(CX_mH_2) - \rho(CX) - \rho(H_2)$. Where $\rho(CX_mH_2)$ is the charge density of the CX_mH_2 systems, $\rho(CX)$ and $\rho(H_2)$ are the independent CX membranes and the two H atoms are separately calculated using the same atomic coordinates and supercell as those in the corresponding CX_mH_2 system. The results for the three systems are shown in figure 2. Figure 2(a) shows that the bonding electron distribution locates very close to the individual hydrogen atoms, in contrast to that located between the two hydrogen atoms for the free H_2 , which indicates that the bond between the two hydrogen atoms has already been broken. Due to the electron transfer, the bonding electron distribution between the hydrogen atoms and the three B atoms indicates that the electron pairing and chemically bonding interaction between the hydrogen atoms and the boron-functionalized monovacancy in graphene is the weakest among three CX_mH_2 systems. In this CB_mH_2 system, each boron atom has three valence electrons ($2s^2 2p^1$). Its two 2s electrons form covalent B–C bonds with the valence electrons

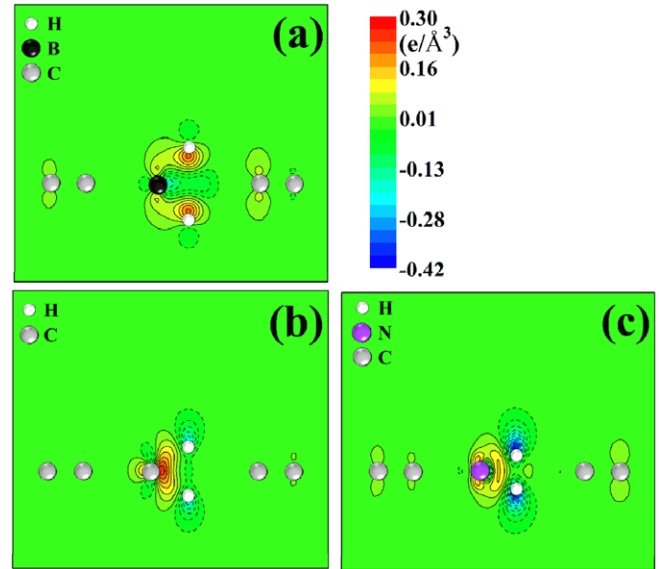


Figure 2. Bonding charge distributions (see text for the definition) in a vertical plane containing the longer diagonal of the 3×3 supercell with H atoms located at the monovacancy of the graphene membrane. A positive value (solid contour line) indicates an increase in electron density and a negative value (dashed contour line) means an electron density loss with respect to the superposition of the atomic electron density. (a), (b) and (c) are for the CB_mH_2 , CC_mH_2 and CN_mH_2 systems, respectively.

of the two adjacent carbon atoms; the remaining one 2p electron participates directly with the aromatic π -bond system of the defected graphene. Even though it might appear that the three adjacent boron atoms do not have any free electron to couple with the hydrogen atom of H_2 , the freely movable adjacent π -electrons can interact partially with the dissociated hydrogen atom to form a weak hyperconjugation coupling. As regards to that, the upper H atom is very close to the out-edge of the π -electron cloud, as shown in figure 3; we believe that there is a strong nanoscale-pulling effect from an electron vortex around the upper and lower sides of the graphene boron-functionalized monovacancy to weaken the H–H bond. The direction of the orbital angular momentum of the upper delocalized π -electrons has a 50% chance to be up or down, respectively. Due to the coupling between the π -electrons and the electron of the H atom, the orbital angular momentum direction of the electron in the H atom is always the same as that of the π -electrons. Then the delocalized π -electrons can pull the H atom away from the centre of the defect by magnetic interaction. The orbital angular momentum of the lower π -electrons around the defect is always in the opposite direction to that of the upper π -electrons, in order to keep a delocalized balance state. The electron vortex phenomenon was first discovered by Uchida and Tonomura [15]; it has been used by Verbeeck *et al* for analysing and manipulating nanomaterials [16]. In contrast to the electron vortex that can travel a macroscopic distance [15, 16], in our case, the electronic vortex is localized within a nanoscale range and is formed from the extremely fast moving π -electron delocalization around the boron-functionalized monovacancy. For the perfect graphene monolayer, their fast moving π -electrons on both

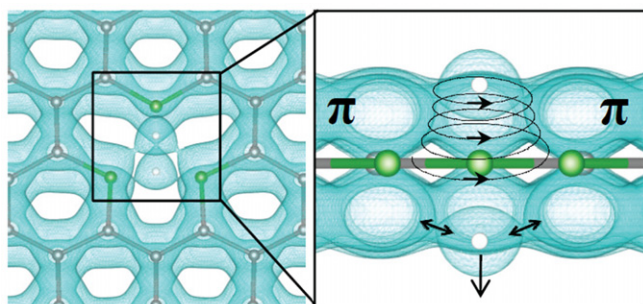


Figure 3. The charge density isosurface of the π -electrons with an energy near the Fermi level in the CB_mH₂ system. The left pattern is a top view with an angle. The right one is a side view to illustrate the electron vortex (curve) around the upper H atom. The downward arrow and the double-headed arrow indicate the nano-pulling effect of the electron vortex and the interaction between the electron of the lower H atom and the π -electrons of the B atoms. Colour code: C, grey; B, green; H, white.

sides of the flat nucleus-lattice are controlled evenly by their nucleuses. In contrast, for the defected graphene monolayer, the static constraint between their delocalized π -electrons and their nucleuses is uneven. Then the delocalized π -electrons on each side of the defected graphene membrane tend to move fast in opposite directions and go outwards from the vacancy. Generally, defects with dangling bonds will attract molecules to approach the defects, but this nanoscale-pulling effect from adjacent π -electrons around the graphene boron-functionalized monovacancy pull the H atom away from the defect. This nano-pulling effect could be used in nanofabrication or bionic material manufacture.

Due to the strong interaction between the outward excursion π -electron and the hydrogen atoms, which is called nano-pulling, the two hydrogen atoms can be pulled away from each other. When hydrogen atoms reach the up- or down-edge of the π -electron cloud, the nano-pulling effect and the hydrogen atoms weaken the hyperconjugation effect and achieve a balanced state. Therefore, the boron-functionalized monovacancy in the CB graphene membrane maybe an ideal H₂ molecule-dissociator, which can separate the two H atoms on different sides of the CB graphene membrane at the same time, for future utilization in areas such as activated hydrogen storage for biomimic chemical synthesis. The activated hydrogen can be released directly through competitive chemical reactions or charging-assisted destabilization [17].

In contrast to what happened in the CB_mH₂ system, figures 2(b) and (c) show that the bonding electron distribution indicates strong covalence bond interactions between the hydrogen and carbon, or the hydrogen and nitrogen atoms, respectively. In particular, the covalence bonds between the hydrogen and nitrogen atoms are even stronger. The reason for this phenomenon is that the carbon and nitrogen atoms adjacent to the monovacancy site have more spare valence electrons to interact directly with hydrogen atoms that are different to those of boron atoms. In the CC_mH₂ system, each of its three adjacent carbon atoms has a spare sp² hybridized electron. This makes the carbon radicals highly reactive and they can easily couple with the hydrogen atoms of H₂

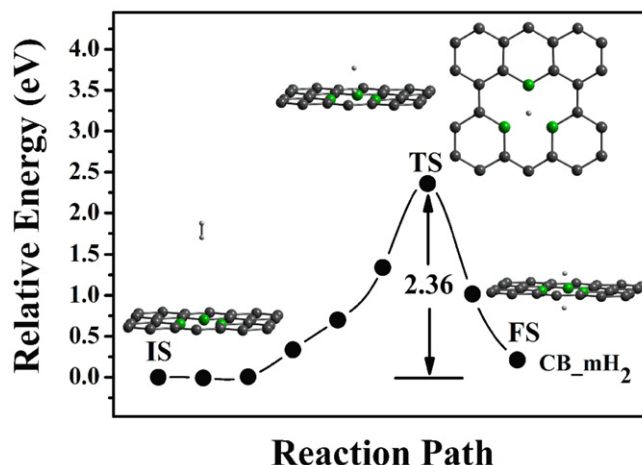


Figure 4. Energy barrier for the transition of a H₂ molecule from the free state to the trapped state at the centre of a boron-functionalized monovacancy in graphene. The insets are the corresponding configurations of IS, TS and FS. For the TS, both the top and side views are given.

through relatively stronger dynamic covalent bonding. Each hydrogen atom will couple dynamically with 1 and 1/2 adjacent radicals during this type of special bonding. As a result, the H–H bond of the CC_mH₂ system is broken from the combined effect of the dynamic atom-radical coupling and the aforementioned ‘electronic vortex’ nano-pulling effect. This makes the distance of its two partially dissociated hydrogen atoms (1.44 Å) smaller than the CB_mH₂ system (1.92 Å). In the CN_mH₂ system, each of its three adjacent nitrogen atoms has one lone-pair electrons, which can couple well with the hydrogen atoms of H₂ through strong dynamic covalent bonding. Each hydrogen atom will dynamically couple with three adjacent electrons during this type of special bonding. As a result, the H–H bond of the CC_mH₂ system is also partially broken from the combined effect of the dynamic coupling of an atom with lone-pair electrons and the aforementioned ‘electronic vortex’ nano-pulling effect. However, the distance between its two dissociated hydrogen atoms is the shortest one (1.14 Å) among the three systems. Due to such strong dynamic coupling between hydrogen atoms and multiple radicals or lone-pair electrons within the monovacancy in the CC and CN membranes, the departure of hydrogen atoms from the CC and CN membranes becomes much more difficult than that from the CB membrane. As a result, the CC and CN membranes are not suitable as the molecule-dissociator of H₂ from this aspect.

The next question is how the free H₂ molecule transfers to the middle of the monovacancy in the graphene membrane. Here, focusing on the boron-functionalized monovacancy in the graphene membrane, we explored the energy barrier for the transition of the H₂ molecule from the free state to the trapped state, as shown in figure 4. We examined several distances between the H₂ molecule and the CB membrane, when the H₂ molecule is on one side of the membrane and have found that when the distance between the lower hydrogen atom of the H₂ molecule and the CB membrane is 5.0 Å or greater, the relaxed H₂ bond is 0.749 Å, which is equal to that of free H₂, indicating no interaction between the H₂ molecule and

the CB membrane. Thus we use the configuration that H_2 is 5.0 Å higher than the CB membrane as the initial state (IS) to simulate a free H_2 molecule and a CB membrane. The configuration of the fully relaxed CB_mH₂ system (trapped state) is defined as the final state (FS). The TS and the energy barrier for H_2 from IS to FS have been calculated using the ‘climbing image nudged elastic band’ method. The energy barrier was computed to be 2.36 eV for CB_mH₂, which is much lower than the bond dissociation potential barrier 4.58 eV of a free H_2 molecule [18]. When the H_2 molecule is moving from the initial location in the IS to the location in the TS and getting closer to graphene monovacancy, the bond length of H_2 gradually increased from 0.749 Å (in the IS) to 1.249 Å (in the TS). The interaction between H atoms becomes weaker and weaker, but it is still stronger than that between the H atom and the π -electrons. When the H_2 molecule passes the TS and approaches the FS, the interaction between H atoms is further weakened. The outward delocalized π -electrons pull the two H atoms away from each other; the final distance between the H atoms is 1.92 Å (in the FS). In other words, the interaction between the two hydrogen atoms became weaker than that of the free H_2 molecule when the H_2 molecule was approaching the centre of the boron-functionalized monovacancy. This is again due to the combined effect of the nano-pulling of the bidirectional electron vortices and the hyperconjugation between the activated hydrogen atom and the π -electrons of the boron-functionalized monovacancy in graphene. According to our electron density analysis for a TS, the two H atoms are not visibly bonded to B atoms in a TS. Only in the FS do the two H atoms bind with the three B atoms to some degree. Thus, it requires four steps for the H_2 molecule bond dissociation process to occur with the boron-functionalized monovacancy as the dissociator. The first step is that a free H_2 molecule transfers to the state in the TS with a longer bond length than that of the free H_2 by overcoming the necessary potential barrier of 2.36 eV. The second step is that the distance between two H atoms in the FS becomes longer than that in the TS while releasing the energy of 2.15 eV. Therefore, these two steps need in total 0.21 eV net energy for the free H_2 to arrive at the location in the FS, which is the temporarily stabilized active hydrogen state. The temporarily stabilized active hydrogen may make its reaction with other chemical components easily due to its more reactive nature.

The third step is the release of the first H atom in the FS. This step can be utilized for chemical synthesis or other applications from one side of the graphene membrane. The fourth step is the release of the second H atom. The binding energies for the first and second H atoms in the states of the third and fourth steps were calculated as shown in figure 5, respectively, by comparing with that of the free H_2 molecule. The third step is realized by dissociating the upper H atom (as the first H atom) in the CB_mH₂ structure (FS) from the membrane by overcoming a binding energy barrier of 2.82 eV, which is presumably due to both the H-atom- π -electrons hyperconjugation and a long range electron spin coupling of the two loosely bound H-atoms. The two H atoms are located symmetrically on each side of the CB membrane, so there is no difference between selecting the upper and lower H

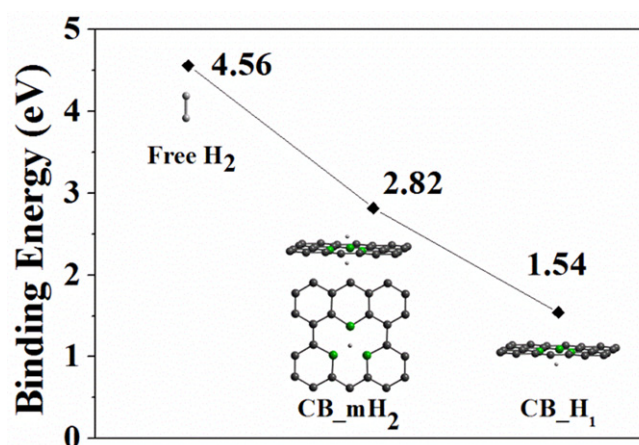


Figure 5. Binding energies for free H_2 , the first (upper) and second (lower) H atoms of the CB_mH₂. CB_H₁ means the CB membrane with only the lower H atom. The line between the data points is to guide the eyes.

atoms as the first H atom to be dissociated. Then, for the fourth step, the lower H atom overcomes a binding energy of 1.54 eV to become a free H atom on the other side of the membrane, which is lower than that of the first dissociated H atom by 1.28 eV. This phenomenon clearly indicates that even though the two dissociated hydrogen atoms are apart at the distance (1.92 Å) of more than twice that of a free H_2 molecule, they still interact with each other through three B atoms, as indicated in figure 2(a). Because of the absence of the long range interaction from the upper H atom, the lower H atom only needs to overcome the constraint from the H-hyperconjugation between the H atom and π -electrons. Then it is easier for the second H atom to be released from the membrane than the first H atom. We also calculated the situation where the two H atoms are released at the same time; we found that the two H atoms would need to overcome a binding energy barrier 4.36 eV, which is higher than the binding energy barrier for each of the H atoms being released one by one. Therefore, the phenomenon of H atoms being released from the boron-functionalized monovacancy one by one should be a high probability event. Each of the above binding energies (2.82 and 1.54 eV) is significantly lower than that of free H_2 (4.58 eV). More importantly, this new discovery of the nano-pulling molecule-dissociator could function as a special enzyme, which can effectively convert one high activation barrier of an impossible reaction to several easily passable lower reaction barriers. This provides a great prospect for future biomimic chemical synthesis.

Based on the calculated energy barriers, we can estimate the bond dissociation effect of the boron-functionalized monovacancy in graphene (CB) for the H_2 molecule relative to free H_2 quantitatively according to the Arrhenius equation [19]:

$$S_{CB/free} = \frac{r_{CB}}{r_{free}} = \frac{A_{CB} e^{-E_{CB}/RT}}{A_{free} e^{-E_{free}/RT}}$$

where r is the bond dissociation rate, A is the interaction (bond dissociation) prefactor and E is the bond dissociation barrier. The binding energy 2.82 eV of the first H atom is

higher than the energy barrier 2.36 eV for the transition of the H₂ molecule from the IS to the FS. Then the binding energy 2.82 eV is selected as the highest energy barrier for the H₂ bond dissociation with the boron-functionalized monovacancy to compare with that of free H₂. Furthermore, assuming that the prefactors of two conditions are identical ($A_{CB}/A_{free} = 1$) and the room temperature T is 300 K, we then obtain a bond dissociation effect of about 10^{30} , which is remarkably high. In contrast to the situation where the two dissociated H atoms locate on the same side of the graphene membrane and have bonds with C atoms [3, 4], now the two dissociated H atoms locate on the different sides of the CB membrane and have little interaction with the CB membrane, which means that the two H atoms can easily be freed.

4. Conclusions

In summary, we have studied the dissociation and separation effect of three types of functionalized monovacancies in graphene for H₂ molecule bond dissociation, using a first-principles density functional theory. We have discovered a novel nano-pulling effect of the boron-functionalized monovacancy in graphene. By the nano-pulling effect, the boron-functionalized monovacancy can split a H₂ molecule into two H atoms further apart from each other than that of the carbon or the nitrogen-functionalized monovacancy in graphene, because there are no free valence electrons in the boron atom to form strong bonding. The different valence electrons of three elements B, C and N mainly contribute to the different phenomenon of the three functionalized monovacancies. Both the energy barriers for the transition of the H₂ molecule from the IS to the FS and of the release of the first H atom from the boron-functionalized monovacancy, are remarkably lower than that of free H₂ molecule bond dissociation. More importantly, the system of the boron-functionalized monovacancy in graphene separates the two partially dissociated H atoms on the different sides of the graphene membrane to prevent the back reaction. The boron-functionalized monovacancy acts just like a pair of nanoscissors to cut the H₂ molecule into two temporarily stabilized active H atoms in CB.mH₂. Therefore, the boron-functionalized monovacancy on graphene can be regarded as an ideal candidate for a molecular dissociator of the hydrogen molecule. This method might be useful for the bond

dissociation of other small molecules and separation of the resultants, through a proper functionalized nanovacancy in graphene, such as splitting H₂O, N₂ and NH₃, etc. It could be used to activate N₂ and H₂ mildly at the same time for biomimic synthesis of NH₃ by lowering activation barriers. In addition, this result may open up new avenues for the development of active hydrogen storage, artificial photosynthesizers, biomimic materials preparation, etc.

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