Hydrogen adsorption on boron doped graphene: an ab initio study

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Abstract
(i) The electronic and structural properties of boron doped graphene sheets, and (ii) the chemisorption processes of hydrogen adatoms on the boron doped graphene sheets have been examined by ab initio total energy calculations. In (i) we find that the structural deformations are very localized around the boron substitutional sites, and in accordance with previous studies (Endo et al 2001 J. Appl. Phys. 90 5670) there is an increase of the electronic density of states near the Fermi level. Our simulated scanning tunneling microscope (STM) images, for occupied states, indicate the formation of bright (triangular) spots lying on the substitutional boron (center) and nearest-neighbor carbon (edge) sites. Those STM images are attributed to the increase of the density of states within an energy interval of 0.5 eV below the Fermi level. For a boron concentration of ∼2.4%, we find that two boron atoms lying on the opposite sites of the same hexagonal ring (B1–B2 configuration) represents the energetically most stable configuration, which is in contrast with previous theoretical findings. Having determined the energetically most stable configuration for substitutional boron atoms on graphene sheets, we next considered the hydrogen adsorption process as a function of the boron concentration, (ii). Our calculated binding energies indicate that the C–H bonds are strengthened near boron substitutional sites. Indeed, the binding energy of hydrogen adatoms forming a dimer-like structure on the boron doped B1–B2 graphene sheet is higher than the binding energy of an isolated H₂ molecule. Since the formation of the H dimer-like structure may represent the initial stage of the hydrogen clustering process on graphene sheets, we can infer that the formation of H clusters is quite likely not only on clean graphene sheets, which is in consonance with previous studies (Hornekær et al 2006 Phys. Rev. Lett. 97 186102), but also on B1–B2 boron doped graphene sheets. However, for a low concentration of boron atoms, the formation of H dimer structures is not expected to occur near a single substitutional boron site. That is, the formation (or not) of H clusters on graphene sheets can be tuned by the concentration of substitutional boron atoms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Two-dimensional crystals of sp² bonded carbon atoms, called graphene, exhibit quite different electronic and structural properties compared with their counterparts, namely graphite (graphene sheets stacked in ABABAB... arrangement), and carbon nanotubes (rolled up graphene sheets forming nanometer-wide cylinders). Indeed, in a recent experimental study, Novoselov et al [1] observed massless two-dimensional (2D) Dirac fermions in free-standing graphene sheets with high crystal quality. In this case, the electron scattering processes are suppressed, and thus, the charge carriers can propagate freely on the graphene surface. Meanwhile, very recently, Meyer et al observed microscopic corrugations on
a single layer suspended graphene sheet, due to the carbon atoms being displaced out of the graphene plane. Such an experimental finding explains the thermodynamic stability of those isolated ‘two-dimensional’ systems; however, ‘further experimental and theoretical studies are needed to clarify the detailed mechanism of the corrugations in graphene’ [2].

On graphene sheets, the sp² orbitals, forming σ bonding states parallel to the graphene surface, connect the carbon atoms arranged in a hexagonal lattice, whereas the p orbitals, perpendicular to the graphene sheet, give rise to delocalized π bonding and π* anti-bonding states. Most of the electronic properties and the chemical reactivity of graphene sheets are governed by those π and π* orbitals: for instance, the already mentioned massless 2D Dirac fermions, and the recently observed control of the electronic properties in thin films composed of bilayer graphene sheets [3]. Focusing on the chemical properties, graphene has been considered as a candidate for hydrogen storage media [4, 5]. Scanning tunneling microscope (STM) images of hydrogen adatoms on graphene surfaces indicate a local electronic charge enhancement and long range electronic perturbation on the graphene sheet, giving rise to a local (√3 × √3)R30° surface periodicity [6]. Hydrogen on graphene surfaces has been the subject of intense studies, not only addressing the realization of fuel cells based upon hydrogen storage, but also the formation of H₂ molecules in the interstellar medium (which is an important problem in astrophysics).

The energetic stability and the equilibrium geometry of hydrogen adatoms on graphene surfaces were investigated in detail by Sha and Jackson [7] and Duplock et al [8]. They found binding energies of 0.67 and 0.76 eV/H atom, respectively, for a single hydrogen adatom chemisorbed on the graphene sheet. Having characterized the energetic and structural properties of hydrogen adatoms on graphene, further experimental/theoretical studies examined the formation of H₂ molecules through H–H reaction processes on the graphene surface: for instance, the Eley–Rideal reaction involving free hydrogen atoms (gas phase) and hydrogen adatoms chemisorbed on the graphene surface [7, 9]. On the other hand, the H–H recombination through hydrogen diffusion, on the graphene surface, represents another reaction path to obtain H₂ molecules from the chemisorbed hydrogen adatoms [10–12]. Based upon those H–H reaction processes, recent experimental studies, supported by ab initio calculations, examined the formation of hydrogen clusters on graphene surfaces [13]. Their findings suggest the formation of H₄ dimer-like structures as an initial stage of the observed hydrogen clusters chemisorbed on the graphene surface. The calculated binding energy of hydrogen adatoms forming a H₄ dimer structure is higher compared with the binding energy of two isolated H monomers.

The binding energy of hydrogen adatoms chemisorbed on graphene sheets, as well as the formation of H clusters, can be tuned by suitable doping processes. For instance, the presence of substitutional boron atoms on graphene improves the hydrogen adsorption on the carbon atoms neighboring the boron substitutional sites [14, 15]. However, those calculated hydrogen binding energy results, as a function of substitutional boron concentration, are quite contradictory. Based upon Raman spectroscopy measurements, Endo et al [16] characterized the equilibrium geometry of substitutional boron atoms on graphite. For a boron concentration of ~2.7%, they found a homogeneous distribution of substitutional boron atoms. Meanwhile, for higher concentration of substitutional boron atoms, about 17%, a detailed experimental study, performed by Hach et al [17], indicates the formation of C₆B configuration. In the C₆B structure, the substitutional boron atoms occupy the opposite sites of a carbon hexagonal ring. Further experimental/theoretical studies have been done aiming to improve our knowledge related to boron doped graphite systems [18–20].

In the present paper we report an ab initio total energy investigation of boron doped graphene sheets, and the chemisorption processes of hydrogen adatoms as a function of boron concentration. Our calculated STM images indicate the formation of bright spots on the boron substitutional sites, which is in agreement with the experimentally obtained STM images [18]. For higher concentration of substitutional boron atoms, around 2.4%, we find that two boron atoms lying on the opposite sites of the same hexagonal ring represents the energetically most stable structure. This geometry represents the building block of the C₆B structure [17]. The formation of a H dimer-like structure on graphene has been confirmed, as well as the increase of hydrogen binding energy near the boron substitutional sites. However, in contrast with the previous studies, here we have considered the most likely configuration for the substitutional boron atoms on the graphene surface. We find that the formation of the H dimer structure, neighboring a single boron substitutional site, is energetically less favorable compared with two isolated H monomers. Meanwhile, the formation of the H dimer structure is expected for higher concentration of boron atoms, i.e., two substitutional boron atoms occupying the opposite sites of a hexagonal carbon ring, B1–B2. In this case, the binding energy of H adatoms is higher compared with the binding energy of an isolated H₂ molecule.

2. Method of calculations

Our calculations were performed in the framework of the spin polarized density functional theory (DFT) [21], within the generalized gradient approximation due to Perdew, Burke, and Ernzerhof [22]. The electron–ion interaction was treated by using norm-conserving, ab initio, fully separable pseudopotentials [23]. The Kohn–Sham wave functions were expanded in a combination of pseudatomic numerical orbitals [24]. A double zeta basis set including polarization functions (DZP) was employed to describe the valence electrons [25]. The self-consistent total charge density was obtained by using the SIESTA code [26]. The graphene sheets were described within the supercell approach, by a single layer of graphene with 84 atoms, separated by 15 Å from their image. A mesh cutoff of 170 Ryd was used for the reciprocal-space expansion of the total charge density, and the Brillouin zone was sampled by using up to 15 special k points. We have verified the convergence of our results with respect to the number and choice of the special k points. All atoms of
graphene sheets were fully relaxed within a force convergence criterion of 20 meV Å\(^{-1}\).

### 3. Results and comments

#### 3.1. Boron

Initially we examined the equilibrium geometry and the electronic properties of a boron doped graphene sheet. For a single substitutional boron atom, B1 in figure 1(a), we obtained a B–C bond length \((d_{B-C})\) of 1.50 Å, while the nearest-neighbor C–C bonds are slightly compressed (by \(\sim 0.01\) Å) compared with the undoped system. The structural deformations of graphene are very localized around the substitutional boron site. Experimental STM measurements indicate \(d_{B-C}\) of 1.59 Å [19], which is in agreement with our calculated results.

The electronic properties of boron doped graphene are summarized in figure 2. Figures 2(a) and (d) present the electronic density of states (DOS) of pristine (dashed lines) and boron doped (solid lines) graphene sheets. We find that the metallic character of graphene has been kept upon the presence of substitutional boron atoms; however, the electronic density of states near the valence band maximum increases compared with the pristine system (shaded regions in figures 2(a) and (d)). Figure 2(b) presents the localization of the electronic states within an energy interval of 0.5 eV below the Fermi level for the structural models B1 (b) and B1–B2 (e), and the electronic distribution of the highest occupied states \((E_F - 0.5\) eV\)) along the C–B bonds for the substitutional boron configurations B1 (c) and B1–B2 (f). Unit: cm/bohr\(^3\).

| Configuration | \(\Delta E\) (eV/B atom) | \(d(B–B)\) in Å |
|---------------|--------------------------|------------------|
| B1–B2         | 0.00                     | 2.87             |
| B1–B3         | 0.17                     | 2.53             |
| B1–B4         | 0.02                     | 7.49             |
| B1–B5         | 0.01                     | 8.64             |
| B1–B6         | 0.08                     | 4.33             |
| B1–B7         | 0.12                     | 3.86             |
| B1–B8         | 0.66                     | 1.58             |

Within our supercell approach, a single substitutional boron atom corresponds to a boron concentration of \(\sim 1.2\%\). Two boron atoms per supercell corresponds to a boron concentration of \(\sim 2.4\%\). In this case, we have considered several plausible Bi–B configurations, indicated in figure 1(b), for boron atoms occupying substitutional sites on the graphene sheet. Our total energy results, summarized in table 1, reveal the formation of preferential domains, or preferential configurations for substitutional boron atoms on graphene, namely, two boron atoms occupying the opposite sites of the same hexagonal ring, B1–B2 in figure 1(b), represents the energetically most stable configuration, whereas B1–B8 is the energetically least favorable structure. The former geometry, B1–B2, was proposed by Hach et al for ‘boron rich carbon structures’ [17]. The structural models B1–B4 and B1–B5 are slightly less favorable compared with B1–B2. Since in B1–B4 and B1–B5 the boron atoms are far from each other, \(d(B–B)\) = 7.5 and 8.6 Å, respectively. We
can infer that at low concentration regime, the substitutional boron atoms may spread out the graphene sheet, whereas under boron rich condition the formation of B1–B2 becomes dominant, giving rise to C6B like structures [17]. Indeed, B1–B2 represents the building block of the proposed C6B structure.

Figure 2(d) (solid line) presents our calculated DOS for the structural model B1–B2. We observe that the electronic density of states increases near the valence band maximum (shaded region) compared with the undoped system (dashed line). The occupied electronic states within $E_F - 0.5$ eV are mainly localized on the substitutional boron and neighboring the carbon atoms, giving rise to the two bright protrusions shown in figure 2(e). Figure 2(f) indicates that such an STM image originates from the $\pi$ orbitals along the B–C bonds.

It is worth pointing out that the unlikely B1–B3 and B1–B7 [15] and B1–B8 [14] arrangements ($\Delta E = 0.17, 0.12, \text{and } 0.66 \text{ eV/B atom}$, respectively) were considered as substrates for hydrogen adsorption on boron doped graphene. Thus, we believe that further studies are necessary, addressing the role played by substitutional boron impurities for hydrogen adsorption processes, now considering the energetically most stable configuration for the substitutional boron atoms, B1–B2.

3.2. Hydrogen

Having established the energetically most probable structures for substitutional boron atoms on graphene, namely structural models B1 (figure 1(a)) and B1–B2 (figure 1(b)), in this section we examine the hydrogen adsorption processes on clean and boron doped graphene sheets.

First, using the 84-atom unit cell (figure 1(a)), we calculate the binding energy of hydrogen adatoms on clean graphene. For a single hydrogen adatom we find a binding energy ($E_{b}^\text{H}$) of 0.98 eV/H atom. The C–H equilibrium bond length is 1.14 Å, which indicates the formation of a C–H covalent bond, while the carbon atom underneath the hydrogen adatom moves upward by 0.5 Å from the flat graphene layer. For an isolated hydrogen molecule, we calculate a binding energy of 4.34 eV/H$_2$ molecule (2.17 eV/H atom). Thus, with respect to the H$_2$ molecule, hydrogen adsorption on graphene is an endothermic process by 1.19 eV/H atom. Our total energy and equilibrium geometry results are in agreement with previous ab initio studies of hydrogen adsorption on the graphene sheet, for instance, $E_{b}^\text{H}$ of 0.7–0.8 eV/H atom and C–H bond length of 1.13 Å [7, 8, 13].

In a very recent study, Hornekær et al observed that the presence of a hydrogen adatom on a graphene surface gives rise to preferential adsorption sites (near the already adsorbed hydrogen adatom) for the subsequent hydrogen sticking process [13]. Indeed we find that a hydrogen adatom lying on ha increases the binding energy of the next hydrogen adatom ($E_{b}^\text{HH}$) on hd or he (cf figure 1(a)). We calculate $E_{b}^\text{HH} = 2.03 \text{ eV/H atom}$ for both hydrogen configurations, ha/hd and ha/he, while Hornekær et al obtained binding energies of 1.9 and 2.1 eV/H atom, respectively. Those results indicate that the formation of ha/hd or ha/he hydrogen dimer-like structures are energetically more favorable compared with two isolated ha monomers, that is, ha + ha $\rightarrow$ ha/hd, ha/he are exothermic processes. Our findings are in accordance with previous studies related to the formation of hydrogen clusters on graphene surfaces. In addition, our calculated binding energies $E_{b}^\text{HH}$ (for ha/hd and ha/he) are comparable with the binding energy of an isolated H$_2$ molecule (2.17 eV/H atom), suggesting that the presence of a single hydrogen adatom (ha) on the graphene sheet somewhat promotes the H$_2$ dissociation near ha.

The binding energy of a single hydrogen adatom, $E_{b}^\text{H}$, increases upon the presence of substitutional boron atoms on the graphene surface. Our results of binding energies are summarized in table 2. For the ha/B1 configuration, depicted in figure 3(a), we find $E_{b}^\text{H} = 1.89 \text{ eV/H atom}$, whereas on the clean graphene surface we have $E_{b}^\text{H} = 0.98 \text{ eV/H atom}$. So, we can infer that the presence of a substitutional boron atom, in the vicinity of the hydrogen adsorption site, strengthened the C–H bond by 0.91 eV. Meanwhile, the hydrogen adsorption on top of the substitutional boron atom, hb/B1, is energetically less favorable by 0.38 eV/H atom compared with ha/B1. At the equilibrium geometry, the C–H bond length is 1.15 Å and the C atom (underneath the hydrogen adatom) moves upward by 0.4 Å. The formation of a C–H covalent bond is depicted in figure 3(b). Figures 3(e) and 3(f) present the occupied electronic states along the C–H and B–C bonds, respectively, within $E_F - 0.5$ eV. Those electronic states are composed of $\pi$ orbitals of carbon and (substitutional) boron atoms on the graphene sheet, and sp$_{\sigma}$ hybridization along the C–H bond (figure 3(e)). Comparing the electronic densities depicted in figures 2(c) and 3(f), B1 and ha/B1 structures, respectively, we can infer that the hydrogen adsorption on ha reduces the electronic density of occupied $\pi$ orbitals along the B–C bonds.

Keeping the B1 configuration adsorbed by a hydrogen adatom (ha/B1), the subsequent hydrogen adsorption has been examined by considering a number of plausible configuration for two hydrogen adatoms on a B1 graphene sheet. Our binding energy results for the hydrogen adatom on the ha/B1 graphene sheet, $E_{b}^\text{HH}$, indicate that ha/hc represents the energetically least stable configuration. We find $E_{b}^\text{HH} = 1.00 \text{ eV/H atom}$, nearly the same hydrogen binding energy.

| Model | ha | hb | ha/hb | ha/hb′ | ha/hc | ha/hd | ha/he |
|-------|----|----|-------|--------|-------|-------|-------|
| Clean | 0.98 | — | — | — | 2.03 | 2.03 |
| B1    | 1.89 | 1.51 | 1.36 | 1.51 | 1.00 | 1.67 | 1.25 |
| B1–B2 | 2.13 | — | — | 1.73 | — | 2.37 | 1.64 |

Table 2. Binding energies ($E_{b}^\text{H}$) of hydrogen adatoms on clean and boron doped graphene surfaces in eV/H atom.
as on clean graphene, $E_{hh}^b = 0.98$ eV/H atom. This result is somewhat expected, since $hc$ is far from the substitutional boron site, B1. Figure 3(c) presents the energetically most stable configuration, $ha/hd$, $E_{hh}^b = 1.67$ eV/H atom. The C–H bond length is equal to 1.14 Å, and its covalent character is depicted in figure 3(d). Similar to the $ha/B1$ system, the electronic states within $E_F - 0.5$ eV are composed of $sp, \sigma$ hybridization along the C–H bonds, and $\pi$ orbitals of carbon and boron atoms, figures 3(g) and (h), respectively. However, in this case, the adsorption of the second hydrogen adatom ($hd$) is not favored by the presence of the first one ($ha$); $E_{hh}^{b2}$ is lower than $E_{hh}^b$. Consequently, $ha + ha \rightarrow ha/hd$ is an endothermic process, thus indicating that the formation of hydrogen clusters is not expected to occur near single boron substitutional sites. Thus, for higher coverage of hydrogen adatoms, we can infer that hydrogen clusters on the clean region graphene surface, i.e., far from boron substitutional sites (with $E_{hh}^b \approx 2.0$ eV/H atom) are more likely than hydrogen adatoms neighboring an isolated boron substitutional site ($E_{hh}^{b2} \approx 1.7$ eV/H atom).

Increasing the concentration of substitutional boron atoms, forming the energetically most probable configuration, i.e., B1–B2 [figure 1(b)], the binding energy of hydrogen adatoms increases compared with the B1 graphene surface. For a single hydrogen adatom, $ha/B1$–$B2$ in figure 4(a), we find $E_{hh}^b$ equal to 2.13 eV/H atom, which is comparable with the calculated $H_2$ binding energy (2.17 eV/H atom). At the equilibrium geometry, the C–H bond length is 1.15 Å, and the formation of C–H covalent bond is depicted in figure 4(b). Figure 4(e) shows that the $sp, \sigma$ orbitals do not lie within $E_F - 0.5$ eV, whereas the $p_\pi$ orbital of the carbon atom C(3) strongly contributes to the electronic states within this energy interval. The former $\sigma$ bonding states, composed of hydrogen $s$ and carbon $p_\pi$ orbitals, are resonant within the valence band of the graphene sheet. In addition, comparing 2(f) and 4(f) we verify that electronic density of $\pi$ orbitals along the B–C bonds increases (asymmetrically) upon hydrogen adsorption.

Different from $ha/hd$ on the B1 graphene sheet, the formation of the $ha/hd$ dimer-like structure on B1–B2, namely $ha + ha \rightarrow ha/hd$, is an exothermic process by 0.24 eV/H atom. Furthermore, $E_{hh}^{b2}$ is higher than the binding energy of the $H_2$ molecule, that is, the formation of $ha/hd$ on the boron doped B1–B2 graphene surface is an exothermic process by 0.20 eV/H atom compared with free $H_2$ molecules. Thus, we can infer that the formation of hydrogen clusters can be improved by the increase of substitutional boron atoms forming the $C_6B$ like structure on the graphene surface. Figure 4(d) presents the total charge density along the C–H covalent bonds. The carbon atoms bonded to hydrogen adatoms exhibit $sp^3$ like hybridizations, where C(3) and C(4) are displaced upward by 0.94 Å with respect to the pristine graphene sheet. The C(3)–C(4) equilibrium bond

![Figure 3](image_url)

**Figure 3.** Equilibrium geometry of hydrogen adsorbed boron doped B1 graphene sheet: (a) a single hydrogen adatom, $ha$, and (c) two hydrogen adatoms forming a dimer-like structure, $ha/hd$. Total charge densities along the C–H bonds for (b) $ha$ and (d) $ha/hd$ models. Partial electronic charge density within an energy interval of $E_F - 0.5$ eV (occupied states) for (e)–(l) a single hydrogen adatom, $ha$, and (g)–(h) dimer-like $ha/hd$ hydrogen structures. Unit, e/bohr³.

![Figure 4](image_url)

**Figure 4.** Equilibrium geometry of a hydrogen adsorbed boron doped B1–B2 graphene sheet: (a) a single hydrogen adatom, $ha$, and (c) two hydrogen adatoms forming a dimer-like structure, $ha/hd$. Total charge densities along the C–H bonds for (b) $ha$ and (d) $ha/hd$ models. Partial electronic charge density within an energy interval of $E_F - 0.5$ eV (occupied states) for (e)–(l) a single hydrogen adatom, $ha$, and (g)–(h) dimer-like $ha/hd$ hydrogen structures. Unit, e/bohr³.
length (1.54 Å) is stretched by 0.1 Å compared with the C–C bond length of undoped systems. The localization of the occupied electronic states, within $E_F = 0.5$ eV, are depicted in figures 4(g) and (h). In the latter diagram we find that the electronic density of the π orbitals along the B–C bonds is reduced compared with the π orbitals of $ha$/B1–B2 (figure 4(f)). Figure 4(g) depicts the $sp_{\sigma}$ orbitals along the C–H bonds. In an STM measurement, those $sp_{\sigma}$ states will give rise to bright spots on the hydrogen adatoms lying on the B1–B2 boron doped graphene sheets. Indeed, recent STM images, supported by ab initio simulations, indicate the formation of bright protrusions attributed to the hydrogen adatoms (forming a dimer-like structure) on clean graphene sheets [11]. On the other hand, quite different STM images are expected for $ha$/B1–B2. Figure 4(e) indicates that, for an STM bias voltage of $\sim0.5$ V below the Fermi level, the tunneling current from the hydrogen adatoms will be negligible compared with the one from neighboring carbon and boron atoms. Thus, in this case, the hydrogen adatom site will appear darker than the neighboring carbon and boron atoms.

4. Conclusions

In summary, we have performed an ab initio total energy investigation of boron doped graphene sheets, and their interaction with hydrogen adatoms. For a single substitutional boron atom our simulated STM images indicate the formation of bright (triangular) spots on the boron substitutional site (center) and the nearest-neighbor carbon atoms (edges), which is in accordance with the increase of the electronic density of states near the valence band maximum. For two boron atoms occupying the substitutional sites on the graphene sheet, corresponding to a boron concentration of $\sim2.4\%$, we find that boron atoms lying on the opposite sites of the same hexagonal ring (B1–B2 structure) represents the energetically most stable configuration. The formation of the B1–B2 structure supports the experimentally proposed $C_6B$ phase for high concentration of substitutional boron atoms in graphene. B1–B2 represents the building block of $C_6B$. On the other hand, the energetic preference of B1–B2 is in contrast with previous ab initio calculations [14, 15]. In those studies, the authors considered the hydrogen adsorption on B1–B3, B1–B7, and B1–B8 configurations which are energetically less stable when compared with B1–B2. Having determined the most likely structure for substitutional boron atoms in graphene sheets, we next examined the hydrogen adsorption on graphene as a function of the boron concentration. For the pristine graphene system, we find that the binding energy of hydrogen adatoms forming H dimer-like configurations ($ha$/hd or $ha$/he) is higher by 1 eV/H atom compared with the binding energy of two isolated H monomers ($E_{bh} = 0.98$ eV/H atom). This is in accordance with the recent experimental/theoretical study of the formation of H clusters on graphene sheets [11, 13]. The presence of a single substitutional boron atom increases the hydrogen binding energy by 0.9 eV/H atom compared with the one on the clean graphene sheet. In this case, the hydrogen adatom lies on top of the carbon atom that is the nearest neighbor to the substitutional B site ($ha$/B1 configuration). However, in contrast to the pristine system, the adsorption of two hydrogen adatoms close to each other, forming a H dimer-like structure, is energetically less favorable compared with two isolated H monomers. This result indicates that the formation of hydrogen clusters on the graphene sheet is somewhat suppressed by the presence of a single substitutional boron atom. Finally, for a boron concentration of $\sim2.4\%$ we find that the binding energy of the H dimer structure ($E_{bh}^*$) is higher than the binding energy of an isolated $H_2$ molecule, where the hydrogen adatoms lie on the carbon atoms neighboring the substitutional boron sites. In this case, boron atoms give rise to preferential adsorption sites for hydrogen adatoms on graphene sheets, and thus improve the formation of hydrogen clusters on graphene sheets. Those results indicate that the formation (or not) of H clusters on graphene sheets can be tuned by the concentration of substitutional boron atoms.

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