Hydrogenated grain boundaries in graphene

W. H. Brito, R. Kagimura, and R. H. Miwa
Instituto de Física, Universidade Federal de Uberlândia, CP 593, 38400-902, Uberlândia, MG, Brazil.
(Dated: January 15, 2013)

We have investigated by means of first principles calculations the structural and electronic properties of hydrogenated graphene structures with distinct grain boundary defects. Our total energy results reveal that the adsorption of a single H is more stable at grain boundary defect. The electronic structure of the grains boundaries upon hydrogen adsorption have been examined. Further total energy calculations indicate that the adsorption of two H on two neighbor carbons, forming a basic unit of graphene, is more stable at the defect region. Therefore, we expect that these extended defects would work as a nucleation region for the formation of a narrow graphane strip embedded in graphene region.

PACS numbers: 73.22.-f, 73.22.Pr, 71.55.-i

Physical and chemical properties of hydrogenated two-dimensional graphene-based (nano)structures have been the aim of recent researches. The adsorption of H atoms can modify the structural, electronic and magnetic properties of the ideal graphene, which is a null-gap semiconductor [1]. It is known that the adsorption of a single H at graphene opens an energy gap and introduces spin-polarized gap states [2]. On the other hand, a fully hydrogenated graphene is an insulator material, known as graphane. Partially hydrogenated graphene structures, such as graphene/graphane superlattices [3], graphene nanoribbons [4] and graphane nanoribbons [5] have been theoretically proposed, and can be produced by removing H atoms from graphene [3] or adsorbing them on graphene [6,10]. These structures can present a suitable band gap energy [3,10] for practical applications in the new nanoelectronic devices.

Grain boundary (GB) defects have been observed in graphene in very recent experiments [11,12]. Theoretical works [13] have also proposed structural models for GB defects, which resemble to those of Refs. [11,14]. Tight-binding calculations suggest that the H adsorption is more stable at the GB defects than in perfect graphene [15]. However, there is no ab-initio investigations on the properties of H adsorption at those observed GB defects, H/GB. Thus, in this work we have investigated, by means of first-principles calculations, the effect of H adsorption on the properties of graphene with grain boundary defects. Our results indicate that the adsorption of a single H is more stable at GB defect. Also, the adsorption of two H on two neighbor carbons, forming a basic unit of graphene, is more stable at the defect region. Thus, we can infer that these extended defects would work as a nucleation region for the formation of a narrow graphane strip embedded in graphene region. The modifications in the electronic structure due to H adsorption at GB defects are also investigated.

Spin-polarized density functional theory (DFT) calculations, within the generalized-gradient approximation (GGA) [17], were performed using the SIESTA code [18], where core states were replaced by norm-conserving pseudopotentials [19] in the factorized form [20]. We have employed a double-zeta plus polarization (DZP) basis set with an energy shift of 100 meV [21], and an energy cutoff of 200 Ry for the real-space mesh. 10 (210) special k-points for geometry (band structure) calculations were used. All atomic positions were fully relaxed until the residual forces were converged to within 10 meV/Å. We have employed a distance of 15 Å between graphene layers and supercells with (60) 60, 96, and 50 carbons atoms to represent the (perfect) defective graphene structures.

We first describe the atomic structure of GB defects in graphene. Here, we have considered three distinct structural models for the GB defects, shown in Fig. 1. These extended defects can be built from a suitable regular arrangement of 5-, 7- or 8-membered carbon rings along a line in graphene. The GB structure shown in Fig. 1(a), named as GB1(5-7), is formed by an alignment of pentagon-heptagon pair separated by hexagons. Figure. 1(b) shows the GB structure named as GB2(5-7), which is a regular sequence of pentagon-heptagon pairs [13]. In these structures, due to the periodicity of the supercell, we have considered two GBs in the unit cell. The third GB structure, shown in the Fig. 1(c), is named as GB(5-8) and consists of a sequence of pentagon-pairs and octagon along the graphene zig-zag direction [12].

Let us now investigate the energetic stability of H atoms adsorbed at graphene with GB defects, H/GB. We first consider a single H atom adsorbed on the top of several non-equivalent carbon atoms at the defect region. These adsorption sites are indicated by the letters A, B, C, D, E and F, as shown in Fig. 1. Also, we have considered the H adsorption at the graphene-like region (site G). To investigate that, we calculated the adsorption energy, $E_{ads}$, which is defined by the following equation:

$$E_{ads} = E[\text{H}/\text{GB}] - E[\text{GB}] - E[\text{H}] + \delta_{\text{BSSE}}$$

where $E[\text{H}/\text{GB}] (E[\text{GB}])$ is the total energy of the fully relaxed hydrogenated (pristine) graphene structure with
GB defects, and $E[H]$ is the total energy of the atomic hydrogen. The last term ($\delta_{\text{BSSE}}$) is used to correct the basis set superposition error [23]. A negative value for $E_{\text{ads}}$ indicates that the adsorption of H is an energetically favourable process. To test our methodology, we have calculated the adsorption energy for a single H at perfect graphene. The calculated adsorption energy of -0.81 eV/H atom is in excellent agreement with other $ab$-initio calculations [24–26].

**TABLE I: Calculated adsorption energies, in eV/H atom, for a single H atom adsorbed at graphene with grain boundary defects.** The letters indicate the adsorption sites (see Fig. 1).

|        | H/GB1(5-7) | H/GB2(5-7) | H/GB(5-8) |
|--------|------------|------------|-----------|
| G      | -0.83      | -0.93      | -0.78     |
| A      | -1.55      | -1.75      | -2.29     |
| B      | -1.39      | -1.54      | -1.89     |
| C      | -1.30      | -1.45      | -1.59     |
| D      | -1.26      | -1.24      | -1.43     |
| E      | -1.18      | -0.99      | -1.31     |
| F      | -0.96      |            |           |

Our calculated adsorption energies, shown in the Table I, indicate that $E_{\text{ads}}$ at the graphene-like region (site G) are within 0.1 eV to that at the perfect graphene sheet. Thus, the error due to the size cell effect is small compared to our calculated energy differences. It is interesting to note that the adsorption energy at the GB defect is negative and smaller than that at perfect graphene for all investigated adsorption sites. This indicates that the adsorption of a single H is energetically more stable and likely to occur at the defective region. Indeed, we find that H/GB(5-8) is a quite stable structure, since the hydrogen adsorption energy (2.29 eV/H) is comparable with the binding energy of an isolated H$_2$ molecule (2.16 eV/H). The flatness of pristine graphene structures is lost due to the H adsorption. For H/GB2(5-7), the hydrogenated carbon and its nearest neighbors move upwards by 0.5 and 0.2 Å, respectively, while the other atoms exhibit negligible displacements. Meanwhile, for the H/GB1(5-7) and H/GB(5-8) systems, the hydrogenated carbon moves upwards by 0.4 Å relative to its nearest neighbors, and a significant displacement is viewed even for the fourth nearest atom of the hydrogenated carbon. At the equilibrium geometry, the C–H bond length is 1.13 Å and the bond length of hydrogenated carbon and its nearest ranges from 1.49 to 1.55 Å, indicating a sp$^3$ hybridization for the carbon atom bonded to H.

Focusing on the electronic properties of the H/GB systems, we performed band structure calculations and scanning tunneling microscopy (STM) simulations for the most stable configurations. Figures 2 (a)–(c) present the electronic band structure of the pristine GB1(5-7), GB2(5-7), and GB(5-8) systems, respectively. The valence and conduction bands exhibit a linear energy–momentum relation nearly of the Dirac point for wave vectors parallel to the GBs. Our STM simulations, for the occupied states within an energy window of 0.2 eV below the calculated Fermi level [Figs. 3 (a)–(c)], indicate the formation of bright lines parallel to the GBs, which is in accordance with the more reactive character of the GBs in comparison with the perfect graphene sheet. Those findings are in good agreement with previous works [12–14]. Figures 2 (d)–(f) show the electronic band structure of H/GB1(5-7), H/GB2(5-7), and H/GB(5-8) structures, respectively. Our results show that the single H adsorption has a strong effect on the electronic properties of GB defects. The systems remain metallic, however, the Dirac point disappears, and it is noticeable the formation of spin-polarized states crossing the Fermi level for the hydrogen adsorbed GB1(5-7) and GB(5-8) systems. In contrast, although the structural similarity with the H/GB1(5-7) system, H/GB2(5-7) exhibits a spin paired state crossing the Fermi level.

The STM images of the GBs are modified upon hydrogen adsorption. Figures 3 (d)–(f) show alternating bright and dark spots along a direction parallel to the GBs. The presence of H adatoms somewhat localizes the electronic states, which is in accordance with the small energy dispersion of the electronic states (near the Fermi level) as depicted in Figs. 2 (d)–(f). In H/GB1(5-7) we find the formation of bright spots on the hydrogen adsorbed site as well as on the nearby C atoms, Fig. 3 (d). Meanwhile, the STM image of the H adatom becomes faded for H/GB2(5-7) and H/GB(5-8). In H/GB(5-8), Fig. 3 (f), we find a very weak spot lying on the H.  

![Fig. 1: Optimized geometries of distinct grain boundary defects, labeled as: (a) GB1(5-7), (b) GB2(5-7), and (c) GB(5-8). The dashed-line box indicate their periodic unit cells. The unit cell parameters a and b, in Å, are 24.5 and 6.6; 28.9 and 9.0; and 27.3 and 5.0 for GB1(5-7), GB2(5-7), and GB(5-8), respectively. The adsorption sites are in gray.](image-url)
adatom, while the nearest neighbor C atom (parallel to the GB) becomes brighter. Indeed, our calculated projected density of states for H/GB(5-8) indicate that the electronic states along the C–H bond are mostly localized between 2 and 3 eV below the Fermi level, while in H/GB1(5-7), the electronic states of H adatoms (mostly) lie at $E_F \pm 0.3$ eV. In this case, in contrast with the H/GB1(5-7) system, the contribution of the H adatom in H/GB(5-8) is not relevant for the spin polarized states near the Fermi level, Fig. 2(f). The STM results for the H/GB2(5-7) system indicate that the electronic states are less localized, Figs. 3(e). The hydrogen adsorbed sites as well as the nearest neighbor C atoms present almost the same brightness along the GB.

Finally, we consider the adsorption of two H atoms on graphene structures. We focus on the most stable configurations for the single H adsorption. Thus, we place the H atoms on sites A and A’ for GB1(5-7) and GB(5-8), and sites A and B for GB2(5-7). The configuration with the H atoms sitting on the opposite sides of the sheet is energetically more favorable than that on the same side. Also, our calculated adsorption energy on the perfect graphene, -1.7 eV/H atom, is in excellent agreement with other ab-initio calculations [24]. For the defective graphene region, we find adsorption energies of -1.86, -1.98 and -2.12 eV/H atom for GB1(5-7), GB2(5-7) and GB(5-8), respectively. Therefore, the adsorption of two H atoms is more stable at the defect region. The structural configuration of the hydrogenated carbons resembles the basic unit of graphene. The above results allow us to infer that the formation of graphene stripes, embedded in graphene, can be ruled by the presence of grain boundary defects.

In conclusion, we have investigated the effect of adsorption of H atoms in the electronic and structural properties of graphene with (extended) grain boundary defects. Our ab-initio calculations indicate that the GB defect could work as nucleation region for graphane strip formation. The electronic structure of such hydrogenated defect is strongly affect by the adsorption of a single H atom. Spin polarized states are observed in H/GB1(5-7) and H/GB(5-8)

We acknowledge support from the Brazilian agencies CNPq and FAPEMIG.

[1] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, Rev. Mod. Phys. 81, 109 (2009), and references therein; K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).

[2] E. J. Duplock, M. Scheffler, and P. J. D. Lindan, Phys.
[3] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim, and K. S. Novoselov, Science 323, 610 (2009); S. Ryu, M. Y. Han, J. Maultzsch, T. F. Heiz, P. Kim, M. L. Steigerwald, and L. E. Brus, Nano Lett. 8, 4597 (2008).
[4] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, Phys. Rev. B 75, 153401 (2007).
[5] J. Lee, and J. C. Grossman, Appl. Phys. lett. 97,133102 (2010); Z. M. Ao, A. D. Hernández-Nieves, F. M. Peeters, and S. Li, Appl. Phys. lett. 97 233109 (2010).
[6] A. K. Singh, and B. I. Yakobson, Nano Lett. 9, 1540 (2009).
[7] Y. Li, Z. Zhou, P. Shen, and Z. Chen, J. Phys. Chem. C 113, 15043 (2009).
[8] P. Sessi, J. R. Guest, M. Bode, and N. P. Guisinger, Nano Lett. 9, 4343 (2009).
[9] D. Haberer, D. V. Vyalikh, S. Taioli, B. Dora, M. Farjam, J. Fink, D. Marchenko, T. Pichler, K. Ziegler, S. Simonucci, M. S. Dresselhaus, M. Knupfer, B. Büchner, and A. Grüneis, Nano Lett. 10, 3360 (2010).
[10] R. Ballog, B. Jørgensen, L. Nilsson, M. Andersen, E. Riensk, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T. G. Pedersen, P. Hofmann, and L. Horneker, Nature Mater. 9, 315 (2010).
[11] P. Y. Huang, C. S. Ruiz-Vargas, A. M. van der Zande, W. S. Whitney, M. P. Levendov, J. W. Kevek, S. Garg, J. S. Alden, C. J. Hustedt, Y. Zhu, J. Park, P. L. McEuen, and D. A. Muller, Nature 469, 389 (2011).
[12] J. Lahiri, Y. Lin, P. Bozkurt, I. L. Oleynik, and M. Batzill, Nat. Nanotechnol. 5, 326 (2010).
[13] O. V. Yazyev, and S. G. Louie, Phys. Rev. B 81, 195420 (2010). O. V. Yazyev, and S. G. Louie, Nature Mat. 9, 806 (2010), J. da Silva Araujo, and R. W. Nunes, Phys. Rev. B 81 073408 (2010).
[14] P. Simonis, C. Goffaux, P. A. Thiry, L. P. Biro, Ph. Lambin, and V. Meunier, Surf. Sci. 511, 319 (2002).
[15] S. Malola, H. Hääkinen, and P. Koshinen, Phys. Rev. B 81 165447 (2010).
[16] W. Kohn, and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[18] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter 14, 2745 (2002); P. Ordejón, E. Artacho, and J. M. Soler, Phys. Rev. B 53, R10441 (1996); D. Sánchez-Portal, P. Ordejón, E. Artacho, J. M. Soler, Int. J. of Quantum Chem. 65, 453 (1997).
[19] N. Troullier, and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
[20] L. Kleinman, and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982); X. Gonze, R. Stumpf, and M. Scheffler, Phys. Rev. B 44, 8503 (1991).
[21] J. Junquera, O. Paz, D. Sánchez-Portal, and E. Artacho Phys. Rev. B 64, 235111 (2001).
[22] H. J. Monkhorst, and J. P. Pack, Phys. Rev. B 13, 5188 (1976).
[23] S. F. Boys and F. Bernardi, Mol. Phys. 19, 553 (1970); C. Hobbs, K. Kantorovich, and J. D. Gale, Surf. Sci. 591, 45 (2005).
[24] Y. Lin, F. Ding, and B. I. Yakobson, Phys. Rev. B 78, 041402(R) (2008).
[25] L. Horneker, E. Rauls, W. Xu, Ž. Sljivancanin, R. Otero, I. Stensgaard, E. Lægsgaard, B. Hammer, and E. Besenbacher, Phys. Rev. Lett. 97, 186102 (2006).
[26] P. O. Lehtinen, A. S. Foster, Y. Ma, A. V. Krasheninnikov, and R. M. Nieminen., Phys. Rev. Lett. 93, 187202 (2004), and references therein.