Thermodynamically stable single-side hydrogenated graphene

H. J. Xiang,1 E. J. Kan,2 Su-Huai Wei,3 X. G. Gong,1 and M.-H. Whangbo2

1Key Laboratory of Computational Physical Sciences, Ministry of Education, and Department of Physics, Fudan University, Shanghai 200433, People’s Republic of China
2Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, USA
3National Renewable Energy Laboratory, Golden, Colorado 60401, USA

(Received 29 August 2010; published 13 October 2010)

The single-sided hydrogenation of graphene was examined by combining the cluster expansion method with density-functional theory to find that hydrogen atoms prefer to form one-dimensional chains, leading to ripples made up of $sp^2$ carbon atoms between them. The formation of such novel structures is due to the competition between electronic kinetic energy and elastic strain energy. Surprisingly, the single-sided hydrogenation of graphene is thermodynamically stable at low hydrogen coverage, and some hydrogenated graphenes are semiconducting, similar to graphene nanoribbons. The new single-side hydrogenated graphene structures account for several puzzling experimental observations. In addition, we propose a low-energy single-side fluorinated graphene structure.

DOI: 10.1103/PhysRevB.82.165425 PACS number(s): 61.48.Gh, 71.20.–b, 73.22.–f, 73.61.Wp

I. INTRODUCTION

Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, has been the focus of recent research efforts,1–3 due to its unique zero-gap electronic structure and the massless Dirac fermion behavior. The unusual electronic and structural properties make graphene a promising material for the next generation of faster and smaller electronic devices. Chemical functionalization is a way to modify the electronic and crystal structure of graphene, which may be important for graphene-based nanoelectronics.4–9 The hydrogenation of graphene,4,5,7 as a prototype of covalent chemical functionalization, is of fundamental importance. The double-sided hydrogenation of graphene is now well understood, at least from the theoretical point of view. For example, Sofo et al.10 predicted theoretically a new insulating material called graphane, in which each hydrogen atom adsorbs on top of a carbon atom from both sides. The formation of graphane was attributed to the efficient strain relaxation for the $sp^3$ hybridization.11

The prediction for the hydrogenated graphene was partially confirmed by Elias et al.12 who demonstrated that graphene can react with atomic hydrogen, which transforms this highly conductive zero-overlap semimetal into an insulator, and hydrogenation of graphene is reversible. However, in the case of graphene on a substrate such as SiO$_2$,12 hydrogenation can occur only on the top basal plane of graphene because the diffusion of hydrogen along the graphene-SiO$_2$ interface is negligible and perfect graphene is impermeable to any atom and molecule.13 Previous theoretical studies14,15 suggest that single-sided hydrogenation of ideal graphene would be thermodynamically unstable. Thus, it remains a puzzle why the hydrogenation of graphene on a substrate is possible and the hydrogenated species are stable at room temperature.12,16

To address the aforementioned issues, we examine the single-sided hydrogenation of graphene by combining the cluster-expansion method17 with density functional theory. We find that hydrogen atoms tend to form one-dimensional (1D) chains leading to ripples made up of $sp^2$ carbon atoms between them. Surprisingly, the single-sided hydrogenation of graphene is thermodynamically stable at low hydrogen coverage, and some of the new single-side hydrogenated graphene are semiconducting, similar to graphene nanoribbons (GNRs). In contrast to the case of the double-sided hydrogenation, the phase separation is unstable in single-side hydrogenated graphene, which suggests that the single-sided functionalization might be a better way of tuning the electronic properties of graphene.

II. COMPUTATIONAL METHOD

It is well known that a hydrogen atom adsorbs on the top of a carbon atom in graphenelike systems. We treat the single-side hydrogenated graphene as an alloy system in which a vacancy or a hydrogen atom could occupy the top sites above the graphene basal plane, as shown in Fig. 1(a). To find the lowest energy structure of graphene with different coverages of hydrogen atoms, we use the state of the art

FIG. 1. (Color online) (a) The CT structure used in the cluster expansion calculations. “T” refers to the top site above the basal plane of graphene. (b) The top view of a 2H-AG structure. The unit cell is enclosed by a rectangle. The numbers denote the $sp^2$ carbon atoms. (c) The decomposition of 2H-AG into two parts: the $sp^3$ hybridized C-H part and $sp^2$ carbon part. (d) The formation energy of 2H-AG as a function of $n/(n+2)^2$ ($n$ is the number of $sp^2$ carbon atoms). The line is fitted according to Eq. (3).
“cluster-expansion” method\textsuperscript{17} established in the alloy theory in which the alloy Hamiltonian is mapped onto a generalized Ising Hamiltonian. In brief, for some adsorption configurations, we perform spin-polarized DFT calculations to relax the cell and internal atomic coordinates. The energies of the relaxed structures are used to extract the interaction parameters of the alloy Hamiltonian. The mapping process was carried out by the ATAT package.\textsuperscript{18}

In our DFT calculations, the local density approximation (LDA) was adopted and the plane-wave cut-off energy for wave function was set to 500 eV. The ion-electron interaction was treated using the projector augmented wave\textsuperscript{19} technique as implemented in the Vienna \textit{ab initio} simulation package.\textsuperscript{20}

III. RESULTS AND DISCUSSION

After obtaining the interaction parameters (nine pair interaction parameters and four three-body interaction parameters) of the alloy Hamiltonian, we can predict the energy of single-side hydrogenated graphene with any adsorption pattern. To identify the most favorable hydrogen adsorption configuration, we define the average adsorption energy at concentration \( y/x \) as

\[
E_a = \frac{E(C, H_x) - x\mu_C - y\mu_H}{y},
\]

where \( E(C, H_x) \) is the total energy of the hydrogenated graphene, and \( \mu_C \) and \( \mu_H \) are set to those of graphene and hydrogen molecule, respectively. It is noted that the difference in \( E_a \) between two adsorption configurations does not depend on \( \mu_H \). If \( E_a \) is negative, the adsorption process is exothermic and the hydrogenated graphene is thermodynamically stable. \( E_a \) for the double-side hydrogenated graphene, i.e., graphene, is as low as \(-0.397\) eV/H, in accord with its high stability. We generate all nonequivalent adsorption configurations for all unique supercells with less than 24 carbon atoms using the linear scaling algorithm recently proposed by Hart and Forcade.\textsuperscript{21} Our calculations using the alloy Hamiltonian show that the adsorption configurations with the lowest average adsorption energies have the adsorption pattern shown in Fig. 1(b). In this structure, the hydrogen atoms form 1D armchair chains. The width of the armchair atom is two according to the conventional definition\textsuperscript{11} of armchair GNPs (AGNR). Hereafter this kind of adsorption configuration is referred to 2H-AG. As can be seen from Fig. 1(c), the \( sp^2 \) carbon atoms form an arch since the angles between a \( sp^2 \) carbon atom and its neighbors tend to be 109.47\(^\circ\). The average adsorption energy is found to be 0.12 eV/H, indicating that the adsorption configuration is thermodynamically unstable at this hydrogen coverage (i.e., \( H \), \( \gamma/6 \)).

The hydrogenated graphene shown in Figs. 1(b) and 1(c) consists of two parts: the \( sp^2 \) hybridized C-H part and \( sp^2 \) carbon part. Thus, we can decompose its formation energy (per unit cell) with respect to graphene and \( H_2 \) into two components

\[
E_f = E_1(HC_{sp^2}) + E_2(nC_{sp^2}),
\]

where \( n \) represents the number of \( sp^2 \) carbon atoms [see Fig. 1(b)]. The formation energy of the \( sp^2 \) carbon part \( E_2(nC_{sp^2}) \) is due to the elastic strain: \( E_2(nC_{sp^2}) = E_c \). The bent \( sp^2 \) carbon part can be seen as a part of a carbon nanotube. For carbon nanotubes, the strain energy per carbon atom is inversely proportional to the square of the radius (\( R \)) of the tube.\textsuperscript{22} Thus, \( E_s = n/2R^2 \) (\( A \) is a constant), and \( R \) can be calculated as \((\pi + 1)/2b_{CC}(2\pi - 2\alpha) \) [\( b_{CC} \) is the \( sp^2 \) C-C bond length (1.42 Å), and \( \alpha \) is the bending angle as a result of the hydrogen adsorption, see Fig. 1(c)]. The reason for the energy decomposition is that the elastic strain energy is not fully described by the short range cluster-expansion Hamiltonian. Finally, we obtain

\[
E_f = E_1(HC_{sp^2}) + nB/(n + 2)^2
\]

with \( B = \frac{64(\pi - \alpha)^2}{3b_{CC}^2} \). This means that when \( n \) goes to infinity, the total strain energy becomes zero, and the formation energy is solely determined by \( E_1(HC_{sp^2}) \). We construct several other adsorption configurations similar to that shown in Fig. 1(b) but with different number of \( sp^2 \) carbon atoms. The formation energies as a function of \( n \) are fitted according to Eq. (3) via parameters \( E_1(HC_{sp^2}) \) and \( B \). The good linear correlation between \( E_f \) and \( n/(n + 2)^2 \) can be clearly seen from Fig. 1(d). The least-squares fitting gives \( E_1(HC_{sp^2}) = -0.236 \) eV and \( B = 21.112 \) eV. The negative value of \( E_1(HC_{sp^2}) \) suggests that the adsorption pattern shown in Fig. 1(c) becomes thermodynamically stable when \( n \approx 86 \).

A previous study suggested that in double-side hydrogenated graphene, the hydrogen atoms tend to adsorb on neighboring carbon atoms in order to maximize the number of \( sp^2 \) C-C bonds.\textsuperscript{11} To see whether the clustering of hydrogen armchair lines leads to a lower average adsorption energy, we double the cell of Fig. 1(b) along the \( x \) direction and move the hydrogen armchair lines next to each other. As expected, the bending angle \( \alpha \) in the optimized structure is much smaller than that of the 2H-AG case. The calculated DFT average adsorption energy for the 4H-AG is 0.039 eV/H, which is indeed lower compared with the case presented in Fig. 1(b). This result prompted us to find out the dependence of the formation energy upon the number of \( sp^2 \) carbon atoms for the 3H-AG and 4H-AG cases. Figure 2 plots the average adsorption energy as a function of hydrogen cover-
This is in agreement with the trend shown in Fig. 2.

The thermodynamically stable single-side hydrogenated graphene structures from our study are nontrivial and unexpected. The peculiar adsorption configuration is a consequence of the competition between electronic kinetic energy and strain energy; the hydrogen atoms tend to be close to each other to lower the kinetic energy of carbon π electrons while the full phase separation between sp² carbon and sp² graphene is prohibited by the large strain caused by the single-sided hydrogen adsorption. Previous studies suggested two possible single-side hydrogenated graphene structures. One structure [Fig. 3(c)] was constructed based on the observation that the optimal way for the one-side chemisorption of two hydrogen atoms on graphene is to occupy the (1,4) positions. This 0.25 H coverage structure has an average hydrogen adsorption of 0.37 eV/H, which is higher than that (about 0.137 eV/H) for the 4H-AG case (see Fig. 2). This suggests that the macroscopic single-sided hydrogen adsorption on graphene is a cooperative phenomenon, which can hardly be described by the adsorption preference of a small number of hydrogen atoms. Another proposed single-side hydrogenated graphene structure [Fig. 3(d)] can be constructed by removing all the bottom hydrogen atoms from graphene and was suggested to be ferromagnetic. This 0.5 H coverage has a very high $E_a$ of 1.61 eV/H, which is much higher than that (about 0.465 eV/H) of the corresponding 4H-AG structure. It should be noted that even with the same H coverage (0.25 or 0.5), the single-side hydrogenated graphene structure based on our new bent models has a much lower energy although the single-side hydrogenated graphene is thermodynamically unstable at this H coverage.

The new bent single-side hydrogenated graphene structures might account for some experimental observations. The formation of bent single-side hydrogenated graphene structures is thermodynamically possible with a negative but small adsorption energy. This is in accord with the fact that hydrogenated graphene is stable at room temperature but the original metallic state can be restored by annealing at 450 °C in Ar atmosphere for 24 h.22

Very recently, graphene films grown on Cu foils have been fluorinated with xenon difluoride (XeF₂) gas. It was found that for single-side fluorinated graphene, the F coverage saturates at 25% (C₃F). Through DFT calculations, Robinson et al. proposed a CₓF structure which can be obtained by replacing H by F in the structure shown in Fig. 3(c). It was suggested that the CₓF structure similar to that shown in Fig. 3(c) has the largest binding energy per F atom. Our calculations show that the 2F-ZG structure with $n=12$ (similar to the structure shown in Fig. 3(b) but with a 25% F coverage) has a lower energy than the previously proposed CₓF structure by about 0.15 eV/F. This result suggests that the bent single-side hydrogenated graphene structures might be also relevant to the single-side functionalization of graphene by other atoms or groups.

Finally, we discuss the electronic properties of new single-side hydrogenated graphene structures, i.e., 4H-AG and 2H-ZG. The band structure for 4H-AG with $n=56$ [Fig. 3(a)] is shown in Fig. 4(a). For comparison, the band structure of 28-AGNR which has the same number of sp² carbon atoms as the 4H-AG is also plotted. The 4H-AG has a similar
band structure as does 28-AGNR except that the 4H-AG has a slightly larger band gap possibly due to the curvature effect. Figures 4(c) and 4(d) show the band structures of the 2H-ZG with $n=28$ [Fig. 3(b)] and 14-ZGNR respectively. It is well-known that a ZGNR has local spin moments at two edges and an antiferromagnetic alignment between two edges results in a small band-gap opening [Fig. 4(d)]. In the case of 2H-ZG, there is no local spin moments. This is because the degenerate edge states can interact with each other resulting in energy lowering by occupying the bonding state. The band gap is closed at the Dirac point $k=(0, 0.34, 0)$.

In summary, we studied the single-side hydrogenation of graphene by combining the cluster-expansion method with density-functional theory, to find that hydrogen atoms tend to form 1D chains with ripples made up of $sp^2$ carbon atoms between them. We reveal that the single-sided hydrogenation of graphene is thermodynamically stable at low hydrogen coverage. The small magnitude of the adsorption energy is in accord with the reversible hydrogenation observed experimentally. In contrast to the case of double-sided hydrogenation, the phase separation in single-side hydrogenated graphene is unstable, hence suggesting that single-sided covalent functionalization might be a better way to tune the electronic properties of graphene. In addition, we find a different single-side fluorinated graphene structure which has a lower energy than the previously proposed model.

**ACKNOWLEDGMENTS**

Work at Fudan was partially supported by the National Science Foundation of China, Pujiang plan, and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning. Work at NREL was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308. M.H.W. thanks the financial support from U.S. DOE under Grant No. DE-FG02-86ER45259.