Sustained ferromagnetism induced by H-vacancies in graphane

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Received 12 May 2010, in final form 15 July 2010
Published 6 August 2010
Online at stacks.iop.org/Nano/21/355201

Abstract

The electronic and magnetic properties of graphane flakes with H-vacancies were investigated using quantum-chemistry methods. The hybridization of the edges is found to be absolutely crucial in defining the size of the HOMO–LUMO gap, which is increased from 3.04 to 7.51 eV when the hybridization is changed from the sp² to the sp³ type. The H-vacancy defects also influence the size of the gap, which depends on the number of defects and their distribution between the two sides of the graphane plane. Further, the H-vacancy defects induced on one side of the graphane plane and placed on the neighboring carbon atoms are found to be the source of ferromagnetism which is distinguished by the high stability of the state with a large spin number in comparison to that of the singlet state and is expected to persist even at room temperatures. However, the ferromagnetic ordering of the spins is found to be limited by the concentration of H-vacancy defects and ordering would be preserved if number of defects does not exceed eight.

1. Introduction

Graphene is the carbon-based wonder material which has gained wide attention due to its many unique electronic and magnetic properties. Despite the high mobility of the charge carriers in graphene resulting from its zero effective mass [1–3], the absence of a gap hinders its application in nanoelectronics. The magnetic properties of graphene arising from spin ordering of the localized states at the zigzag edges [4, 5] or by the presence of defects [7–11] might facilitate its application in carbon-based spintronics. If the localized states occupy the same sublattice then they can induce a sublattice imbalance and, according to Lieb’s theorem [6], that can lead to the ground state being ferromagnetic [7, 8]. Room-temperature ferromagnetism in graphene has been obtained experimentally [13]. However, there are some issues involved in maintaining the ferromagnetic state, whose stability depends on the concentration of the localized states, distance between states and size of the graphene flakes through the size of the band gap. Thus, the gapless regime leads to a quasi-localized nature of the localized states that makes the exchange coupling between two defect-induced moments indistinct [7–12]. Therefore, for bulk graphene possessing no gap, such an exchange coupling [9] creates some inconsistencies in applying Lieb’s theorem [6], namely the rule of the ferromagnetic ordering of spins of the localized states placed on the same sublattice.

Recently discovered graphane [19–23]—hydrogenated graphene—has given a new impetus to the investigation of carbon-based materials due to the predicted advantages in its application in nanoelectronics and spintronics. Termination of the carbon atoms by hydrogens leads to the generation of an sp³ carbon network removing the π bands from its band structure and thereby generating a gap. It has been theoretically predicted that fully hydrogenated graphane is non-magnetic and a wide gap semiconductor [19, 24]. However, H-vacancy defects in graphane generate localized states characterized by non-zero magnetic moments (each defect has \(\mu = 1.0\mu_B\) [25], where \(\mu_B\) is the Bohr magneton (figure 1)). As graphane is characterized by a wide gap, and the value of the charge transfer integral \(t_\sigma \sim -7.7\) eV [18]) is higher than that in graphene \(t_\sigma \sim -2.4\) eV [18]), according to the Hubbard model [7, 8], these should stabilize the ferromagnetism in graphane (for example through an increase of the critical value of the on-site repulsion term [10]).

We report here on our investigation of the electronic and magnetic properties of graphane and their modification once the H-vacancy defects are introduced in the lattice. Our study is performed via quantum-chemistry methods using
spin-polarized density functional theory with the semilocal gradient corrected functional UB3LYP/6-31G in the Jaguar 7.5 program [26]. The H-vacancies are introduced in the originally optimized structure of defect-free graphane in the chair conformation (for the size of the graphene flake see figure 1), whose carbon atoms at the edges are terminated by two hydrogen atoms, thereby preserving the sp$^3$ network over the whole lattice. The electronic properties are defined for the fully relaxed lattice of graphane possessing the vacancies.

2. Single H-vacancy defect

The size of the band gap of graphene nanoribbons decreases rapidly with increasing nanoribbon width as a result of the vanishing of the confinement effect [14–16], similar to that in graphene [1, 5, 17], until it saturates to a value of ≈3.5–4.5 eV. Therefore, for graphene flakes confined by the edges from all sides of size 10 Å × 16 Å, suggesting a strong confinement effect, the large HOMO–LUMO gap (the gap between the highest occupied and lowest unoccupied molecular orbital) in comparison to the band gap obtained for nanoribbons [14, 15, 19, 24] is expected. Defect-free graphene flakes of size 10 Å × 16 Å with edges possessing sp$^3$ hybridization are found to be characterized by degenerate bands and by a HOMO–LUMO gap of 7.51 eV (HOMO = −6.09 eV and LUMO = 1.42 eV), as shown in figure 2(a). For comparison we have examined flakes of size 18 Å × 16 Å and found a decrease in gap to 7.15 eV (HOMO = −5.87 eV and LUMO = 1.27 eV) due to the suppression of the confinement. The edges in the sp$^3$ hybridization, for which the edge carbon atoms are terminated by a single hydrogen, possess localized states. In this case the orbital degeneracy is lifted and the localized states induce the π and π$^*$ bands (HOMO = −4.64 eV and LUMO = −1.58 eV) in the gap of graphene that decrease the HOMO–LUMO gap to 3.04 eV. In the available experiment [20, 21], only a transformation of graphene from the conductor to an insulator due to its hydrogenation was reported, but the size of the gap and the type of edge hybridization were not indicated. Since we found that the gap is sensitive to edge hybridization and can be increased from 3.04 eV to a maximum of 7.51 eV by transformation of the edge hybridization from the sp$^3$ to sp$^4$ type, attention to hydrogenation of the edges should be paid in further experimental investigations.

A single H-vacancy defect in the graphene lattice generates an unsaturated dangling bond on the carbon atom—π unpaired electron (perpendicular p$_z$ orbital). Moreover, bonding of the carbon atom carrying the defect with its neighbors is changed from the sp$^3$ hybridization to sp$^2$, thus providing a modification of the bond length from 1.55 to 1.52 Å. The perpendicular p$_z$ orbital and the C–C bonds possessing sp$^2$ hybridization participate in the formation of the localized state characterized by an unpaired spin (see the spin density in figure 1). Therefore, this localized state generates a defect level in the gap (see the bands in figure 2(b)) and induces spin-polarization in the system such that the bands for the spin-up and spin-down states, in the following α- and β-spin states respectively, can be characterized by a different energy. For the α-spin state, the defect level (π) appears close to the valence band (HOMO = −4.55 eV), thereby suppressing the size of the HOMO$^*_α$–LUMO$^*_α$ gap to Δ$^*_α = 6.06$ eV, while for the β-spin state the π$^*$ level occurs closer to the conduction band (LUMO = −0.84 eV) and the HOMO$^*_β$–LUMO$^*_β$ gap is Δ$^*_β = 5.29$ eV.

3. Different distribution of the H-vacancy defects

For several H-vacancy defects, the ordering of spins of the localized states and the size of the gap are defined by the distance between the defects and the distribution of those defects between the sides of the graphene plane. The side dependence is related to the sublattice symmetry. For the chair conformation of graphane, the carbon atoms belonging to different sublattices are terminated by hydrogen atoms from different sides of the plane. It was already known that in graphene [27], when the localized states occupy the same sublattice and if their spins have antiparallel alignment, then the contribution of the π states to the total energy diminishes as a result of the destructive interference between the spin-up and spin-down tails. Therefore, according to Lieb’s theorem [6], for the localized states occupying the same sublattice a ferromagnetic ordering of their spins would be energetically favored, but for the states on different sublattices, one expects antiferromagnetic ordering [7–10].

For vacancies equally distributed between both sides of the graphene plane (AB-distribution), the energetically favorable spin ordering is the antiparallel alignment of spins between one side (A sublattice) and the other (B sublattice). Thus, for an even number of vacancies in the AB-distribution, all spins are paired but the band degeneracy can be slightly lifted. In figure 2(c) we present the bands for two H-vacancy defects in the AB-distribution separated by a distance $d = 3a_{C–C}$, where $a_{C–C}$ is the length of the C–C bond. Therefore for the α- and β-spin states, the obtained gap of size Δ$^*_{α,β} = 5.41$ eV is defined by the energy gap between the π (HOMO = −4.56 eV) and the π$^*$ (LUMO = −0.85 eV) defect levels. For an odd number of defects, one localized state would have an unpaired spin, thus generating an extra level π for the α- and π$^*$ for the β-spin states. However, when several H-vacancy defects are located on the same side of the graphene plane a parallel alignment

Figure 1. The spin density for a single H-vacancy defect in graphene plotted with isovalue of ±0.001 e Å$^{-3}$. 
of their spins would be preferred because they belong to the same sublattice (AA-distribution). In figure 2(d) we show the energetics of the bands for graphane with two H-vacancy defects separated by a distance of \( d = 4a_{C-C} \) in its triplet state. Each spin state induces a defect level in the valence band of the \( \alpha \)-spin state (\( \pi \) states) and in the conduction band of the \( \beta \)-spin state (\( \pi^* \) states). Therefore, the size of the HOMO–LUMO gap for the \( \alpha \)-state is defined by the conduction band and the defect level \( \pi \) in the valence band, while for the \( \beta \)-spin state it is defined by the valence band and the defect level \( \pi^* \) in the conduction band (\( \Delta_\alpha = 6.08 \text{ eV}, \Delta_\beta = 5.24 \text{ eV} \)), which is similar to the case of the single H-vacancy (see figure 2(b)). However, the state characterized by antiparallel alignment of two spins (the singlet state), possesses \( \pi \) and \( \pi^* \) defect levels for both the \( \alpha \)- and \( \beta \)-spin states and the size of the gap is defined by the energy gap between these defect levels, \( \pi \) and \( \pi^* \), i.e., \( \Delta_\pi \approx \Delta_\beta \) (for example see figure 2(c)).

The destructive and constructive contributions of the spin tails of the localized states decrease with increasing distance between the defects [27]. Therefore, we have calculated the difference in the total energy between the triplet and singlet states (\( E_{\pi,\beta}^{\text{relax}} \)) depending on the distance between the two H-vacancy defects. If \( E_{\pi,\beta}^{\text{relax}} \) energy is negative the ferromagnetic ordering of spins is energetically preferred, with an antiferromagnetic ordering otherwise. We have calculated the two components: the energy \( E_{\pi,\beta}^{\text{relax}} \) is considered before relaxation of the lattice induced by the presence of defects and the \( E_{\pi,\beta}^{\text{relax}} \) component after relaxation. These energies for the AA- and AB-distributions, and splitting of the \( \pi \) levels in the valence band (\( \epsilon_1-\epsilon_2 \)) are presented in table 1. For the AB-distribution the distance between the two defects should be \( >a_{C-C} \), because for \( d = a_{C-C} \) the spins of the two localized states are paired, which leads to transformation of a single bond in sp\(^3\) hybridization between the nearest-neighbor carbon atoms to a double bond in the sp\(^3\) hybridization (\( \sigma \) and \( \pi \) bonds) of length 1.36 Å. Such a defect forms the \( \pi \) and \( \pi^* \) defect levels, which are energetically close to the edges of the conduction and valence bands of graphane. Therefore, the size of the HOMO–LUMO gap defined by the defect levels is 6.38 eV, which is much larger than that for the levels formed by the non-bonded perpendicular \( p_z \) orbital (\( \Delta = 3.71 \text{ eV} \) in figure 2(c)).

A significant energy difference between the triplet and singlet states was found only for \( d \leq 2a_{C-C} \) in the AA-distribution, for which the relaxation of the graphane lattice stabilizes the state with ferromagnetic spin ordering, and for \( d < 2a_{C-C} \) in the AB-distribution. As a result, for the nearest location of the defects, the ordering of spins occur according to Lieb’s theorem [6]. When the defects are spatially separated (\( d > 2a_{C-C} \)) the energy difference between the state with a large spin number and the singlet state diminishes because of decoupling of the magnetic moments of the localized states, and the random spin distribution with a minimum number of unpaired spins would be energetically favored. Therefore, for an even number of defects the system would prefer to remain in the singlet state independent of the distribution of defects over

![Figure 2. Energetics of the bands in graphane with sp\(^3\) hybridized edges (solid lines) and the defect levels (\( \pi \) and \( \pi^* \)) induced by H-vacancies (dashed lines): (a) defect-free graphane; (b) graphane containing a single H-vacancy; (c) graphane containing two H-vacancies distributed between the two sides of the graphane plane (AB-distribution) and separated by a distance of \( d = 3a_{C-C} \) (antiferromagnetic spin ordering); (d) graphane containing two H-vacancies located on one side of the graphane plane (AA-distribution) and separated by a distance of \( d = 4a_{C-C} \) (ferromagnetic spin ordering). The \( \alpha \)- and \( \beta \)-spin states correspond to spin-up and spin-down states. The spin density plotted with isovales of \( \pm 0.001 \text{ e Å}^{-1} \) is also presented.](image)

| Distance, \( d \) | \( E_{\pi,\beta}^{\text{relax}}(\epsilon_1-\epsilon_2) \) (eV) | \( E_{\pi,\beta}^{\text{relax}} \) (eV) |
|----------------|---------------------------------|-----------------|
| AA-distribution (ferromagnetic ordering) |
| 2a_{C-C} | -1.52 | -1.23 | 2.82 \times 10^{-1} |
| 4a_{C-C} | -0.26 | -1.32 \times 10^{-2} | 1.52 \times 10^{-2} |
| 6a_{C-C} | 7.11 \times 10^{-5} | -1.15 \times 10^{-2} | 1.53 \times 10^{-2} |
| 8a_{C-C} | 1.76 \times 10^{-5} | -7.93 \times 10^{-3} | 6.52 \times 10^{-3} |
| AB-distribution (antiferromagnetic ordering) |
| a_{C-C} | 1.34 | 2.98 | — |
| 3a_{C-C} | 4.30 \times 10^{-3} | 1.18 \times 10^{-2} | — |
| 5a_{C-C} | -1.08 \times 10^{-4} | 6.13 \times 10^{-3} | — |
the sublattices, while for an odd number of defects the triplet state is preferred.

We have calculated the fluctuation of the gap size with an increasing number of defects for the system in its singlet state when the size of the gap is defined by the energy difference between the induced defect levels, \( \pi \) and \( \pi^* \), formed by the perpendicular \( p_z \) orbitals. For the AB-distribution \((d > 2a_{C-C})\), the size of the gap can fluctuate from 1.2 to 3.7 eV depending on the distance between the defects and their locations. The change in the gap size is related to the degree of the broken sublattice symmetry. Moreover, with an increasing concentration of the H-vacancies \( (N > 8) \) we found that the number of localized states can be smaller than the number of defects. For the AA-distribution the size of the gap is found to gradually decrease from 3.75 to 2.72 eV with an increasing number of defects from \( N = 2 \) to 18. Additionally, with a growing number of defects a significant distortion of the planarity of graphane, such as buckling of the lattice inherent for the AA-distribution, was observed.

### 4. Stable ferromagnetism

A prediction of the ordering of the AA-distributed localized states on the graphene surface is controversial. According to results in [29] for semihydrogenated graphene, i.e. graphene hydrogenated from one side (the so called graphane), the non-hydrogenated side of graphane possesses the localized states and the spins all of them are ferromagnetically ordered. We believe that this behavior is highly debatable because it is known for the carbon-like materials, such as diamond and graphic structures, that the total magnetization is suppressed by increasing the vacancy concentrations, and particularly for graphic structures this occurs more rapidly [11]. In contrast, the authors of [25] did not consider the ferromagnetic ordering of the states in defected graphane at all because they found that for the vacancy defects located on the neighbors \((d = 2a_{C-C})\), the spins are paired, indicating a non-magnetic state. When the distance exceeds \( 2a_{C-C} \), for which pairing of the spins can not occur, the interaction between the localized states vanishes, thereby favoring the antiferromagnetic ordering of spins. However, we believe that pairing of the spins of the localized states located on the neighboring carbon atoms is unlikely, considering the significant distance between the vacancies (\( \sim 2.55 \text{ Å} \)). Moreover, pairing may occur only when the spins are antiferromagnetically ordered (that for the states localized on the same sublattice is against Lieb’s theorem [6]) and it implies the formation of the bond, which again seems unlikely because of the large distance between the localized states (the typical C–C bond length in organic compounds is \( \sim 1.4 \text{ Å} \) against \( \sim 2.55 \text{ Å} \) for the states separated by \( d = 2a_{C-C} \) in graphane). Therefore, the question of the ordering of the spins of the localized states in their AA distribution is unclear as yet, which we set out to investigate here.

We found that for the AA-distribution of the localized states formed by the H-vacancies, the ferromagnetic ordering of their spins is possible when the vacancies are placed on the neighboring carbon atoms (see \( E_{\downarrow \downarrow}^0 \) for the AA-distribution in table 1), thereby generating a state characterized by a large spin number (see an example for graphene in [28]). Just as in [25] it was noticed that increasing the distance between the vacancies leads to vanishing of the \( \pi - \pi^* \) interaction between the localized states resulting in the antiferromagnetic ordering of spins. Therefore, we investigate here the stability of the ferromagnetic ordering of the spins of the localized states placed on the neighboring carbon atoms \((d = 2a_{C-C})\) and formation of domains of defects depending on the concentration of the defects in the domain and the number of domains.

We found that with increasing concentration of defects \((N)\) the stability of the state with a large spin number, i.e., the difference in total energy between the state with a large spin number and the singlet states, can increase. Therefore, for two parallel lines of defects \( E_{\downarrow \downarrow}^0 = -3.32 \text{ eV} \) for \( N = 4 \) (figure 3(a) for the spin density distribution of \( N = 4 \)), \( E_{\downarrow \downarrow}^0 = -5.03 \text{ eV} \) for \( N = 6 \) and \( E_{\downarrow \downarrow}^0 = -6.56 \text{ eV} \) for \( N = 8 \). However, for \( N = 8 \) the states characterized by the lower spin number are close in energy to the state with the larger spin number \((E_{\downarrow \downarrow}^0 = -0.035 \text{ eV}, E_{\downarrow \downarrow}^0 = -0.065 \text{ eV} \) and \( E_{\downarrow \downarrow}^0 = -0.12 \text{ eV} \) thereby destabilizing it and limiting the number of defects having ferromagnetically ordered spins. A further increase of the defect concentration \((N > 8)\) leads to significant suppression of the energy difference between the ferromagnetic and singlet states. Thus, \( E_{\downarrow \downarrow}^0 = -0.25 \text{ eV} \) for \( N = 10 \), \( E_{\downarrow \downarrow}^0 = 0.17 \text{ eV} \) for \( N = 12 \) and \( E_{\downarrow \downarrow}^0 = -0.14 \text{ eV} \) for \( N = 14 \). Therefore, just as for graphene [7–10], there is a critical value of defect concentration above which the ferromagnetic ordering of the spins of the localized states occupying the same sublattice no longer exists. Another destabilizing factor for ferromagnetism in graphene containing many H-vacancies in the AA-distribution is the lattice relaxation leading to the buckling of the graphane structure \((E_{\downarrow \downarrow}^0 = 1.49 \text{ eV} \) for \( N = 4 \) and \( E_{\downarrow \downarrow}^0 = 1.29 \text{ eV} \) for \( N = 8 \)). There is also a significant decrease in stability when the defects are divided in groups, because the state characterized by
antiferromagnetic ordering of spins between the groups is close in energy to that of the state with ferromagnetic ordering of all spins (see the spin density distribution for $N = 4$ in figure 3(b)). Finally, fully hydrogenated graphene is a wide gap semiconductor and possesses no localized states at the edges in sp$^3$ hybridization (i.e. when the carbon atoms connected to two neighbors are terminated by two hydrogen atoms, while the carbon atoms connected to three neighbors are terminated by a single hydrogen) which could interact ($\pi-\pi$ interaction) with states formed by the H-vacancy defects. Hence, increasing the size of the graphene flakes should not drastically alter the interaction of the localized states and their ordering, which was the case in graphene [9].

To summarize, for the AA-distribution of the H-vacancies the size of the HOMO–LUMO gap can be tuned by the level of hydrogenation—the gap slowly decreases with increasing number of defects, while for the AB-distribution the size of the gap fluctuates in the range of 1.2–3.7 eV, depending on the level of the broken sublattice symmetry. Moreover, formation of the H-vacancy defects redistributed over one side of the graphene plane (AA-distribution) and located on the neighboring carbon atoms belonging to the same sublattice will generate a stable state characterized by a large spin number (ferromagnetic ordering). For a better stabilization of this state, the reorganization of the graphene lattice in response to the occurrence of defects should be minimized. Deformation of the graphene lattice can be minimized for free standing graphene in the low-temperature regime and through interaction of graphene with a substrate under the condition that the sp$^3$ hybridization of graphene lattice is preserved. If the rigidity of graphene on a substrate could be achieved, graphene containing H-vacancies on one side of the plane can even become a room-temperature ferromagnet, which obviously has enormous potential for application in nanoelectronics and spintronics. Because each defect forms a perpendicular $p_z$ orbital possessing unpaired spin and, therefore, its contribution to the magnetization is $1 \mu_B$, the magnitude of magnetization of such a room-temperature ferromagnet can ideally be regulated by the number of H-vacancy defects. However, the number of defects to achieve the stable ferromagnetism at room temperature should be limited, because above a critical value the ferromagnetic ordering of spins would be unstable.

Acknowledgment

The work was supported by the Canada Research Chairs Program.

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