Magnetization of Graphane by Dehydrogenation

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Using first principles calculations, we show that each hydrogen vacancy created at graphane surface results in a local unpaired spin. For domains of hydrogen vacancies the situation is, however complex and depends on the size and geometry of domains, as well as whether the domains are single- or double-sided. In single-sided domains, hydrogen atoms at the other side are relocated to pair the spins of adjacent carbon atoms by forming π-bonds. Owing to the different characters of exchange coupling in different ranges and interplay between unpaired spin and the binding geometry of hydrogen, vacancy domains can attain sizable net magnetic moments.

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Graphene[1], a truly two-dimensional (2D) crystal of honeycomb structure, has sparked considerable interest not only because of its charge carriers behaving like massless Dirac fermions[2,3,4], but also the unusual magnetic properties displayed by its flakes and nanoribbons[5,6,7,8,9,10]. In addition to numerous experimental and theoretical studies on the physical properties of graphene, efforts have been also devoted to synthesize various types of derivatives of graphene. More recently, a 2D hydrocarbon material in the family of honeycomb structure, namely graphane is synthesized[11]. Interesting properties such as reversible hydrogenation-dehydrogenation with changing temperature[11], the electronic structure with a wide band gap[12,13] have been revealed soon after its synthesis. In this letter, we reveal that graphane can be magnetized by dehydrogenation of domains on its surfaces. Large magnetic moments can be attained in a small domain on the graphane sheet, depending on whether the defect region is one-sided or two-sided. Our predictions are obtained from the state-of-the-art spin-polarized first-principles plane-wave calculations[14,15] within the LDA noncollinear calculations including spin-orbit interaction, using (11×11×1) supercells. Details of our method can be found in[16,17].

Graphene, in its chair conformation as illustrated in Fig. 1(a), is derived by the adsorption of a single hydrogen atom to each carbon atom alternating between the top (A) and bottom (B) side in the honeycomb structure. A charge of 0.1 electrons is transferred from H to C leaving behind positively charged H atoms on both sides of a double layer of negatively charged (-0.1 electrons) C atoms. Graphane having a 2D quadrapole structure has the work function Φ≈4.97 eV, which is ≈ 0.2 eV larger than that of graphene. In contrast to semimetallic graphene, graphane is a semiconductor with a wide direct band gap of 3.42 eV calculated by LDA but corrected to be 5.97 eV with GW0 self-energy method, as shown in Fig. 1(b). Doubly degenerate states at the Γ-point at the top of the valence band are derived from 2pz- and 2pz-orbitals of carbon atoms. The edge of the conduction band is composed mainly from C-pz orbitals. Calculated phonon bands all having positive frequencies confirm the stability of 2D graphane. High frequency vibration modes associated with C-H bonds are well separated from the rest of the spectrum, in Fig. 1(c).

The creation of a single H-vacancy at the hydrogen covered surfaces gives rise to the spin polarization in the non-magnetic perfect graphane. Desorption of a single H atom from graphene is an endothermic reaction with 4.79 eV energy. Various techniques, such as laser beam resonating with surface-hydrogen bond[18], stripping with ionic vapor[19] and scission of C-H bonds with subnanometer Pt clusters[20], can be used to create H-vacancy(ies). Upon desorption of a single hydrogen atom, local bonding through sp3 hybrid orbital is retransformed into planar sp2 and perpendicular pz (π) orbitals. At the vacancy site one unpaired electron accommodated by the dangling pz orbital contributes to the magnetization by one µB (i.e., Bohr magneton). The exchange interaction between two H-vacancies calculated in a (11x11x11) supercell is found to be non-magnetic for the first and second nearest neighbor distances due to spin pairings. Since the π–π interaction vanishes for farther distances, antiferromagnetic (AFM) state between two H-vacancies for the third and fourth nearest neighbor distance is energetically favorable. The occurrence of long range spin interactions in carbon based structures was explained before by the superexchange[21] and magnetic tail interaction[22].

As for the islands of H-vacancies at the single (top) side of graphane, we consider various geometrical domains, where H atoms at their edges and inside are removed as seen in Fig. 2. For a triangular domain specified as ∆∗ at the top side, H atoms attached to three carbon atoms located at each edge are removed. Hydrogen atom which is normally adsorbed on the central C atom at the bottom side moves to the corner. Under these circumstances, spins of three hydrogen-free C atoms are antiferromagnetically ordered to yield a net magnetic moment of 1 µB. Noncollinear calculations with spin-orbit interaction fix the directions of spins, which are tilted relative to...
FIG. 1: (Color online) (a) Top and side views of atomic structure showing of graphane primitive unit cell with Bravais lattice vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) and buckling of alternating carbon atoms, A and B, in honeycomb structure \( \delta \), bond lengths \( d_{C-C} \) and \( d_{C-H} \) optimized using LDA. Large green (light) and small orange (dark) balls indicate C and H atoms, respectively. (b) Energy band structure is calculated by using LDA and corrected using GW\(_0\) (shown by blue lines and orange dots). For graphene, linear band crossing at Dirac point is shown by dashed grey lines. (c) Calculated phonon bands and density of states DOS projected to C and H atoms.

FIG. 2: (Color online) Calculated magnetic state of various domains of single-sided H-vacancies, where all H atoms attached to C atoms from upper side in the unshaded region (delineated by dash-dotted lines) including edges, are removed. The triangles are specified by \( \Delta^s_n \) with \( n \) indicating the maximum number of C atoms at one edge and \( s \) signifies the single-sided dehydrogenation. Similar symbols are used also for hexagonal, \( \Delta^s_3 \) and lane \( L^s_n \) (\( n = 4,5 \)) domains. Total magnetic moment \( \mu_T \) and its components \( \mu_x, \mu_y, \mu_z \) are given in units of the Bohr magneton \( \mu_B \). Magnetic moments on C atoms are shown by red (black) arrows. Relocations of H atoms at the other side of graphane are shown by curly arrows. For the sake of clarity \( \pi \)-bonds formed after the relocation of bottom H atoms are indicated only for \( \Delta^s_4, L^s_4 \) and \( L^s_5 \) structures.

\( \mu_B \). The tendency to pair the spins of adjacent C atoms to form \( \pi \)-bonds are seen better in lane domains. Let us consider \( L^s_4 \) and \( L^s_5 \) in Fig.2. Because of relocation of H atoms at the bottom side, two pairs of nearest neighbor C atoms form \( \pi \)-bonds and hence pair their spins. At the end, \( L^s_4 \) has \( \mu_T = 0 \). For \( L^s_5 \) having odd number of H-vacancy, while two pairs of C atoms are bound by two \( \pi \)-bonds, C atom at the center has an unpaired spin and attains \( \mu_T = 1 \mu_B \). In a similar manner, the hexagonal domain \( H^s_3 \) has total of seven C atoms at its center and corners, all H atoms stripped from top side. At the bottom side, H atoms are relocated and hence the spins of adjacent C atoms are paired to result in a total net magnetic moment of \( \mu = 1 \mu_B \).
FIG. 3: (Color online) Net magnetic moments in Bohr magneton within the triangular $\Delta_d^2$, hexagonal $H_d^3$, rectangular $R_d^4$ and lane $L_d^5$ domains, which are delineated by dash-dotted lines and have $n$ carbon atoms at their edges. Here $d$ signifies the double-sided dehydrogenation. Random shaped domain including both one and two-sided H-vacancy parts is also illustrated.

Graphene can be tuned by changing the size and geometry of a given double-sided H-vacancy domain. In this case the situation is not complex and allows us to figure out the magnetic moment of the entire structure easily. Based on noncollinear calculations including the spin-orbit coupling, the direction of the unpaired spins on the $A$-type C atoms freed from H atoms is found to be opposite to that of the spins of $B$-type C atoms. However, instead of AFM spin ordering, lowest energy state of lane defects consisting of even number of C atoms is NM due to the entirely paired $p_z$ orbitals. Also, large double-sided domains including lane defects with equal number of $A$- and $B$-type C atoms are found to be NM. The resulting net magnetic moment of a double-sided H-vacancy domains can be given by $\mu_T = (N_t - N_b)\mu_B$, where $N_t$ and $N_b$ denote the number of stripped H atoms from the top and bottom sides, respectively. Accordingly, the net magnetic moment induced in $\Delta_d^2$, $\Delta_d^3$, $\Delta_d^4$ and $\Delta_d^5$ domains are 2, 3, 4 and 5 the $\mu_B$ respectively. The same argument can be applied to rectangular $R_d^4$, hexagonal $H_d^3$ and lane $L_d^5$ domains. Even the magnetic moment of a domain having arbitrary shape including various single-sided and double-sided H-vacancy parts, as indicated in Fig.3 can be retrieved by the arguments discussed above. Non-integer value of $\mu_T$ is due to severe distortion of structure. We also note that our results regarding to the unpaired spin of a domain and their net magnetic moment are in compliance with Lieb’s theorem[23], which distinguishes $A$- and $B$-sublattices in honeycomb structure.

In conclusion, we showed that the interaction between unpaired spins associated with H vacancies in graphene gives rise to interesting magnetic structures. We revealed simple physical mechanisms underlying the magnetism of single-sided and double-sided vacancy domains. For single-sided domains, owing to the tendency to pair the spins of $\pi$-orbitals of adjacent C atoms, some of the adsorbed H atoms at the bottom side are relocated. At the end, the net magnetic moments can be attained in vacancy domains depending on their size and shape. For double-sided domains, interactions underlying the generation of net magnetic moment are relatively straightforward and are in good agreement with Lieb’s theorem. Since the exchange coupling between different domains are hindered by domain walls, very dense data storage can be achieved through uniform coverage of identical domains. It is also noted that a graphene flake comprising a domain with large magnetic moment can be utilized as a non-toxic marker for imaging purposes. While magnetic 2D systems attract a great deal of attention due to their tunable properties at nanoscale, our results suggest that the size and ordering of magnetic moments of hydrogen vacancy domains with thin walls can be used for future data storage and spintronics applications.

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