

Ferromagnetism in Semihydrogenated Graphene Sheet

J. Zhou,[†] Q. Wang,[‡] Q. Sun,^{*,†,‡} X. S. Chen,[§] Y. Kawazoe,^{||} and P. Jena[‡]

Department of Advanced Materials and Nanotechnology, and Center for Applied Physics and Technology, Peking University, Beijing 100871, China, Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, Shanghai Institute of Technical Physics, Chinese Academy of Science, Shanghai 200083, China, and Institute for Material Research, Tohoku University, Sendai, 980-8577, Japan

Received June 27, 2009

ABSTRACT

Single layer of graphite (graphene) was predicted and later experimentally confirmed to undergo metal-semiconductor transition when fully hydrogenated (graphane). Using density functional theory we show that when half of the hydrogen in this graphane sheet is removed, the resulting semihydrogenated graphene (which we refer to as graphone) becomes a ferromagnetic semiconductor with a small indirect gap. Half-hydrogenation breaks the delocalized π bonding network of graphene, leaving the electrons in the unhydrogenated carbon atoms localized and unpaired. The magnetic moments at these sites couple ferromagnetically with an estimated Curie temperature between 278 and 417 K, giving rise to an infinite magnetic sheet with structural integrity and magnetic homogeneity. This is very different from the widely studied finite graphene nanostructures such as one-dimensional nanoribbons and two-dimensional nanoholes, where zigzag edges are necessary for magnetism. From graphane to graphone and to graphone, the system evolves from metallic to semiconducting and from nonmagnetic to magnetic. Hydrogenation provides a novel way to tune the properties with unprecedented potentials for applications.

Because of their unique properties, carbon-based low dimensional nanostructures have been of interest to scientists for many years. Among these “graphene”, a two-dimensional planar structure that can be viewed as a single layer of graphite, has been proposed as a versatile material for many potential applications.¹ Recently fully hydrogenated graphene, which is referred to as “graphane”, has been predicted² theoretically and synthesized³ experimentally by exposing graphene in hydrogen plasma environment. More importantly, graphane is a semiconductor while graphene is a conductor. Hydrogenation of graphene is reversible,³ providing the flexibility to manipulate its coverage. For example, one can remove the hydrogen atoms from one side of graphane, while keeping the other side hydrogenated. This will result in a half-hydrogenated graphene which we refer to as “graphone”. It is interesting to know the effect of partial hydrogen coverage on the electronic structure and properties of graphone.

Many studies, both experimental and theoretical, have revealed that hydrogen can not only induce magnetism in nonmagnetic materials but also can change the magnetic configuration in some magnetic materials.^{4–9} For example,

hydrogenation of Rh clusters can change its magnetic properties¹⁰ and proton irradiation can induce ferromagnetism of graphite. Both graphene and graphane sheets are known to be nonmagnetic. Is it possible that graphone with half of the carbon atoms saturated with hydrogen can be magnetic? Using density functional theory with generalized gradient approximation for exchange and correlation energy, we show that graphone is indeed ferromagnetic. Partial saturation of carbon atoms in graphene breaks its π -bonding network and the p-electrons associated with the unhydrogenated carbon atoms are localized and unpaired. The magnetic moments couple ferromagnetically giving rise to an infinite magnetic sheet with structural integrity and magnetic homogeneity. In addition, the electronic structure is also changed by partial hydrogenation. Graphone becomes an indirect band gap semiconductor with a small band gap, very different from the original graphene (with zero band gap) and graphane (with large band gap).

It has been theoretically predicted that zero-dimensional graphene nanodots, one-dimensional graphene nanoribbons, and two-dimensional graphene nanoholes can be magnetic when having zigzag edges. However, Okada¹¹ has demonstrated that armchair edge nanoribbons are more energetically favorable than zigzag ones. Therefore, one of the challenges has been to controllably synthesize a two-dimensional infinite ferromagnetic graphene sheet without zigzag edges. Here we

* To whom correspondence should be addressed: sunqiang@pku.edu.cn.

[†] Peking University.

[‡] Virginia Commonwealth University.

[§] Chinese Academy of Science.

^{||} Tohoku University.

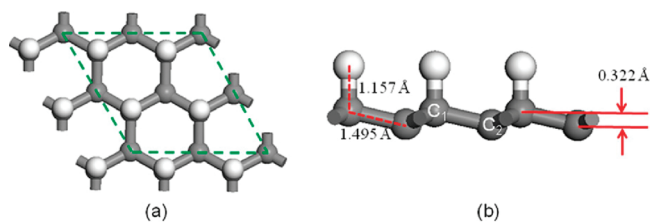


Figure 1. Optimized geometric structure of graphone. (a) Top view with the rhombus marked in green shows the supercell, (b) side view shows C–C and C–H distances.

show that this can be achieved by tunable hydrogenation of graphene.

Our first-principles calculations are based on spin-polarized density functional theory (DFT) with generalized gradient approximation (GGA)¹² for exchange correlation potential. Perdew–Burke–Ernzerhof (PBE) functional for the GGA as implemented in Vienna ab initio simulation package (VASP)¹³ and pseudopotentials with $2s^22p^2$ and $1s^1$ valence electrons of C and H atoms, respectively, are used. We constructed supercells consisting of eight carbon atoms and four hydrogen atoms as shown in Figure 1. Vacuum space of 15 Å normal to graphene plane was used to avoid interactions between two layers. Reciprocal space was represented by Monkhorst–Pack special k-point scheme¹⁴ with $7 \times 7 \times 1$ grid meshes. The structures were relaxed without any symmetry constraints with a cutoff energy of 400 eV. The convergence of energy and force were set to 1×10^{-4} eV and 0.01 eV/Å, respectively. The accuracy of our procedure was tested by calculating the C–C bond length of graphene; our calculated result of 1.41 Å is in good agreement with the experimental value of 1.42 Å.

We first relaxed the geometric structure of graphone in which C₁ atoms were hydrogenated and C₂ atoms remain unsaturated. Note that in the fully hydrogenated nanostructure, graphane, all the C atoms form a zigzag configuration similar to sp^3 hybridized form. The C atoms in the optimized graphone sheet become more planar-like as compared to graphane. The relaxed bond lengths of C–C and C–H are, respectively, 1.495 and 1.157 Å. This C–C bond length lies between that in graphene and graphane structure. The distance between planes composed of C₁ atoms and C₂ atoms is 0.322 Å. All the H atoms are adsorbed on C₁ atoms with C–H bonds arranged normal to graphene plane. We note that similar to graphane, the sp^2 hybridized C₁ atoms became sp^3 hybridized upon hydrogenation, while the C₂ atoms remain sp^2 .

Now readers may ask whether the graphone sheet is stable? To answer this question we carried out molecular dynamics simulations at room temperature ($T = 300$ K) with a time step of 1 fs. After running 3000 steps, the geometry is still kept, suggesting that the graphone sheet is stable. In fact, the C–H binding energy is much larger than the thermal energy corresponding to the room temperature. In Figure 2, we show the fluctuations of energy and temperature with time during the simulation.

Next we discuss the magnetic property of the graphone sheet. It is known that in graphene the p orbitals perpen-

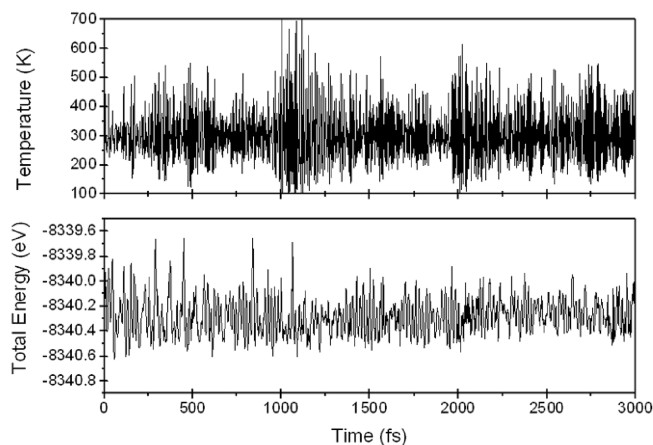


Figure 2. Changes of temperature and energy with time obtained from molecular dynamics simulation of graphone sheet.

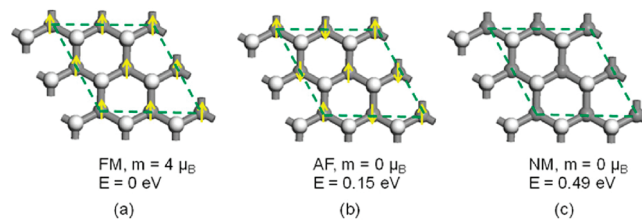


Figure 3. Different magnetic configurations of graphone with their magnetic moments and relative energies for (a) ferromagnetic, (b) antiferromagnetic, and (c) nonmagnetic configurations.

dicular to the plane of the carbon ring system combine to form an extensive π -bonding network. The resulting delocalized π -electrons lead to a metallic and nonmagnetic 2D sheet. When half of the carbon atoms are hydrogenated, strong σ -bonds are formed between C and H atoms and the π -bonding network is broken, leaving the electrons in the unhydrogenated C atoms localized and unpaired. We have found that the C₂ atom carries a magnetic moment of about $1 \mu_B$. In order to study the preferred coupling of these moments, we considered the following three magnetic configurations as shown in Figure 3: (1) ferromagnetic (FM) coupling; (2) antiferromagnetic (AF) coupling; and (3) nonmagnetic (NM) state, where the calculation is spin unpolarized. We found the ground state to be FM, which lies 0.15 and 0.49 eV lower in energy than that of AF and NM states, respectively. Since our calculations are based on a supercell that consists of four unit cells, the energy of the FM state for one unit cell composed of two C atoms and one H atom is 36 and 120 meV lower in energy than those of the AF and NM states, respectively. This shows that semihydrogenation can lead to a ferromagnetic sheet. We can use the energy difference between FM and AF states and the mean field theory to estimate the Curie temperature of magnetic graphone sheet which gives 278 and 417 K when graphone is respectively treated as 3D and 2D.

To visualize the distribution of spins on the graphone sheet, we plot spin density in Figure 4. This clearly indicates that the induced magnetic moments are localized on C₂ atoms, while the hydrogenated C₁ atoms and H atoms carried very small magnetic moments (less than $0.1 \mu_B$). Conventionally magnetism is attributed to d- or f-electrons. Here we show

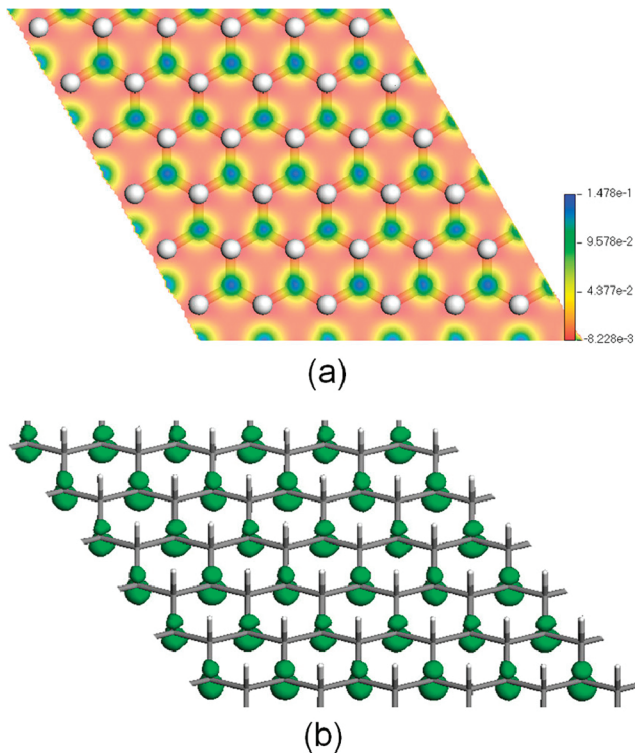


Figure 4. Calculated spin density ($\rho_\alpha - \rho_\beta$) of graphane. (a) 2D plot (b) 3D isosurface with value of 0.26 electrons/ \AA^3 .

that the unpaired 2p electrons in the unhydrogenated carbon sites contribute to magnetism. Since the valence electrons in p-states are more delocalized than those in d- or f-states, they have much larger spatial extension that promotes long-range exchange coupling interaction. Therefore, the long-range magnetic coupling between 2p moments can be attributed to the extended p–p interactions. In fact, the extended tails of wave functions have also been proposed to mediate long-range magnetic interactions between defect-induced moments in cation-vacancy-induced magnetism in BN.¹⁵

In order to understand in more detail the changes in electronic structure in the graphane sheet, we plot the band structure in Figure 5, where $K = (-1/3, 2/3, 0)$ represents the coordinate of Dirac point of graphene. We see that the spin up channel is located at lower energy relative to the spin down channel, but the two share similar distribution in reciprocal space. Examination of the states at near the Fermi level shows that the magnetic property is mainly contributed by the p-electrons of C atoms. Unlike the original graphene, which is metallic, the band structure shows that graphane is an indirect bandgap semiconductor with valence band maximum (VBM) located at the K point similar to that in graphene, and conduction band minimum (CBM) at the G (Γ) point. This is caused by breaking of the π -orbital network due to partial hydrogenation. The band gap of graphane sheet is found to be 0.46 eV, which is much smaller than that of graphene.

From above, we have seen that ferromagnetism can be introduced if one can synthesize a graphane sheet from a graphene sheet by removing the hydrogen atoms on one side.

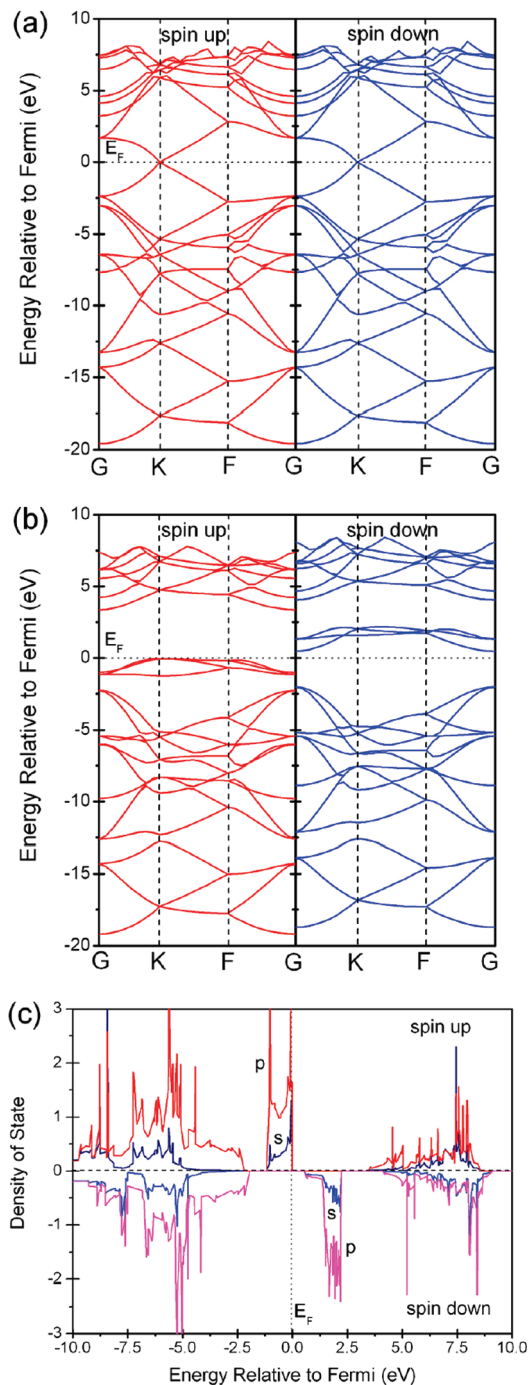


Figure 5. Calculated band structures of (a) graphene and (b) graphane. $G = (0, 0, 0)$, $K = (-1/3, 2/3, 0)$ and $F = (0, 1/2, 0)$. G presents the Γ point and K is the Dirac point of graphene. (c) PDOS of graphane with green curve representing spin up s-electrons, red the spin up p-electrons, blue the spin down s-electrons, and magenta the spin down p-electron.

The next question arises; if one further removes half of the hydrogen atoms from graphane, is the sheet still magnetic? We have found that the sheet becomes nonmagnetic. This is because in this case two unsaturated C atoms alternatively form nearest neighbors, their p_z orbitals form π -bonding, which quenches magnetism. On the basis of this finding, we can conclude that only half-hydrogenation can introduce magnetism. Controlling the coverage of hydrogenation and the geometry is the key to observe the predicted ferromagnetism.

In conclusion, we have demonstrated theoretically that it is possible to introduce ferromagnetism into graphene by surface modification with hydrogenation. This method has the following advantages over the existing ones: (1) It is not necessary to substitutionally dope^{16–18} C atoms by foreign atoms such as transition metal atoms^{16,17} or B and N.¹⁸ (2) It is not necessary to cut the two-dimensional graphene into finite systems with zigzag edges like one-dimensional nanoribbon or zero-dimensional quantum dots.^{19–21} (3) It is not necessary to introduce carbon vacancies like nanoholes in graphene, where magnetism appears at the edge of the vacancy.^{22–25} The disadvantages of the above processes are the following: (1) Integrity of graphene structure is destroyed by vacancies or by substitution with foreign atoms or cutting into nanosize, where magnetism is inhomogeneously distributed. (2) In practical applications, nanoribbons need to be assembled, and the magnetic moments in the zigzag edges can be easily quenched in the assembly. (3) Magnetism can also be introduced by transition metal adsorption, but due to the strong d–d interactions, it is easy for transition metal atoms to form clusters. All these methods are difficult to control and they are not reversible. Therefore, reversibility, controllability, integrity of structure, and homogeneity of magnetism make the graphone sheet very appealing for further experimental study.

Acknowledgment. This work is partially supported by grants from the National Natural Science Foundation of China (10874007, 10725418, 10990100), the Foundation of National Laboratory for Infrared Physics, the US National Science Foundation, and the US Department of Energy. The authors thank the crew of the Center for Computational Materials Science, the Institute for Materials Research, Tohoku University (Japan), for their continuous support of the HITACH SR11000 supercomputing facility.

References

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Filsrov, A. A. *Science* **2004**, *306*, 666–669.

- (2) Sofo, J. O.; Chaudhari, A. S.; Barber, G. D. *Phys. Rev. B* **2007**, *75*, 153401–153404.
- (3) Elias, D. C.; Nair, R. R.; Mohiuddin, T. M. G.; Morozov, S. V.; Blake, P.; Halsall, M. P.; Ferrari, A. C.; Boukhalov, D. W.; Katsnelson, M. I.; Geim, A. K.; Novoselov, K. S. *Science* **2009**, *323*, 610–613.
- (4) Esquinazi, P.; Spemann, D.; Hohne, R.; Setzer, A.; Han, K.-H.; Butz, T. *Phys. Rev. Lett.* **2003**, *91*, 227201–227204.
- (5) Esquinazi, P.; Hohne, R.; Han, K.-H.; Setzer, A.; Spemann, D.; Butz, T. *Carbon* **2004**, *42*, 1213–1218.
- (6) Lee, K. W.; Lee, C. E. *Phys. Rev. Lett.* **2006**, *97*, 137206–137209.
- (7) Hara, M.; Hatakeyama, N.; Akamaru, S.; Watanabe, K.; Nishimura, K.; Mori, K.; Matsuyama, M. *J. Magn. Magn. Mater.* **2009**, *321*, 423–428.
- (8) Marcos, J. S.; Fernandez, J. R.; Chevalier, B. *J. Magn. Magn. Mater.* **2007**, *310*, 383–385.
- (9) Chevalier, B.; Pasturel, M.; Bobet, J.-L.; Isnard, O. *Solid State Commun.* **2005**, *134*, 529–533.
- (10) Nayak, S. K.; Weber, S. E.; Jena, P.; Wildberger, K.; Zeller, R.; Dederichs, P. H.; Stepanyuk, V. S.; Hergert, W. *Phys. Rev. B* **2007**, *56*, 8849–8854.
- (11) Okada, S. *Phys. Rev. B* **2008**, *77*, 041408–041411.
- (12) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- (13) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (14) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13*, 5188–5192.
- (15) Dev, P.; Xue, Y.; Zhang, P. *Phys. Rev. Lett.* **2008**, *100*, 117204–117207.
- (16) Sevincli, H.; Topsakal, M.; Durgun, E.; Ciraci, S. *Phys. Rev. B* **2008**, *77*, 195434–195440.
- (17) Zanella, I.; Fagan, S. B.; Mota, R.; Fazzio, A. *J. Phys. Chem. C* **2008**, *112*, 9163–9167.
- (18) Owen, F. J. *J. Chem. Phys.* **2008**, *128*, 194701–194704.
- (19) Pisani, L.; Chan, J. A.; Montanari, B.; Harrison, N. M. *Phys. Rev. B* **2007**, *75*, 064418–064426.
- (20) Topsakal, M.; Sevincli, H.; Ciraci, S. *Appl. Phys. Lett.* **2008**, *92*, 173118–173120.
- (21) Fernandez-Rossier, J.; Palacios, J. J. *Phys. Rev. Lett.* **2007**, *99*, 177204–177207.
- (22) Huang, B.; Liu, F.; Wu, J.; Gu, B.-L.; Duan, W. *Phys. Rev. B* **2008**, *77*, 153411–153414.
- (23) Choi, S.; Jeong, B. W.; Kim, S.; Kim, G. *J. Phys.: Condens. Matter* **2008**, *20*, 235220–235223.
- (24) Palacios, J. J.; Fernandez-Rossier, J.; Brey, L. *Phys. Rev. B* **2008**, *77*, 195428–195441.
- (25) Yazyev, O. V.; Helm, L. *Phys. Rev. B* **2007**, *75*, 125408–125412.

NL9020733