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2010 New J. Phys. 12 125012

(http://iopscience.iop.org/1367-2630/12/12/125012)

New Journal of Physics
The open-access journal for physics

Graphene hydrate: theoretical prediction of a new insulating form of graphene

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New Journal of Physics **12** (2010) 125012 (7pp)
Received 1 July 2010
Published 13 December 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/12/125012

Abstract. Using first-principles calculations, we show that the formation of carbohydrates directly from carbon and water is energetically favored when graphene is subjected to an unequal chemical environment across the two sides, with a difference in the chemical potential of protons and hydroxyl groups. The resultant carbohydrate structure is two-dimensional (2D), with the hydrogen atoms exclusively attached on one side of the graphene and the hydroxyl groups on the other side, the latter forming a herringbone reconstruction that optimizes hydrogen bonding. We show that graphene undergoes a metal–insulator transition upon hydration that is readily detectable from the significant shift in the vibration spectrum. The hydrate form of graphene offers new applications for graphene in electronics, either deposited on a substrate or in solution.

S Online supplementary data available from stacks.iop.org/NJP/12/125012/mmedia

Carbohydrates, $C_m(H_2O)_n$, are of great importance since they play a crucial role in various life functions, most notably as the medium for the storage and transport of energy in living systems [1]. In the structure of carbohydrates, the protons and the hydroxyl groups separately bond to each carbon atom. It is an intriguing possibility to create a macroscopically large, planar carbohydrate structure based on graphene, a newly discovered carbon allotrope [2] that has attracted much interest in its novel two-dimensional (2D) material structures and electronic device applications [3]. Recent theory [4] and experiment [5] have shown that it is possible to hydrogenate graphene at room temperature to produce graphane, and this process is reversible. In organic chemistry, on the other hand, it is readily possible to insert water molecules into alkene species through hydration reactions, for example, converting ethylene into ethanol. Both

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of these processes involve opening the double C–C bond so that protons or the hydroxyl group can be attached to C atoms. Hydration of graphene, however, is elusive because its planar geometry puts severe constraints on the final configuration: if the proton and hydroxyl groups are on the same side of the C-atom plane, the 2D periodicity of the lattice places them so close that they recombine to form water molecules. Therefore, hydration of graphene is not feasible unless the protons and hydroxyl groups can be placed on opposite sides of the C-atom plane.

These considerations have motivated our investigation into what would emerge if graphene could be subjected to two very different chemical environments, one on each side. The difference in chemical environment could be the ion concentration, pH value or ionic potential. The result of this process may open up new possibilities for device applications of graphene in solution; for instance, DNA sequencing through ionic transport and novel battery technologies based on graphene membranes. In this paper, we examine the properties of a 2D crystalline hydrate structure obtained from graphene, where the hydroxyl groups spontaneously lock into a herringbone structure on one side of the basal C-atom plane, while protons are chemisorbed on the other. We show that this structure, which we refer to as 'graphanol' or 'poly-ethanol', is stable at room temperature. We note that a similar structure to siloxane was recently studied [6], but a small unit cell was used, which prevents the system from reconstructing to the most favorable configuration. We show that upon hydration, graphene, which is a semi-metal in pure form, transforms into an insulator with a substantial direct gap. Due to charge transfer and alignment, a macroscopic net dipole moment arises perpendicular to the C-atom plane. Hydration has a dramatic impact on the vibrational spectra, with new peaks arising and the bond stretching mode of graphene shifting to lower energy.

For the present study of graphanol, we use first-principles calculations based on density functional theory. The geometry and formation energies were calculated using projector-augmented plane waves (PAW) as implemented in VASP [7] with an energy cutoff of 400 eV. The core electrons are treated as PAW pseudopotentials [8]. The system is treated as slabs separated by 30 Å as specified in the periodic boundary condition perpendicular to the membrane. Structure optimization is complete when the magnitude of the force on each atom is less than 0.04 eV $Å^{-1}$, and stress on the cell is less than 0.01 GPa. The optimized geometry was checked with SIESTA code [9], which employs local atomic orbitals, with an energy cutoff of 70 Ryd. The lattice constants obtained from the two approaches differ by less than 1%. The local orbital method was also used for the calculation of the projected density of states (DOS), density of charge difference and molecular dynamics (MD) simulations of graphanol and hydrogen energy barriers for transport across the graphene membrane. In the latter, a 4×4 supercell of graphene was used, with a time step of 1 fs, and constant temperature was maintained by a Nosé thermostat. In all calculations, the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional and a $4 \times 4 \times 2$ k-point mesh were used unless otherwise specified.

Upon hydration, with the protons and hydroxyl groups chemisorbed on each side of graphene (figure 1), the planar graphene structure is converted into a puckered diamond-like sp^3 structure with the C–C bond length increasing from 1.42 to 1.56–1.57 Å. The in-plane lattice constant increases by 5% compared to that of graphene. The C–C bond elongation is expected because of the loss of the π bonds. The C–H and C–O bond lengths are 1.11 and 1.43 Å, respectively, typical values for hydrocarbons and alcohols. In principle, the hydroxyl group can rotate freely about the C–O bond; our MD simulation at 300 K, however, shows that these groups spontaneously form a herringbone structure in which the proton in one of the hydroxyl groups points to one of its neighboring oxygen atoms. This structure changes

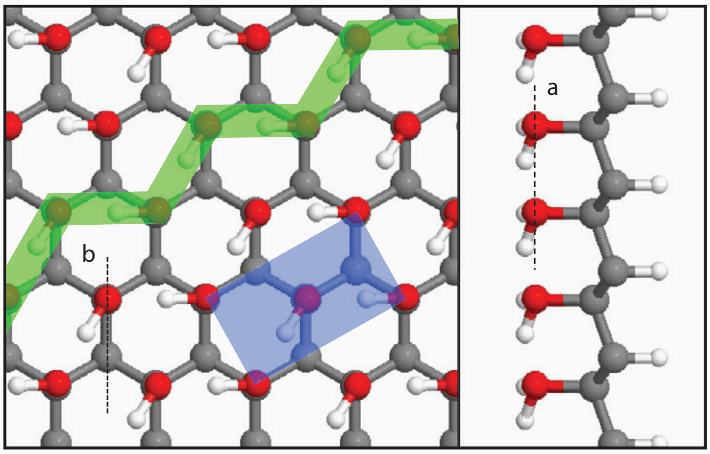

Figure 1. Top view (left) and side view (right) of the herringbone structure of graphanol with protons (white) and hydroxyl groups (oxygen in red) residing exclusively on one side of the membrane, both of the groups chemisorbed on carbon atoms (gray). One of the zigzag herringbone lines (green stripe) and a unit cell (blue rectangle) are highlighted in the top view. The dashed lines marked as 'a' and 'b' denote the slicing planes in figures 3(a) and (b).

the periodicity of the 2D crystal to a rectangular lattice, as shown in figure 1. Compared to the structures with periodicity restricted to that of the graphene unit cell, the formation of the herringbone structure lowers the energy by about 126 meV per hydroxyl group (with a hydrogen bond length of 159 pm), which is in the range of typical energies for hydrogen bonding. The overall binding energy indicates that the system is more stable than its isomer ketene (C_2H_2O) and diketene ($C_4H_4O_2$) by 0.97 and 0.43 eV per C_2H_2O unit, respectively. This indicates that graphene upon hydration will not disintegrate into small species, which is consistent with numerous experimental observations that graphene is an extraordinarily strong material in various environments. Our MD simulation, run for 3 ps, shows that the system can be trapped in a stable configuration even at 800 K in vacuum.

Similar to hydrogenation of graphene, the hydration of graphene leads to a semimetal–insulator transition of pristine graphene, as shown in figure 2. Our DFT calculation shows that graphanol with the herringbone hydroxyl surface has a direct gap of 3.22 eV, which is less than the 3.48 eV of graphane. This result is also consistent with a previous tight-binding study where either H^+ or OH^- absorbate on graphene was found to strongly suppress conductivity over a range of energy [10]. The plot of the DOS projected to local atomic orbitals (figure 2, right panel) reveals that the top of the valence band predominantly resides on the hydroxyl group and the carbon atoms, while the bottom of the conduction band is related to the single hydrogen and the carbon atoms. This indicates that an excitation of the system would be accompanied by a transfer of electronic charge across the C-atom plane, from the hydroxyl to the hydrogen-terminated side.

To understand the bonding nature of the system, we show in figure 3 the charge density difference between the graphanol structure and the superposition of charge of the individual free atoms placed at the same positions as in graphanol. As is clear from these plots, the herringbone reconstruction is driven by the hydrogen bond interaction between the depleted proton *s* orbital and one of the lone pair orbitals of the oxygen. The attraction between these two requires that

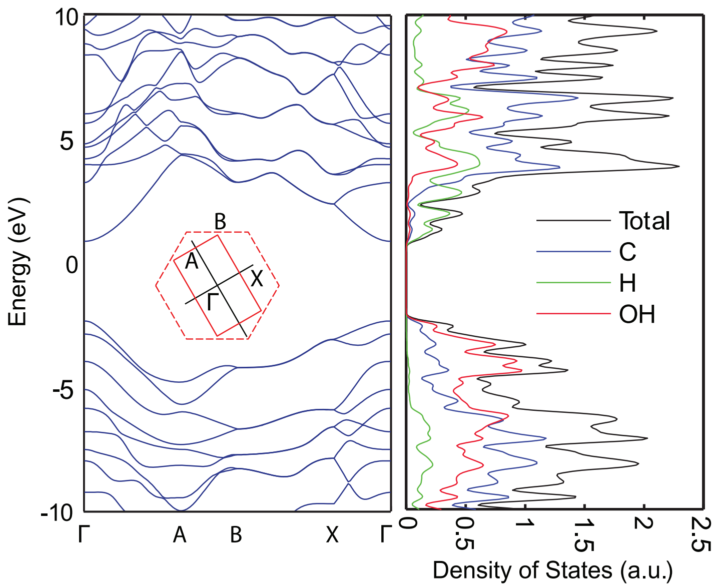

Figure 2. Band structure (left) and DOS projected to atomic orbitals (right). The first Brillouin zones of graphanol (solid red) and graphene (dashed red) are shown as insets, with the high-symmetry points labeled.

the O–H bond point in the direction of a neighboring oxygen, whose O–H bond in turn rotates away from that direction by 60° so that one of its lone pairs engages in strong interaction with the proton, along the zigzag line. This pattern matches the sixfold symmetry of graphene and results in a herringbone structure across the 2D crystal. Both C atoms in the unit cell of the herringbone structure have sp^3 hybridized orbitals, which form covalent bonds to the oxygen atoms on one side and to the hydrogen atoms on the other side, as is clear from figure 3(b). The charge difference is integrated in the plane of the membrane and plotted in figure 3(c) along the direction perpendicular to the plane. This leads to a net dipole moment of 0.2 eÅ (0.95 D) per unit cell, pointing toward the single protons. Compared to the dipole of a water molecule projected in one O–H bond direction, this value is reduced by a factor of 2, due to the separation of the positive and negative charges that form the dipole, by the intervening plane of C atoms, which mediates and partially screens their interaction. Remarkably, a macroscopic dipole moment should arise since all OH^-–H^+ units in the hydrate are aligned in the perpendicular direction as long as the C-atom plane remains flat.

Because of the thinness of the graphene membrane, the vibrational properties of the single atomic layer change dramatically upon hydration. We calculated the vibrational spectra at the Γ point of both graphene and graphanol using first-principles MD simulation of a 4×4 supercell that runs for 3 ps. The vibrational modes are extracted by Fourier transforming the velocity autocorrelation function. The C–C bond stretching mode is red-shifted from 214 meV (1726 cm^{-1}) for graphene to 152 meV (1226 cm^{-1}) for graphanol due to the added mass of the adsorbates and reduced bond order upon hydration. On the other hand, a new prominent higher-energy peak arises at 358 meV, which corresponds to the C–H bond stretching mode. Other peaks at 342, 190 and 104 meV, respectively, correspond to the O–H bond stretching mode, the O–H bond scissor mode and the C–H bond scissor mode. (See movies 1–9 in the supplementary data for the vibrational modes, available at stacks.iop.org/NJP/12/125012/mmedia.) The herringbone graphanol structure we consider here is metastable. Its formation from graphene

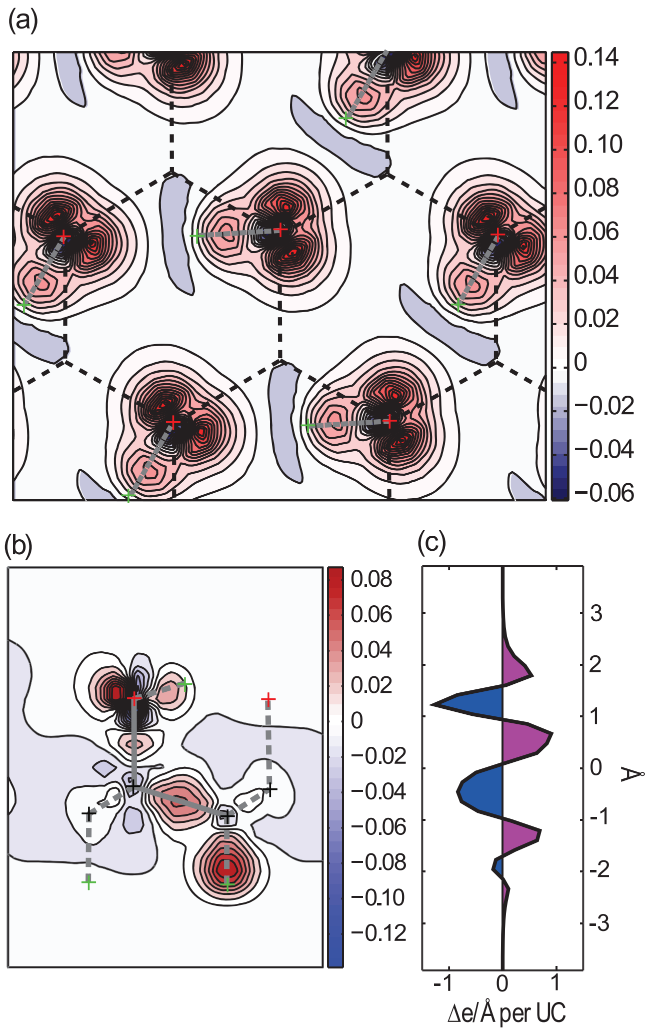

Figure 3. (a, b) Charge difference distribution (in units of eÅ^{-3}) of the system shown on the planes indicated in figure 1 as lines 'a' and 'b'. (c) Integrated charge difference along the direction perpendicular to the C-atom plane. The colored crosses mark the projected position of the atoms (green for H, red for O and gray for C), while the in-plane (out-of-plane) bonds are marked with solid (dashed) lines.

and H_2O is endothermal by 0.78 eV per C_2H_2O unit according to our calculations. Therefore, we do not expect these membranes to remain stable if an ensemble of them are randomly dispersed in solution where the protons and hydroxyl groups can directly interact with each other. We emphasize that the interesting properties of graphanol manifest themselves in single-layer graphene devices where the ions of opposite nature are strictly separated by a single-layer graphene. The experimental synthesis of graphane involved low-energy plasma that provides the kinetic energy to overcome the barrier for chemisorption [5]. For graphanol, the adsorbates on each side of the C-atom plane, namely the proton and hydroxyl groups, are opposite in nature. We suggest that graphanol can be synthesized in solution by controlling the pH value so that protons dominate on one side of the graphene membrane and the hydroxide anions dominate on the other. The formation of graphanol from graphene, proton and hydroxide anions

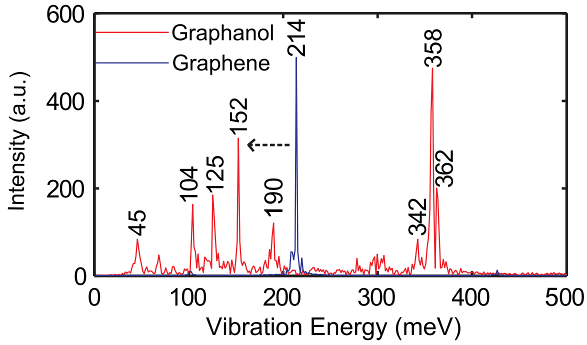

Figure 4. Calculated vibrational spectra (at Γ, the center of the Brillouin zone) of pristine graphene (blue) and of graphene upon hydration (red).

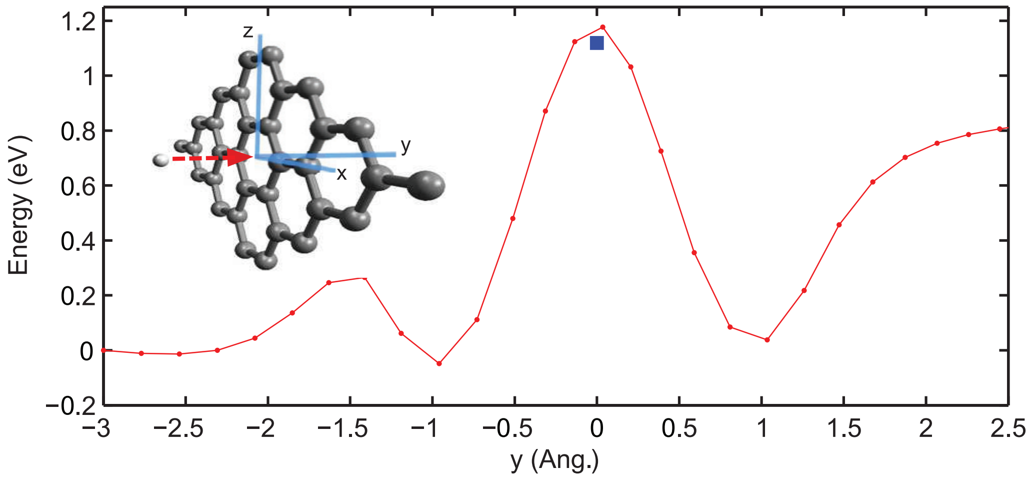

Figure 5. Estimation of the energy barrier for penetration of graphene by a proton. The proton (white sphere in the inset) moves through the center of a hexagonal ring in graphene with a minimum starting kinetic energy. The energy profile (red line) is the potential energy of the system (total energy minus the kinetic energy of the ions) at various proton–graphene distances in the MD simulation. The blue square marks the energy when the structure is relaxed with the proton fixed at the center of the hexagonal ring of graphene, giving a barrier of 1.17 eV.

is strongly exothermic, releasing 2.56 eV per C_2H_2O unit. One way to control this reaction in experiment is to apply a potential difference across the membrane in water, a setup that would establish the concentration difference and also a strong electric field across the membrane that helps overcome the barrier of chemisorption. Furthermore, in such a scheme, the reaction can likely be reversed by switching the direction in which the potential difference is applied. Indeed, recent experiments [11] observed such reversible conducting-to-insulating behavior in a gated graphene device and the origin of the transition was attributed to water.

An obvious question in the proposed graphene hydration scheme is whether ions of one type can penetrate the graphene membrane and end up on the wrong side. The hydroxyl ions are too large to achieve this, given the size of holes on the grahene layer, since the hexagonal carbon network of pristine graphene is dense and impenetrable to small gas molecules, such as helium [12]. The only relevant issue then is the possible penetration of the membrane by the protons. In order to address this, we have performed spin-resolved MD simulations to establish the energy barrier for proton penetration. Figure 5 shows the energy profile when a proton moves through graphene. The proton starts with a kinetic energy that is barely enough to penetrate graphene at the center of the hexagonal ring. The highest point of the profile corresponds to an upper bound of the required system energy for the penetration. We estimate a lower bound of the barrier by relaxing the structure with the proton held fixed at the center of the hexagonal ring. The barrier found is 1.17 eV. For hydrogen atoms and larger species, such as the hydroxyl groups, the penetration barrier is much higher. These barriers prevent protons or hydroxide anions from diffusing to the other side of graphene and recombine to form water instead of forming graphanol. It is worth pointing out that because of the strong interaction of the protons and hydroxyl groups across the atomically thin membrane, the formation of graphanol is favored (by 2.25 eV per C_2H_2O unit) over the formation of hydrogen and oxygen gas, in contrast to the situation in a bulk metal, for which hydrolysis of water could occur. The graphene hydration process described above represents a unique case where the reaction conditions are directly manipulated on a sub-nanometer length scale. Considering graphene as a giant flat molecule, a view originally suggested by Pauling [3], this reaction would consist of assembling a different type of a single macromolecule where the two ion species on each side of the C-atom plane interact strongly. Graphene is a mostly inert, strong and atomically thin material of semi-metallic character. Its range of applications could be broadly extended by introducing its insulating counterpart, the graphanol structure discussed here. For instance, such a thin membrane could prove very useful in studies of electronic DNA sequencing in ionic solution [13], where an insulating membrane could be essential in confining the electronic tunneling current to the nucleic bases for an easily detectable signal. Other possible applications may include electronic devices in which both the conducting and insulating parts are composed of single planes of C atoms, patterned from the same piece of graphene to form areas of pure graphene and graphanol, as required by the circuit design.

Acknowledgments

WW acknowledges support from the Nanoscale Science and Engineering Center of Harvard University, which is funded by the National Science Foundation.

References

[1] Lehninger A L, Nelson D L and Cox M M 2005 *Lehninger Principles of Biochemistry* 3rd edn (New York: Freeman) p 238
[2] Novoselov K S *et al* 2004 *Science* **306** 666
[3] Geim A K 2009 *Science* **324** 1530
[4] Sofo J O, Chaudhari A S and Barber G D 2007 *Phys. Rev.* B **75** 153401
[5] Elias D C *et al* 2009 *Science* **323** 610
[6] Nakamura J *et al* 2009 *Appl. Phys. Lett.* **94** 3
[7] Kresse G and Furthmuller J 1996 *Phys. Rev.* B **54** 11169
[8] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758
[9] Soler J M *et al* 2002 *J. Phys.: Condens. Matter* **14** 2745
[10] Robinson J P *et al* 2008 *Phys. Rev. Lett.* **101** 196803
[11] Echtermeyer T J *et al* 2008 *IEEE Electron Device Lett.* **29** 952
[12] Bunch J S *et al* 2008 *Nano Lett.* **8** 2458
[13] Branton D *et al* 2008 *Natl Biotechnol.* **26** 1146