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Effects of the substrate on graphone magnetism: A density functional theory study

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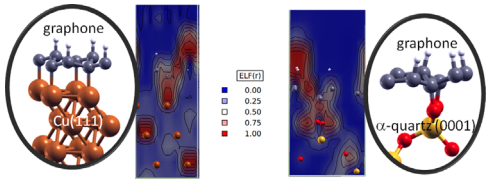
HIGHLIGHTS

- A DFT study of the adhesion of graphone to quartz and copper is presented.
- The magnetization of graphone adsorbed on copper is reduced by four times.
- In the case of adsorption on quartz, the magnetization is halved.
- The electron pairing of unpaired p-electrons plays a key role in quenching.
- Even a very small anisotropy can induce ferromagnetism above room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

The magnetism of graphone, a single-side-hydrogenated graphene derivative, has been related to the localized and unpaired p-electrons associated with the unhydrogenated carbon atoms. In the present density functional theory study, the effects the adhesion to either Cu(111) or α-quartz (0001) surface on the magnetic properties of graphone have been investigated. The total magnetization of the graphone adsorbed to copper and quartz surface is reduced by four and two times, respectively, with respect to the isolated graphone. We have shown there is electronic charge transfer from surface towards three-fold coordinated C atoms of graphone, but the main role in the partial magnetism quenching is played by bond formation and the consequent electron pairing of p-electrons. The critical temperature has been investigated on the basis of the mean field theory to evaluate the stability of the magnetism at ordinary temperature.

1. Introduction

Graphene, a monolayer and planar honeycomb structure of carbon atoms, has attracted great attention in the last years, due to its unique properties deriving from a very simple atomic structure [1]. It combines atomic thinness, high-carrier mobility, linear optical absorption, field-effect sensitivity, and high mechanical strength. A rich amount of papers has flourished investigating the fundamental physics and the practical applications of this wonderful material [2]. More recently, derivatives of graphene have been of large interest because of the possibility to add new functionalities to graphene and tune its electronic properties [3]. Among these graphene-related materials, we can mention, for example, graphane, a two-dimensional hydrocarbon constituted by graphene fully-hydrogenated on both sides of the plane [4]. The

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atomic configuration of graphane is related to the carbon atom sp^3 hybridization making it an insulator with a band gap of ~5 eV. The modification of graphane by removing hydrogen on one side results in a new different structure termed graphone. Density functional theory (DFT) calculations have estimated that graphone has a narrow band-gap of 0.5 eV and it is predicted to exhibit magnetic properties [5]. This features make graphone very interesting as a light magnetic material to be considered for substitution of metals and rare earths. For example, if we suppose that graphone could be packed in a graphite-like structure, the $T=0$ K saturation magnetization of graphone can be estimated to be around 450 gauss, comparable to the saturation magnetization of nickel, which equals 510 gauss [6], but with about one fourth of the weight. Recently, it has been found experimentally that highly hydrogenated graphene exhibits a weak ferromagnetism [7]. Graphone could be used as biocompatible magnetic material in biosensors or in carbon-based spintronic applications.

Graphone has been investigated in several studies [5, 8–19], and a possible technique for its synthesis has been proposed by Zhou and Sun [9] by *ab initio* calculations. However the synthesis of graphone remains an open challenge for the experimentalists. The magnetism of graphone has been related to the localized, unpaired p-electrons associated with the unhydrogenated carbon atoms. P-electrons are characterized by much larger long-range exchange coupling than D- or f- electrons giving rise to long-range coupling between 2p magnetic moments. Notably, it has been found that a direct substitution of C atoms with B atoms decreases the p–p interactions which weaken the nearby C magnetic moments [20]. The stability of isolated graphone has been questioned: prior MD simulations reported isolated graphone to be stable at room temperature after 3 ns runs [5], but more recent calculations [10] over longer runs and larger system sizes confuted this stability. On the other hand, long nanoribbons of graphone have been predicted to spontaneously roll up to form spiral shapes and to be stable up to 1000 K [10].

In the bottom-up approach the direct synthesis of hydrogenated graphene could be achieved by using chemical vapor deposition (CVD). For example, the growth of graphane-like films during plasma-assisted CVD has been reported to occur on Ti/Cu substrates at the temperature of 650 °C [21]. As for graphene, after the growth the films can be transferred to arbitrary substrates; often silicon dioxide surfaces for several applications and characterizations. In a previous paper [22], we have investigated the interaction between graphane and the surface of the copper substrate.

In this paper, we study the adhesion of graphone to copper and α-quartz by DFT calculations, using an exchange-correlation functional corrected for long range interactions. We calculated the effects of the adsorption on magnetism in the resulting systems. We want to investigate under which circumstances the interaction of graphone with a substrate can just reduce or completely quench its magnetism and at the same time whether it can rather protect unpaired p-electrons from the interaction with environment. The critical temperature has been investigated on the basis of the mean field theory to evaluate the stability of the magnetism at ordinary temperature. Graphone can form several conformational isomers in a similar way to graphane and the “boat”, which allows carbon dimers to be in the same plane, is the conformer with the lowest total energy. This conformer does not show magnetism, so that we have concentrated our study to the magnetic isomer, the “chair” conformer, where the first-neighbor C atoms are never in the same plane.

2. Methods

The computational approach was based on a pseudo-potential plane-wave method using PWSCF code as implemented in the QUANTUM-ESPRESSO package [23]. We used the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) exchange-correlation functional [24] including the empirical correction of the long range forces (DFT-D) [25]. The pseudo-potential plane-wave calculations were performed using Vanderbilt ultra-soft pseudo-potentials [26]. The convergence of the total energy has been checked by varying the cut-off and the grid of kpoints to reach a good compromise between accuracy and computational times. All geometry optimizations were performed with cut-off for the wave functions of 30 Ry, cut-off for the charge density of 300 Ry and $6\times6\times1$ Monkhorst–Pack grid, allowing a convergence of the total energy below 0.0002 Ry/atom. The final self-consistent calculations of the optimized structure properties used a cut-off for the wave functions of 40 Ry, a cut-off for the charge density of 400 Ry and $10\times10\times1$ Monkhorst–Pack grid granting a convergence below 0.00007 Ry/atom. The Cu(111) surface was modeled by the repeated slab geometry which contains six Cu atomic layers with the in-plane 2×2 unit cell. For the α-quartz structure, the in-plane 1×1 unit cell of the (0001) surface was chosen, composed by three atomic tri-layers, the bottom layer being passivated by H atoms. The 2×2 cell of graphone can be matched properly to copper and α-quartz surfaces. The vacuum gap between graphone and slab periodic image was set to 20 Å. The graphone, the top four copper layers and the top two α-quartz tri-layers were fully relaxed with a convergence threshold of 0.001 Ryd/Å on the inter-atomic forces. We optimized the unit cell of each structure by imposing that the stress on the cell is less than 0.04 GPa. Dipole corrections have been also included in the calculations. The partial atomic charges by the Bader method [27] have been calculated as post-process analysis of a self-consistent total energy calculations performed using PAW pseudo-potential, with the cut-off values of 100 Ry for the kinetic energy and 600 Ry for the electron density.

3. Results and discussion

3.1. Isolated graphone

The lattice cell of isolated graphone has been fully optimized resulting in a lattice parameter $a=$ 5.030 Å. This parameter preserves a low stress on the cell also when the interface with Cu(111) slab is considered. Upon geometry optimization, carbon atoms are disposed into two distinct layers, where in one layer each carbon atom C_1 has three single bonds with carbon atoms and one single bond with hydrogen atom out of plane, while in the other layer each carbon atom C_2 has three single bonds with carbon atoms and one p-electron unpaired. We reported the geometrical parameters in Table 1, where Δz is the distance from the layer containing the sp^3 hybridized hydrogenated C_1 atoms to the layer containing the not saturated sp^2 hybridized C_2 atoms. The magnetic properties are due to the localized and unpaired electrons in the three-coordinated C_2 atoms. This is different from graphene, where π-electrons are delocalized, and from graphane, where the electrons are forming strong σ bonds. We have found that the

Table 1
Geometrical parameters for isolated graphone by varying the magnetic state and graphane. Bond lengths are in Ångstrom, angles are in degrees.

	$d(C_1–C_2)$	$d(C_1–H)$	Δz	$a(H–C_1–C_2)$
Graphone FM/AF	1.49	1.16	0.33	102.85
Graphone NM	1.47	1.17	0.25	99.85
Graphane	1.53	1.11	0.45	107.50