



Hydroxylated graphyne and graphdiyne: First-principles study



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ABSTRACT

First-principles calculations are performed to study the favorable geometries and corresponding electronic properties of hydroxyl functional group (–OH) decorated monolayer graphyne and graphdiyne (MGY and MGDY). The energetically favorable high coverage –OH decoration configuration shows ordered chiral-like structure on adjacent big triangle carbon rings and hexagon due to the stabilization of the hydrogen bonding between these groups. In contrast to the hydrogenated graphyne and graphdiyne, it is an unstable geometry when all carbon bonds are saturated to single bond. It is found that –OH can introduce magnetism in the systems but the magnetic properties can only survive at low –OH concentration. –OH pair forming hydrogen bond between two –OH groups are usually nonmagnetic due to the antiferromagnetic coupling between them.

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1. Introduction

Graphene, a two dimensional (2D) sheet of sp^2 -hybridized carbon atoms, has received significant attention because of its importance in fundamental physics and potential applicability in nanoelectronics [1–4]. However, due to the zero-gap electronic structure of pristine graphene, its direct utilization in various devices is limited. Thus, considerable efforts have been made to widen the electronic band gap of graphene. 2D carbon materials with suitable band gap include graphyne [5], which is composed of two types of hybridized carbon atoms, namely, sp and sp^2 -hybridized carbon. γ -Graphyne is made up of hexagonal carbon rings and acetylene linkages, i.e., the sp^2 -hybridized carbon atoms that form hexagons joined together by acetylene linkages (–C≡C–). New carbon modalities, similar to the formation of graphyne, can be achieved by increasing the number of alkyne linkages between the hexagon rings, e.g., if the linkage is butyne, the system is γ -graphdiyne. Thus far, there have been considerable experimental efforts [6–8] to synthesize these unusual materials for implementing them in nanoelectronics. Interestingly, graphdiyne films have been grown on the surface of copper via a cross-coupling reaction using hexaethynylbenzene [9]. The preparation of γ -graphyne is reasonable because previous theoretical work has

demonstrated that γ -graphyne is more energetically favorable than γ -graphdiyne.

Much attention has been paid to γ -graphyne and γ -graphdiyne, hereafter referred to as graphyne and graphdiyne, respectively, due to their excellent electronic properties, including small carrier effective mass [10,11], high carrier mobility at room temperature [12], and hydrogen storage capacity [13–15]. In addition, its outstanding mechanical properties [16–18] enable many functional applications. To expand their applications to nanoelectronics, modulation of their electronic properties is essential. Similar to graphene, recent works have demonstrated that cutting, strain, and doping are all important for modulating the electronic properties of graphyne. For instance, Pan et al. [19] found that both graphyne and graphdiyne nanoribbons are semiconductors and their band gaps decrease with an increase in ribbon width. The band gap of graphyne can be continuously tuned under uniform strain [11]. Bu et al. indicated that doping with a unit of BN can effectively modulate the energy gap of graphdiyne. Meanwhile, its direct band type remains unchanged regardless of the doping rate [20]. Similar to graphene, several recent works have demonstrated that the electronic properties of graphyne can be chemically modified through adsorption. For example, the adsorption of transition metals to large graphyne and graphdiyne pores yield excellent spin electronic structure, suggesting their potential use in spintronics [21]. Tan et al. [22] found that at low coverage, the hydrogen atoms prefer to chemically adsorb to the acetylene carbon atoms. Moreover, the band gap of hydrogenated graphyne is tunable over a wide range from 0.45 to 4.43 eV with changing hydrogen coverage. Koo et al. [23,24]

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found that hydrogen or halogen atoms can tune the band gap of graphyne by 3–5 eV by varying concentration. Moreover, they found that halogen atoms can form sp^2 bonds with sp -hybridized carbon atoms, which differs from graphene. Kang et al. [25] found that the electronic properties of graphyne can be tuned by altering the oxygen coverage, which indicates that oxygenation is a promising method for functionalizing graphyne to achieve the designated properties. Previous experimental and theoretical investigations have confirmed the existence of oxygen atoms and OH groups on graphene that may exhibit some ordered adsorption structures. Further analysis has shown that functional groups, such as oxygen and hydroxyl (–OH) groups, and combinations of the two, have significant impacts on the electronic structure of graphene [26,27]. Recently, graphdiyne has been synthesized in an alkaline solution on copper foil via a cross-coupling reaction with a monomer of hexaethynylbenzene [9]. XPS spectra of graphdiyne films show the presence of oxygen, so it is possible that graphdiyne has similar properties as graphene. To assess their applicability in nanoelectronics, it is important to study the influence of –OH groups on the electronic structures of graphyne and graphdiyne.

2. Computational method

We performed first-principles calculations using density functional theory (DFT) implemented with the Vienna ab initio simulation package (VASP) [28,29]. The projector augmented-wave (PAW) method [30,31] was used for describing the interactions between valence and core electrons, and the electron–electron interaction was treated with a generalized gradient approximation (GGA) using the exchange–correlation function proposed by Perdew, Burke, and Ernzerhof (PBE) [32]. A kinetic energy cutoff of 400 eV was selected for the plane wave basis set. In the calculations, G-centered k-point mesh generated by the Monkhorst–Pack scheme was used for the numerical integrations over the Brillouin zone. The k-point was set to $5 \times 5 \times 1$, $7 \times 7 \times 1$, and $7 \times 7 \times 1$ for structure optimization, energy, and density of states (DOS) calculations, respectively. All of the studied systems were fully relaxed (the lattice constants and atomic coordinates are all simultaneously optimized) when their atomic forces became less than 0.01 eV/Å, and the energy convergent criterion was set to 10^{-5} eV. A dipole correction was applied because of the impact of the adsorption of the –OH group on various potential distributions. Since the cohesive energy per atom does not provide a suitable measure for evaluating the relative stability between systems with different compositions, we apply the formation enthalpy, ΔG [33,34], to quantitatively evaluate the relative stability. ΔG is expressed as,

$$\Delta G = E_{tot} - \sum \chi_i \mu_i. \quad (1)$$

The term E_{tot} is the cohesive energy per atom of the hydroxylated system considered here, χ_i (i denotes H, C, O) is the molar fraction of the atoms in the structures that obey $\sum \chi_i = 1$. μ_i is the chemical potential of the constituents at a given state. μ_C is considered the cohesive energy per atom of pure graphyne. μ_H is taken as the binding energy per atom of H_2 , and μ_O is the binding energy per atom of O_2 .

3. Results and discussion

3.1. Stable hydroxylated structures of graphyne and graphdiyne

We first consider a single –OH group on graphyne. Similar to hydrogenated graphyne, several adsorption configurations are considered, including in-plane, out-of-plane, and oblique-plane geometries, as well as the orientation of different O–H bonds. It should be noted that the above three geometries are defined by the

angle between the C–O bond and the graphyne/graphdiyne plane. The C–O bonds with 0° and 90° geometries are defined as having in-plane and out-of-plane configurations, respectively, whereas those geometries between 0° and 90° are defined as having oblique-plane configurations. Our calculations indicate that the out-of-plane configuration is most favorable. Similar to hydrogenated graphyne, a single –OH group can easily adsorb on a sp -hybridized carbon atom of an acetylene chain, referred here as MGY–OH. We define the acetylene chain as L1, as shown in Fig. 1(a). The –OH group is found to induce a slight local distortion of the graphyne plane. As is shown in Table 1, the carbon atom covered by an oxygen atom extrudes out of the graphyne plane by approximately 0.701 Å. The oxygen atom is positioned on top of an L1 sp -hybridized carbon atom of with the O–C bond nearly perpendicular to the graphyne plane. The O–H bond length is 0.978 Å, which is in agreement with the O–H bond length of graphene oxide [26,27]. The C–O bond length is 1.401 Å, slightly shorter than the C–O bond in graphene oxide, and the C–O–H bond angle is 108.22° , slightly smaller than the bond angle in H_2O . As shown in Fig. 2(a), if we define ΔG of graphyne as the reference, ΔG of MGY–OH is 0.127 eV lower than the ΔG of pure graphyne, which indicates that the formation of MGY–OH is energetically more favorable than that of pristine graphyne.

When we apply the second –OH group on graphyne, there are still several possible adsorption configurations. The optimal structure exhibits out-of-plane geometry, as shown in Fig. 1(b), referred to as MGY–2OH. As shown in Fig. 2(a), the ΔG of MGY–2OH is 0.247 eV lower than MGY–OH, which indicates that the formation of MGY–2OH is energetically more favorable than that of MGY–OH. Adsorption of the first –OH group on one sp -hybridized carbon atom leaves an unpaired electron of its nearest sp -hybridized carbon atom, which will serve as the reaction center of subsequent –OH group adsorption. The results indicate that the second –OH group also favors adsorption on the sp -hybridized carbon atom that belongs to L1. Moreover, the two –OH groups prefer to adsorb on opposite sides of the graphyne plane, and the two O–H bonds point in the opposite direction. As shown in Table 1, the two MGY–2OH –OH groups will lead to a larger undulation (0.917 Å) of the graphyne plane. The C–H bond length is 1.385 Å, which is slightly smaller when compared with the single –OH group on graphyne. The O–H bond length is exactly the same as shown in Fig. 1(a) (0.978 Å). The C–O–H bond angle is approximately 0.77° larger when compared with the single –OH group on graphyne.

The above mentioned calculations demonstrate that the adsorption of an –OH group to sp -hybridized carbon atoms is easy and tends to saturate an entire acetylene chain and then another. Hence, in consideration of the structure shown in Fig. 1(b), it is natural to expect the formation of a novel 2D hydroxylated graphyne material, whereby all sp -hybridized carbon atoms are saturated with sp^2 -hybridized carbon atoms attached to –OH groups, as shown in Fig. 1(c), referred to here as MGY–6OH. As shown in Fig. 2(a), the formation enthalpy of MGY–6OH decreases significantly with respect to pristine graphyne by approximately 0.751 eV, which implies an energetically stable configuration exhibiting significant potential for experimental fabrication. The calculations indicate that the structural fluctuation of MGY–6OH is 0.014 and 0.231 Å smaller than that of MGY–OH and MGY–2OH, respectively. The C–O bond length is 1.395 Å, and the $\angle COH$ is approximately 108.7° , as listed in Table 1.

We further increased the –OH group coverage rate on graphyne, specifically increasing the –OH group coverage on the carbon atoms located in the hexagonal ring of MGY–6OH. As shown in Fig. 1(d), the calculations suggest that the geometry is energetically favorable. We denote this new structure as MGY–12OH, where only carbon–carbon double bonds (–C=C–) exist in acetylene carbon chains and single carbon bonds (–C–C–) exist in hexagonal rings. Table 1 clearly shows that the C–O bond length and the $\angle COH$ in

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