Li-decoration on the edge oxidized graphyne and graphdiyne: A first principles study

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ABSTRACT

In recent years, the new two-dimensional planar carbon allotropes, graphyne and graphdiyne, have received significant research attention. Accordingly, the present study is devoted to investigate how the electronic structures of graphyne and graphdiyne nanoflakes are modified upon the edge oxidizing as well as Li-decoration. Different oxygen containing groups such as carbonyl, ketone, hydroxyl, carboxylic, formyl, and epoxide are considered for oxygenation of these carbon surfaces. The stability of oxidized surfaces with respect to the bare sheets has been discussed in terms of Gibbs free energy of formation. We showed that carbon surfaces terminated with carboxylic group are more stable than other oxidized surfaces. It is also found that the band gap in considered surfaces can be tuned (0.53–1.51 eV) by changing the type of oxygen containing group. Moreover, we report the binding energies for the Li adsorption at hollow sites on the basal plane and on the oxygen of functional group. Our calculations reveal that the interaction between oxygen group and carbon atoms at the edge increases the reactivity of considered sheets toward Li adsorption. The band gap of fuctionalized surfaces can be engineered by selective lithiation over a wide range between 0.01 and 1.31 eV. We found that the oxygen species plays the key role on the Li adsorption on the edge oxidized surfaces leading to either semiconducting or metallic behaviors. However, this study offers critical information for further theoretical and experimental studies on oxidized carbon materials for their possible applications in lithium ion batteries as well as hydrogen storage materials.

1. Introduction

The capability of carbon atoms to form complicated networks surprises the world with various allotropes and fantastic physical properties. In the recent two decades, different carbon structures from fullerene, to carbon nanotubes, and to graphene have been discovered. These nanomaterials with sp^2-like hybridized carbon atoms have been of intense interest and have made significant contribution to the development of modern nanotechnology. Besides the naturally existing allotropes many artificial allotropes have also drawn worldwide attention in recent years [1–6]. As new forms of non-natural carbon allotropes related to graphite/graphene, graphyne (GY) and graphdiyne (GDY) have been the subject of interest for their outstanding structural and electronic properties. It has been predicted that GY, assembled layers of sp- and sp^2-hybridized carbon atoms, has a high possibility of synthesis [7]. GDY has been successfully synthesized on the surface of copper via a cross-coupling reaction using hexaethynylbenzene

[8,9]. Planar GY and GDY are consisting of carbon hexagonal rings and butadiene linkages [10,11]. The presence of acetylenic groups means that GY and GDY can exist in geometries other than the hexagonal lattice of graphene which in turn introduces a rich variety of optical and electronic properties that are quite different from those of graphite [12–14]. Moreover, the porous structure and large surface area in GY and GDY may allow potential applications in energy storage materials [15–17]. They are also promising candidates for the anode material in lithium battery applications because of their higher lithium mobility and higher lithium storage capacity than graphite [18–22]. There have been experimental efforts to synthesize GY and GDY nanoflakes providing evidence that the synthesis of GY and GDY is possible [23–26].

Like graphene, the edge sites of GY and GDY with dangling bonds are more reactive than the basal plane of strong covalent bonding with highly delocalized π electrons. These dangling bonds at the edge are at disposal for covalent attachment of various chemical moieties to impart solubility and reactivity of the surface. It has been shown that functionalization changes the morphology, elastic, and electronic properties and also modifies transport characteristics of nanostructures [27,28]. On the other hand, these

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nanomaterials can be decorated with metals to increase the sensitivity, selectivity, limit of detection, or a combination of these properties. Recently, extensive researches have been initiated toward the development of metal decorated nanostructures for their promising energy storage application. The energetics and dynamics of Li atom on the GY has been studied by Zhang et al. [18]. They found that the high Li mobility and high storage capacity make GY a promising candidate for the anode material in Li-ion battery applications. Moreover, the application of Li decorated GY as the hydrogen storage materials was modeled by Srinivasu and Ghosh [19]. Also, Li et al. [15] and Hwang et al. [17] showed that the GY can be used as an ideal framework material to hold the Ca atoms. In another work, the electronic and magnetic properties of single 3d transition metal atom (V, Cr, Mn, Fe, Co, and Ni) adsorbed GY and GDY were systematically studied using density functional theory (DFT) [29]. Besides the energy storage applications, the sensitivity of GY(GDY)-based gas sensors can also be improved by metal decoration [30–33]. However, in order to develop efficient energy storage materials and high performance gas sensors, tuning the electronic properties of these surfaces for the desired reactivity and sensitivity is a critical step. In this contribution, we perform first principles calculations within DFT framework to study the impact of Li-decoration on the reactivity of edge oxidized GYs and GDYs. Several oxygen containing groups such as carbonyl, ketone, hydroxyl, formyl, carboxylic, and epoxide are considered for oxygenation of these carbon surfaces. The electronic properties of obtained graphyne oxide (GYO) and graphdiyne oxide (GDYO) substrates and the extent in which these functional groups affect the strength of the interaction with Li adsorbents are investigated. In fact, we explore the reactivity enhancement of GY and GDY surfaces after oxygenation and metal decoration.

2. Computational details

All calculations are performed using DFT methods as implemented in GAUSSIAN09 suit of programs [34]. The structures are relaxed and the electronic properties of the systems are calculated with generalized gradient approximation (GGA). The Perdew–Burke–Ernzerhof (PBE) functional has been used to treat the exchange correlation part of the density functional [35]. The basis set is split-valence double-zeta with inclusion of polarization functions, 6-31G (d). Although the DFT-GGA methods have been widely used to study the metal decorated carbon surfaces and achieved good agreements with experiments [36,37], one has to be aware that the approximate functional suffers from the disregarding long range interactions and underestimated the binding energy of the charge transfer complex. Therefore, in order to taking into account the van der Waals forces in our adsorption systems, we have also computed the binding energies by M06-2X functionals which has been developed for treating noncovalent interactions [38].

The model GY and GDY are nanoflakes containing 66 and 90 carbon atoms, respectively (Fig. 1). These flakes are functionalized by a single oxygen containing groups including carbonyl (–CO), ketone (–O), hydroxyl (–OH), formyl (–COH), carboxylic (–COOH), and epoxide ($\triangle$). To avoid boundary effects, atoms at the open ends of the sheet were saturated with hydrogen atoms. All structures have been fully relaxed to account for any rearrangement in the carbon surface (CS) due to the presence of oxygen groups. The binding energy between lithium atom and functionalized CS is calculated by

$$E_{bind} = E_{Li_n-CS} - (E_{CS} + n\, E_{Li}) \qquad (1)$$

where n is the number of adsorbed Li atoms, E_{Li_n-CS} is the total energy of the Li$_n$-CS structure, E_{Li} is the total energy of a single Li atom, and E_{CS} is the total energy of functionalized CSs.

It is should be mentioned that as we are employing a finite localized basis set, our calculations are subject to basis set superposition error (BSSE). It is common to estimate BSSE by using the counterpoise correction method, however, such calculations are very demanding due to the large number of configurations studied here and the different spin polarized ground states of the fragments. On the other hand, previous studies indicate that basis set truncation introduces an error in the computed binding energy smaller than 4% [39]. For this reason, we neglect the BSSE correction in this work.

3. Results and discussion

3.1. Edge oxygenation of GY and GDY

The relative stability of edge modified GYs and GDYs are very important in practice. Since these structures have different chemical compositions, the binding energy per atom does not provide a suitable measurement for the comparison of their relative stability. Therefore, we adopt the approach used in tertiary phase thermodynamics to account for chemical composition and to analyze the relative stability of GYOs and GDYOs [40]. We define the Gibbs free energy of formation δG for edge modified CSs as

$$\delta G = E_c - n_H\mu_H - n_O\mu_O - n_C\mu_C \qquad (2)$$

where E_c is the cohesive energy per atom of functionalized CSs, and n_i is the molar fraction of atom i (i = C, O, H) in the CSs. The binding energy per atom of H$_2$ and O$_2$ molecules are chosen as μ_H and μ_O, respectively, and μ_C is the cohesive energy per atom of the single GY or GDY sheets.

The calculated δG for considered GYOs and GDYOs are shown in Fig. 2. The δG values of the hydrogen saturated GY and GDY are taken as reference. The dependence of δG on the type of functional is similar in the GY and GDY surfaces. The most stable structures correspond to CSs terminated with –COOH group, having greatest negative δG value which may be due to the resonance stabilization. This is consistent with the observation of Uthaisar et al. [41] who point out the stability of graphene nanoribbons functionalized with carboxylic acid groups. Moreover, Gao et al. [42] suggested that thermal decarboxylation of graphene oxide occurs at higher annealing temperature. Fig. 2 also indicates that, due to the ring strain in the three-membered ring, the CSs modified by epoxide group are less stable and have larger δG than the H-saturated CSs. The energies of highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), their gap (E_g), and the Fermi energy (E_F) of each structural model are presented in Table 1. A quick look at the data in Table 1 reveals that, in general, the oxygenation leads to shift of HOMO and LUMO levels to higher and lower energies, respectively. Thus for all considered GYOs and GDYOs, the band gap reduction can be seen as compared to their corresponding bare CSs. The only exception is GDY_COOH for which a slight band gap increase is observed. The change in the electronic structures of studied CSs can be due to the interaction between the edge carbon atom and oxygen atom which is likely because of the difference between electronegativity of oxygen atom relative to the edge carbon atoms. However, the band gap reductions of the oxygenated CSs are sensitive to the functional group. The greatest reductions in E_g are observed for the carbonylated and formylated CSs. In these cases the large shifts of HOMO and LUMO levels reduce the band gap of bare GY(GDY) from 1.42 (1.49) eV to 0.53(0.54) eV in GY_CO(GDY_CO) and to 0.81 (0.83) eV in GY_COH (GDY_COH). However, we have demonstrated that the tunable E_g (0.53–1.51 eV) can be engineered by edge functionalization of these CSs.