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First principles studies on band structures and density of states of graphite surface oxides

ABSTRACT

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Graphite oxide constitutes carbon network with oxygen atoms both on hexagonal arrangement and the edge sites. Structural and electronic properties for graphite-oxygen complexes have been explored using first-principles total-energy calculations within the local density approximation (LDA). Band structures and density of states for the propose carbon 3D models are reported. A finite energy gap and planarity of graphene layer emerges for the oxygen-functionalized graphite, therefore its value varies with the ratio of carbon to oxygen and sites on carbon network.

Keywords: *Graphite oxides; Band structure; Density of states; Local Density Approximation; First-principles.*

INTRODUCTION

The application of graphite materials are determined by its surface functional groups, which anchored on or within the graphite structure. Various methods are available for producing oxygen functionalities on graphite. Surface graphite-oxygen complexes, i.e graphite oxides (GO) are formed on graphite by gas-phase oxidation in graphitization-activation process; by reacted with various oxidizing agents, e.g, CO₂ [1] and chemical oxidizing agents in solutions, e.g., HNO₃ [2]. Intensive research were carried out both experimentally and theoretically for characterization of surface functional groups of the modified graphite materials, since these groups significantly facilitate electrical conductivity and capacitance processes [3, 4]. Oxidation processes could both increase and decrease capacitance, i.e. acid oxidation of graphite with concentrate nitric acid rise capacitance up to 10 fold whilst high pressure steam oxidation reduced capacitance. Some authors suggested that this condition are arise due to the change in surface functional groups that in further change the crystallography of graphite [5]. The change in crystallography led to change of electrical resistivity of graphite [6].

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Graphite is consisted of comprehensively stacked layers of condensed hexagonal rings. Two layers are needed to build the unit cell in graphite since the two sheets are translated from each other by a C-C distance ($a_{CC} = 1.42 \text{ \AA}$) [7]. The three-dimensional structure of graphite is therefore held together by weak interlayer van der Waals forces including some electronic delocalization [8]. These π bonds, perpendicular to the graphene sheet, are responsible for this weak interaction between carbon layers in graphite. However there is no information about the about the type and how many functional groups that can affect crystallography that could ultimately affect the electrical and electrochemical properties of graphite materials. Despite this widespread importance, numerical accesses to this crucial parameter remains quite elusive both from an experimental and theoretical point of view. In the following, we present computational methods allowing deriving electronic structures directly from crystalline structures. The method being straight forward, cheap and reliable for digging up electronic structure of graphite materials [9].

EXPERIMENTAL

The electronic properties were investigated using the ABINIT density functional code [10] within the local density approximation (LDA) scheme. This numerical technique in spite of not explicitly accounting for the van der Waals part of the interlayer interaction, has been proved to give the correct equilibrium structure and to be accurate enough to tackle the complex band structure of 3D graphites in the vicinity of fermi energy. A standard non-relativistic pseudopotential was used for the carbon element, and the plane wave basis set was given 35 H of cutoff energy. The total system consists of a 8×8 graphene supercell (32 C atoms) with one or some functional groups attached on the edges or basal of graphite layer as shown in Figure 1. Graphite and GO are modeled has two or three layers of graphene. The sampling of the Brillouin zone is done using a $5 \times 5 \times 2$ Monkhorst-Pack 15 grid ensuring the convergence of Kohn-Sham states i.e, K, G (usually denoted as Γ), A and M. The structures were optimized prior to the electronic study. For the calculation of the density of states

(DOS) we use a $15 \times 15 \times 2$ Monkhorst-Pack grid and a Gaussian smearing of 0.5 eV. The structures of GO were obtained from optimized and non-optimized cell geometric. This basic structure of carbon atoms was then decorated with oxygen atoms on one of graphene or both graphenes and the type functional group could be epoxide, ketone, ether and ester. One to four of oxygen on the surface represented a low oxidation level of graphite. More than eight of oxygen atoms were considered to be high level oxidation level.

RESULTS AND DISCUSSION

The unit cell ($a = 4.92$, $b = 4.92$ and $c = 6.80$) of the GO layer of model contains 16 carbon atoms in a hexagonal framework. The results show graphite layers both warp and unwarp around the oxide sites. The deformation depends on the existing oxides. Most of mid to high oxidation level GO wrinkle after subjected optimization. Such that situation also found in GO containing epoxide functional groups. Figure 1 illustrate some wrinkle structures of GO. In these structures, the existing of oxygen atom stretches the underneath C-C bonds but not to damage the sp^2 carbon framework. As the increasing of the lattice constant, the epoxide in GO disintegrates into a more stable unzipped phase with sp^2 bond underneath the oxygen atom broken [11].

The planar structures of the graphite are maintained by existence of symmetrical arrangement in hexagonal framework. Planarity of graphene structures can be broken by the existence of out-of-plane epoxides, ketones, and dioxin. Therefore, energy for symmetrical arrangement of the ethers in Figure 1(B) are much more lower than its formation energy. Conversely, planarity of graphene can be maintained on the presence of a carboxylic structure accompanied by the destruction of σ - bonds in the carbon chain. Figures 1(E) and 1(F) represent the carboxylic groups on graphite structures before and after optimized, respectively for illustrated planarity in carboxylic GO. Practical implications for this situation are the oxidation of carbon to the carboxylic structure can be used in forming the nano-size carbon without damaging the weak bonds between layers.

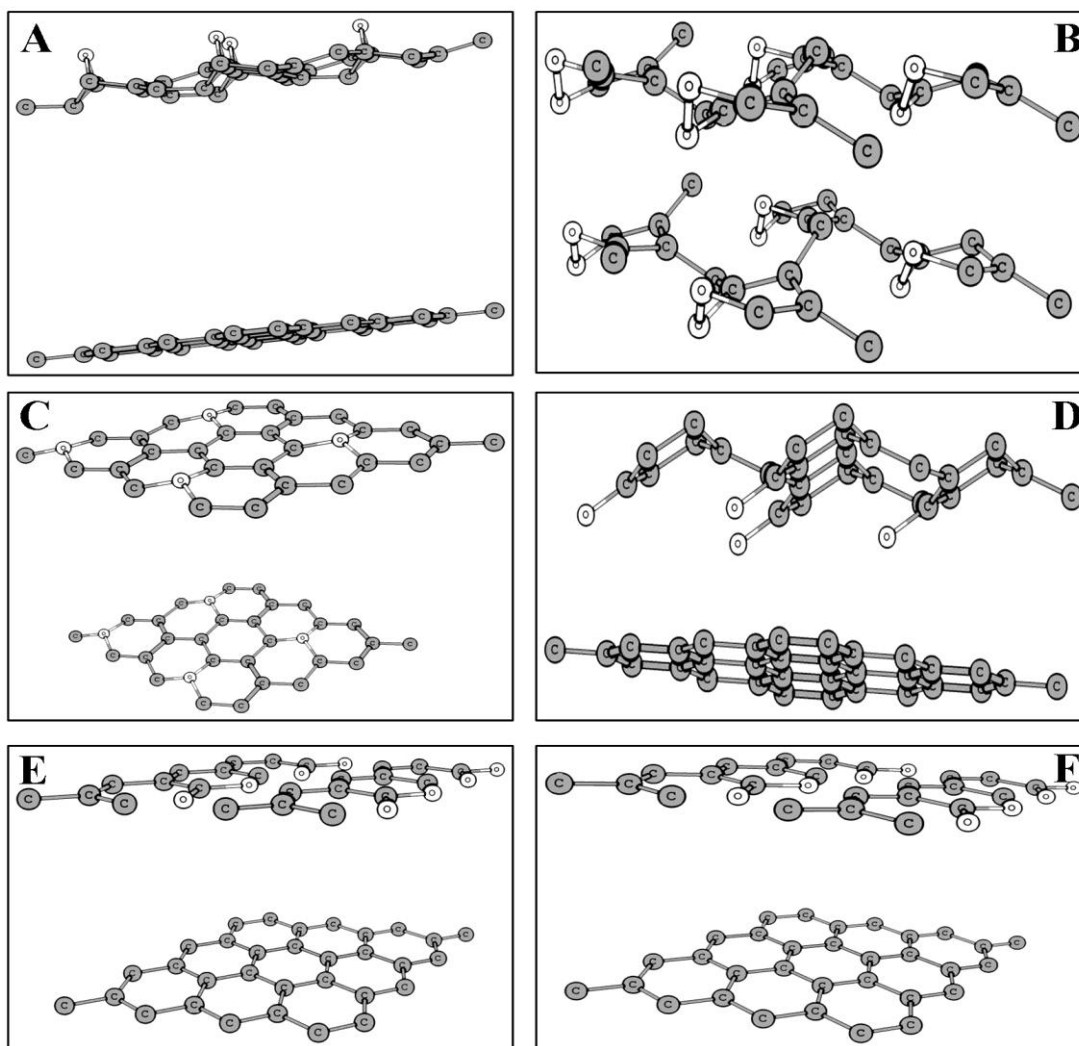


Fig. 1. Some graphite oxides from various functional groups show buckle structures A. epoxide type, represents bond between the carbon - oxygen in the basal plane of graphite structure, B. dioxine, C. ether, D. ketone, E and F. carboxylic.

The changes that occur in every interaction of electrons before and after oxidation can be described by the density of states (DOS) plot in Figure 2. The binding of various groups also disrupts the electronic structure of GO by spoiling the local electron states. It can be inferred from the figure that two lines in panel A significantly reduce its size and peaks (see Figure 2(B), (C) and 2(D)). It can be shown that electrons in p-orbital were dominated the states. Since the plots are sum of electrons in those typical orbitals, then the electrons will be populating p-orbital degenerated from π -bondings to unpaired electrons.

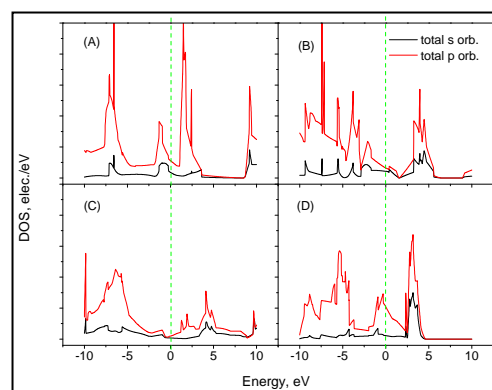


Fig. 2. Plot DOS for the graphite (A) and GO. GO are modeled as eight atoms for one unit cell contain one oxygen atom in edge (B), basal (C) of planar layer and out-of-plane (D) site. Plots are constructed from total local DOS each atoms. Black and red lines represent DOS of electron in s and p – orbitals, respectively.

Each DOS of typical GO are used for determine type of bonding that dominate in the C – O bonding. In Figure 4, most of electrons are in the valence bands except for graphite. This indicates that after oxidation electronic character of graphite significantly changes.

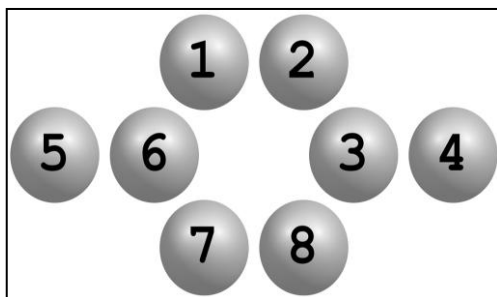


Fig. 3. Template for atoms and atom positions in modeled graphite and GO unit cell. Each of circles represents atoms C or O in those positions represented by the numbers.

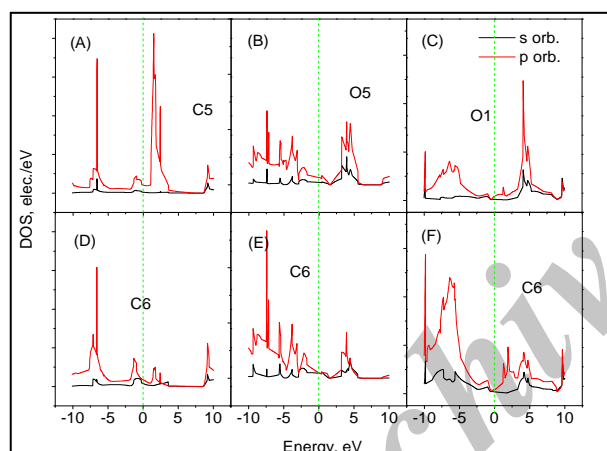


Fig. 4. Plot DOS for atom pairs that contributed GO (C – F). A and B are included as references. C5, C6, O1 and O6 denoted as carbon and oxygen atom those in position 1, 5 and 6 of graphite unit cell. A and B are atom pair in graphite; C and D are atom pair in edge site of graphite oxide; E and F are atom pair in basal site of GO.

The electronic band structure and the corresponding DOS of graphite and GO are shown in Figure 5. Band structures of GO are denser than graphite has, this feature is confirmed with DOS plots. The magnitude of DOS increase 2 – 4 times from graphite to GO and the band gaps can be calculated from band structures.

In spite of the most GO showed the dense band structure, some type of GO have inverse effect on the band gaps. As shown in Table 1, some GO have 0.2 – 0.8 eV direct band gap. This feature

is formed due to breakage of planarity and molecular symmetry of GO. Since all carbon atoms bond in GO have three nearest neighbors, then the symmetry of the in-plane sp^2 character has been disrupted along with the varying bond angles and bond lengths.

Carbonyls at the edges are either isolated and arranged in 1,5 conjunction, in which five neighboring carbonyl groups that represent the most stable oxygen configuration [12]. Studies also show that oxygen functionalities of GO, for example, ethers in the edge site, are stabilized by inducing repulsive forces, such as electrostatic stabilization between negatively charged carboxylate groups at the edges sites of hexagonal arrangement. Such functional groups influence the selective molecular intercalation or the adsorption of ions and molecules, leading to a variety of covalent modifications. On the basal plane, out-of-plane groups, much less stable oxides, such as epoxides are present. Epoxides are typically present at a lower concentration in comparison to the carbonyls [13].

Parabolic band at gamma-point (G) in GO (inverse of antiparabolic in graphite), suggesting to quasi-free electron states, is at much higher energies which indicates a larger ionization energy for GO. This ionization energy is defined as the difference between the vacuum level and the valence band maximum and an explicit calculation of this energy indicates a difference of about 1 eV between graphite and GO.

The band gap also has a strong correlation with the atomic ratio of O/C [14], therefore the level of oxidation affects significantly the electronic structure of GO. Oxygen atoms have a larger electronegativity than carbon atoms. GO becomes a p-doped material where the charge flow creates negative oxygen atoms and a positively charged carbon grid [15]. At a low oxidation the band gap is small and gives GO the characteristics of a semiconductor. In addition, the existence of unpaired electrons in oxygen atoms should yield either ferro or paramagnetic properties. The ratio of carbon and oxygen atoms is the yardstick of the oxidation efficiency. In progressively oxidized GO this ratio approaches the value of two.

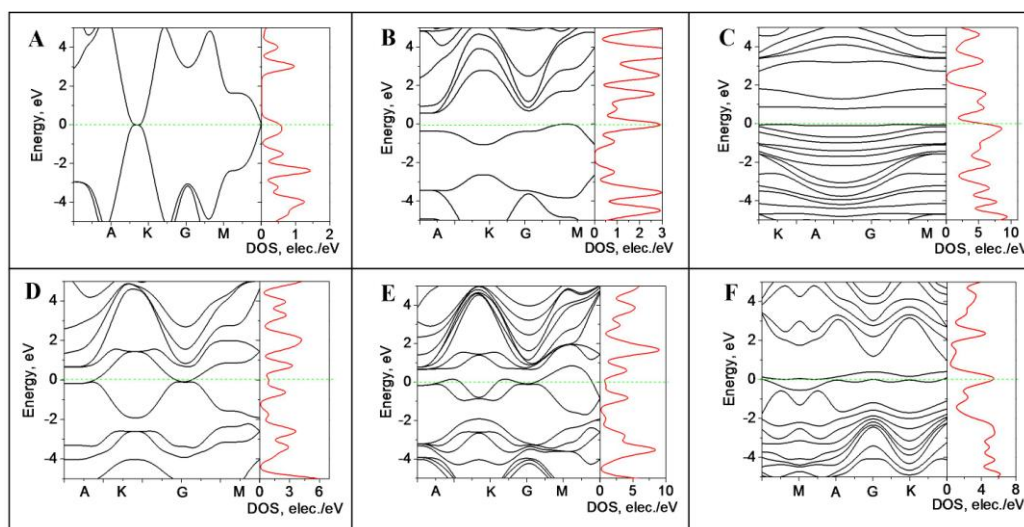


Fig. 5. Band structures (black plots) and total DOS (red plots) for modeled graphite (A) and GO, i.e., (B) oxygen atom in the basal site of hexagonal-ring arrangement as found in ether (C) oxygen atom in the edge site of hexagonal-ring arrangement as found in ketone, (D) epoxide, (E) asymmetric carboxylic and (F) optimized asymmetric carboxylic.

Table 1. Band gaps values of some GOs

No	Graphite Oxide	Oxidation Level	Layer Arrangement	Band Gap, eV
1	Ether, edge site	Low	Symmetric	-
2	Ether, edge site	Low	Asymmetric	0.161
3	Ether, basal site	Low	Symmetric	0.575
4	Ether, basal site	Low	Asymmetric	0.170
5	Ketone	Low	Symmetric	0.507
6	Ketone	Low	Asymmetric	0.782
7	Epoxide	Low	Symmetric	-
8	Epoxide	Low	Asymmetric	-
9	Carboxylic	Low	Asymmetric (ABA)	-
10	Ether, basal site	High	Symmetric	0.281
11	Ether, basal site	High	Asymmetric	-

CONCLUSIONS

Reaction of oxygen with carbon surfaces is one of the simplest reactions involving elemental carbon. It is also the most important reaction which is the key to very diverse technological applications. First principles study of GO have not only confirmed experimental findings, but in addition quantified these properties and found interesting new features. The hexagonal arrangement in GO with ethers have a moderate wrinkling and relatively less planar. In asymmetric

GO, the wrinkled layer maintain a hexagonal structure that is close to adjacent flat layer. Furthermore, planarity of graphene structures can be broken by the existence of out-of-plane epoxides, ketones, and dioxin. Conversely, planarity of graphene can be maintained on the presence of a carboxylic structure accompanied by the destruction of σ - bonds in the carbon chain. The binding of various groups also disrupts the electronic structure of GO by affecting the local electron states. DOS plots describe that electrons in p-orbital were dominated the states and most of

electrons are in the valence bands except for graphite. This indicates that after oxidation electronic character of graphite significantly changes. Band structures of GO are more denser than graphite. This feature is confirmed with DOS plots. The magnitude of DOS increase 2 – 4 times from graphite in GO. In spite of most of GO showed the dense band structure, some type of GO have inverse effect on the band gaps with the band gap values ranging from 0.2 to 0.8 eV at the point near fermi energy. The band gap also has a strong correlation with the atomic ratio of O/C, therefore the level of oxidation affects significantly the electronic structure of GO.

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