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Structural and electronic properties of graphene oxide for different degree of oxidation^{*}

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Abstract

In the last year, the investigation of two-dimensional materials as graphene oxide is a fundamental goal to produce innovative devices with wide range of applications in many areas. In the present work, we report a systematic study of structural and electronic properties of graphene oxide for different oxidations levels (25%, 50%, 75%, 100%) using density functional calculations for electronic ground state and a statistical approach on carbon-carbon bond length obtained after the geometric optimization of graphene covered with epoxide and hydroxyl functional groups. The theoretical models proposed and studied here are accord with the well-known experimental data. Our statistical results of the carbon-carbon bond length shown that hydroxyl groups disturbs the structure of graphene more than epoxide groups, however, both hydroxyl and epoxide groups are responsible of the change of hybridization sp^2 to sp^3 , while the degree of oxidation increase. In addition, our electronic structure calculations confirm that with low degree of oxidation, the graphene oxide is semiconductor, and with full degree of oxidation graphene oxide is an insulating material. The minimum of total energy is found when the graphene oxide has full coverage. This work can contribute to understand the plasticity and ductility properties of graphene oxide recently reported.

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1. Introduction

The two-dimensional materials have emerged as potential platforms for exploring novel and unique properties not found in other materials. In the last decade, graphene or graphene-based materials have been intensively investigated due to its excellent electronic, optical, mechanical and thermal properties and their wide range of applications [1]. Although, there are many methods to prepare graphene, the oxidation/reduction of flake graphite [2, 3] is the more used process to prepare graphene at low cost and mass production. However, the final product is a structure decorated of reactive oxygen functional groups, called graphene oxide (GO) [4], this interesting carbon nanomaterial can be dispersed in aqueous solutions and depending of the degree of oxidation, GO is a semiconductor or insulating material [2, 4], these features increase the range of applications such as field-effect transistors, polymer composites, sensors, conductive coatings, energy storage and biomedical applications among others [1-3, 5]. These oxygen functional groups disturb the quasi-plane structure and intrinsic properties of graphene; nonetheless, their structural and electronic properties can be recovered by chemical or thermal reduction of GO [2]. In this way, we can find a structure of GO with different degrees of oxidation and with different types of functional groups (i. e., hydroxyl, epoxide, carbonyl and carboxyl groups). Experimental and theoretical reports have confirmed mainly the presence of hydroxyl and epoxide functional groups and depending of oxidation or reduction process used, exist various theoretical models of GO proposed, but until now, this structure has been the subject of considerable debate over the years [2, 4, 6].

A recent experimental and theoretical report [7] shows that epoxide to ether functional group transformation is the responsible of an unusual plasticity and ductility of GO; this interesting result can be used to tune the mechanical properties of GO. Other previous works [4, 6] has demonstrated the configuration most energetically favorable is when the functional groups are in the opposite sides of the structure of GO, and the epoxide groups prefer a configuration 1,2-ether instead of 1,3-ether oxygen.

In this study, we present a systematic study, based on density functional calculation for electronic ground state and a statistical approach of some structural properties to investigate: (i) carbon-carbon bond length, (ii) the most stable structures according to the oxidation degree and (iii) the functional groups responsible of the change of the hybridization sp^2 to sp^3 . For this goal, two types of GO are studied: GO with epoxide groups and GO with hydroxyl groups, using different oxidations levels (25%, 50%, 75%, and 100%). We also investigate the binding energy between graphene and epoxide/hydroxyl functional group at low degree of oxidation.

Nomenclature

GO	graphene oxide
BE	binding energy
C-C	carbon-carbon bond length

2. Computational method

2.1. Electronic structure calculations

To begin, we choose a unit cell of eight carbon atoms; it was progressively cover with epoxide and hydroxyl functional groups, where each carbon atom corresponds to 12.5% of functionalization. Consecutively, the pseudopotential density functional SIESTA package [8] was employed for electronic ground state calculations using the generalized gradient approximation (GGA-PBE) [9], with energy cutoff 450 Ry, and a k-point 16 x 16 x 1 mesh in the Monkhorst-Park scheme [10]. The norm-conserving pseudopotentials were used for carbon, oxygen and

hydrogen atoms. The geometric optimizations [4] of carbon-carbon and carbon-oxygen functional groups bond lengths, as well as the total energies were performed with accuracy 0.04 eV/Å and 1 meV, respectively.

2.2. Binding Energy

The binding energy E_{BE} , between epoxide or hydroxyl groups and graphene was calculated [4] at low oxidation level (25% and 12.5%) using the standard formula of chemisorption:

$$E_{BE} = E_{GO} - E_G - E_{FG} \quad (1)$$

where, the E_{GO} , E_G , E_{FG} are the total energy of supercell of GO, energy of graphene and energy of the functional group (epoxide or hydroxyl), correspondingly. The energy value of epoxide group was calculated from the energy of molecular oxygen:

$$E_{epoxide} = \frac{E_{O_2}}{2} \quad (2)$$

and for calculating the energy value of hydroxyl group we took it from water in gaseous phase

$$E_{hydroxyl} = E_{water} - \frac{E_{molecular\ hydrogen}}{2} \quad (3)$$

All global minimum energies were obtained after the geometric optimization.

3. Results and Discussions

3.1. Total minimum energy

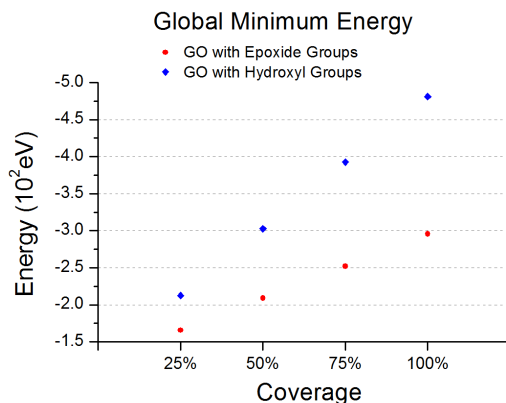


Fig.1. Global minimum energy obtained from geometric optimization of graphene functionalized with hydroxyl and epoxide groups, as function of energy (keV) and coverage percentage.

In the Fig 1, is shown the global minimum energy after the geometric optimization of each structure of GO with different degree of oxidation. We observe that GO with epoxide groups is less stable than GO with hydroxyl groups. At 25% and 50% of coverage, GO with hydroxyls has approximately the same value of energy that GO with epoxides at 50% and 100%. This can be interpreted as; the hydroxyls groups stabilize the structure of GO two more times the epoxide groups. In both case GO with epoxide/hydroxyl groups reach their global minimum energy at 100% of oxidation level.

3.2. Carbon-carbon bond length in GO

To explore C-C bond lengths in the structure of GO, we have used the following equation:

$$\Delta_{(C-C)_i} = L_G - L_{GO} \quad i = 1, 2 \dots 8 \quad (4)$$

Where,

i = Number of C-C bonds

$\Delta_{(C-C)_i}$ = Difference of C-C bond length (Å)

L_G = C-C bond length of graphene (Å) = **1.42 Å**, traditional value reported [1, 2]

L_{GO} = C-C bond length of graphene oxide (Å), values found in this study.

The optimum result is when $\Delta_{(C-C)_i} = 0$, i. e., C-C bond lengths of GO are equal to the value reported for graphene (1.42 Å). Experimentally, it has been demonstrated that functional groups damage the structure of graphene, consequently, this value changes in GO. By a statistical analysis, we demonstrate in the Fig. 2, how change C-C bonds length with the degree of oxidation. At 100% of coverage both epoxide and hydroxyl groups affect the original structure of graphene, at 75% of coverage, epoxide group damage the 50% of the structure and hydroxyl groups affect the 62.5% of the structure, at 50% both epoxide and hydroxyl group affect the 75% of the original structure, and finally at 25% of coverage the structure is more affected by hydroxyl group than epoxide group and the spread of the hydroxyl data group is broader in comparison to the narrow spread reported to epoxide data group.

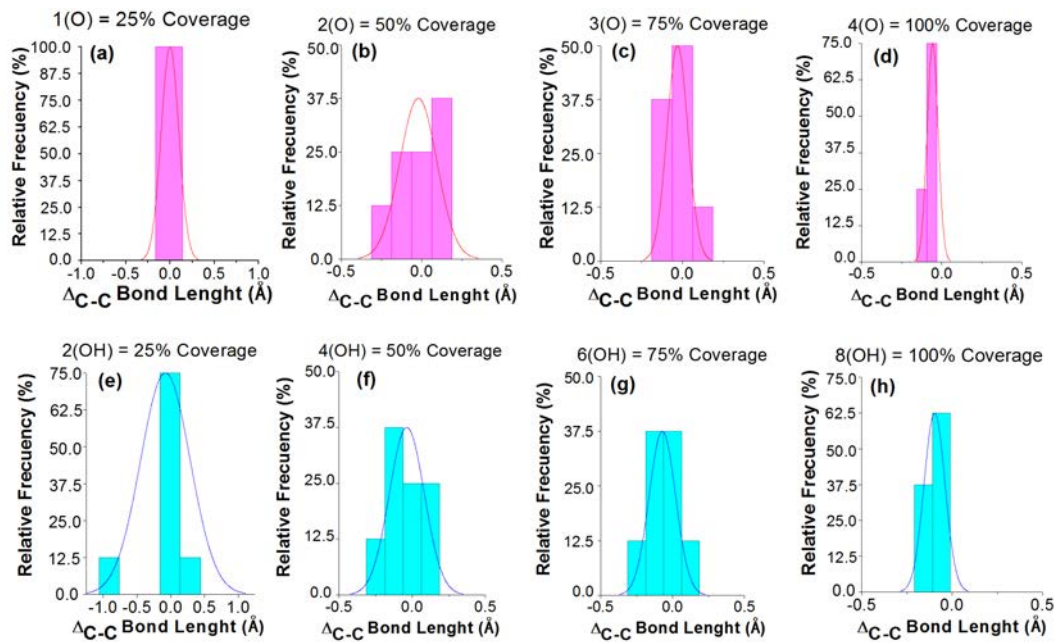


Fig 2. Distribution of Δ_{C-C} bond length in GO: (a) Distribution of Δ_{C-C} bond length in GO covered at 25% with epoxide group, (b) Distribution of Δ_{C-C} bond length in GO covered at 50% with epoxide group, (c) Distribution of Δ_{C-C} bond length in GO covered at 75% with epoxide group, (d) Distribution of Δ_{C-C} bond length in GO covered at 100% with epoxide group; (e) Distribution of Δ_{C-C} bond length in GO covered at 25% with hydroxyl group, (f) Distribution of Δ_{C-C} bond length in GO covered at 50% with hydroxyl group, (g) Distribution of Δ_{C-C} bond length in GO covered at 75% with hydroxyl group, (h) Distribution of Δ_{C-C} bond length in GO covered at 100% with hydroxyl group.

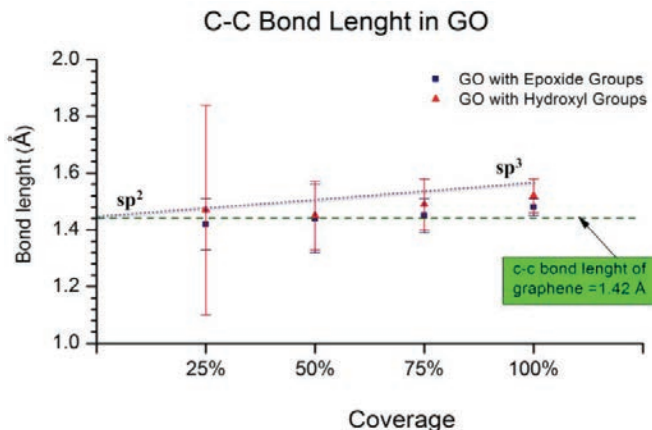


Fig 3. Evolution of hybridization sp^2 to sp^3 : dependence of carbon-carbon bond length (Å) in GO, as function of the degree of oxidation and epoxide or hydroxyl functional groups employed.

The statistical analysis outlined above is complemented with the Fig 3, where can be observed clearly the change of hybridization sp^2 to sp^3 , by oxidation level increase. This is due to the C-C distances in graphene are 1.42 Å and correspond to hybridization sp^2 , while the C-C distances in diamond are 1.54 Å and correspond to hybridization sp^3 . GO changes completely to hybridization sp^3 at 100% of coverage with functional groups hydroxyl and epoxide.

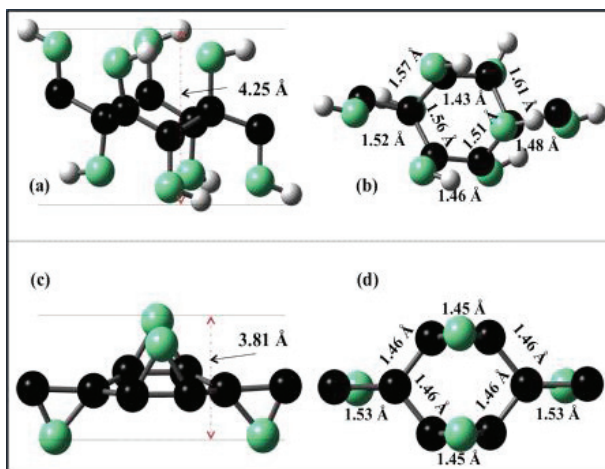


Fig 4. Structural properties of the most stable models: (a,b) GO with hydroxyl groups at 100% of coverage and (c,d) GO with epoxide groups at 100% of coverage. The black, green and gray balls correspond to carbon, oxygen and hydrogen atoms, respectively.

The Fig.4 shows graphically the structural properties of the most stable configurations of GO with hydroxyl/epoxide groups at 100% of coverage, obtained after of geometric optimization. It evidences that hydroxyls disturb the structure of GO more than epoxides. The distance out-of-plane is 4.25 Å for GO with hydroxyls (Fig 4. a) and 3.81 Å for GO with epoxides (Fig. 4. c). The C-C bonds length of pristine graphene change from 1.45 Å to 1.61 Å (Fig 4. b, d) in both cases, clearly it detects the hybridization sp^3 , as diamond (1.54 Å).

3.3. Binding energy

The BE was calculated from equation (1). For epoxide groups, we have used the equation (2) to calculate its energy. BE of one epoxide group on the structure of graphene is 2.31 eV and correspond to 25% of coverage with two carbon atoms bonded. For hydroxyl group, it was employed the equation (3) to obtain its energy. So, the BE of one hydroxyl group on the structure of graphene is 0.83 eV that correspond to 12.5% of coverage with one carbon atom bonded. These values of BE are consistent with other values previously reported [11]. The ratio value of $E_{BE[-O-]}/E_{BE[-OH]}$ is 2.78; this value shows that for removing one epoxide group, the energy necessary is around three times more in comparison with one hydroxyl group.

3.4. Density of States

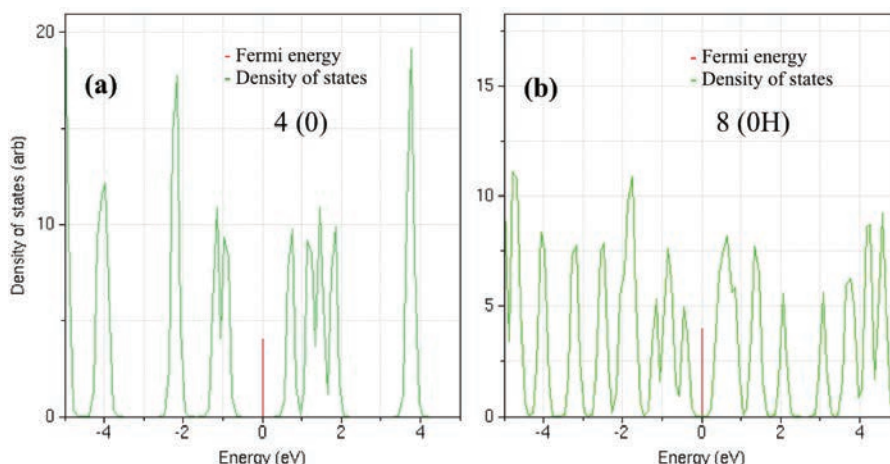


Fig 5. Density of states of the most stable models: (a) GO with epoxide groups at 100% of coverage and (b) GO with hydroxyl groups at 100% of coverage.

The electronic densities of states of the most stable configurations calculated in this work are reported in the Fig. 5. On the first one we can see that the energy gap for GO with epoxide is ~ 1.8 eV and for GO with hydroxyls is ~ 0.7 eV. We can think that GO with hydroxyl groups is a semiconducting material, however, the structure considered here does not take in account that GO presents both hydroxyl and epoxide groups at experimental level [2]. Moreover, our results allow to show that epoxide groups increase the energy gap in GO around three times more than hydroxyl groups, changing the electrical properties of GO from semiconducting to insulating material depending on the increasing of the oxidation degree.

4. Conclusion

In summary, we have presented a systematic study of structural and electronic properties of GO i.e., graphene functionalized with epoxide and hydroxyl functional groups, for different oxidation levels. The structures of GO studies are in accordance with the well-known experimental data and other theoretical previous reports. In particular, our result based on electronic energy shown that the most stable structures of GO (either epoxide or hydroxyl group) are at 100% of coverage. However, these results are not in a well agreement with a previous report [4], but fully consistent with the results obtained in graphene entirely covered with hydrogen atoms [6]. In addition, epoxide groups disturb the structure of graphene less than hydroxyl groups, in any degree of oxidation. Furthermore, structure of graphene most damaged is at 25% of functionalization with hydroxyl groups, with these results, we demonstrate how difficult it is to recover the intrinsic structural and electronic properties of pristine graphene after the chemical or thermal reduction of GO.

Acknowledgements

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