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First principles study on optical response of graphene oxides: From reduced graphene oxide to the fully oxidized surface

F. Nasehnia [a], S. Mohammadpour Lima [b], M. Seifi [a,*], E. Mehran [a]

[a] Department of Physics, University of Guilan, P.O. Box 41335-1914, Rasht, Iran
[b] Department of Physics, Islamic Azad University, Chalous Branch, Chalous, Iran

ABSTRACT

The electronic structure and linear optical properties of oxygen-functionalized graphene are investigated by means of density functional theory (DFT). Our calculations show that oxygen atoms are chemisorbed on the graphene plane and each oxygen atom bonds with two carbon atoms to form a three-membered epoxide group. For different oxygen coverages ranging from 2% to 50% (O/C ratio), the most favorable configurations are calculated. In order to calculate the linear optical response of the structures, the dielectric tensor is derived within the random phase approximation (RPA). Dielectric function, absorption coefficient, optical conductivity, loss function, reflectivity and the refraction index are calculated for both in-plane (p) and perpendicular (s) polarizations of the electric field of the incident light. The calculations are performed in the infrared (only the electronic contributions), visible (VS) and ultraviolet (UV) regions and show different characteristic features depending on the degree of oxidation. The optical spectra are anisotropic along the two polarizations of the electric field of the incident light.

1. Introduction

During the last decade, graphene has attracted the interest of scientists owing to its fascinating structural and electronic properties as well as promising applications in modern semiconducting devices [1–5]. Most of the graphene's remarkable properties such as long spin relaxation time, high transport mobility and low optical absorption stem from its peculiar linear energy–momentum dispersion relation. As a consequence of its unique electronic structure, graphene possess a universal dynamic optical conductivity of $\sigma_0 = e^2/4\hbar$ [6] over a wide energy range. Due to its zero band gap, graphene is an inappropriate material for use in logical devices. Therefore, a lot of effort has been conducted to opening its band gap in a controlled way in order to combine the advantage of graphene and modern electronic devices [7]. One promising way to open a robust and tunable band gap in graphene is atomic covalent functionalization [8–11] by hydrogen [12,13], fluorine [14,15] and oxygen [16] that has been extensively investigated in recent years.

Chemical modification of graphene sheets by O adatoms (adsorbed O atoms) has some advantages compared to other adatoms. The main advantage is the existence of a promising and

low-cost method to produce oxygen functionalized graphene by controlling reduction (deoxidation) of graphene oxide (GO) [17–19]. The basic route for production of GO (suspended) is the Hummers method [20] based on acidic treatment of graphite. After production of GO using this method, it can be reduced in a controlled way to achieve partially oxidized graphene (POG) or reduced graphene oxide (RGO with 7–8% oxygen). However, complete reduction is difficult to achieve and some functional groups, unintentionally remain on the both sides of the graphene sheet. In a recent study, Wang et al. synthesized GO structures with tunable oxygen concentration [21].

Exact structure of GO has been the subject of much debate over the past few decades and there is still no unique commonly accepted model for it [18]. This ambiguity is due to differences in production methods. Depending on the production method, GO may contain following functional groups: epoxide species (C=O), hydroxyl (C—OH), carboxyl (COOH), epoxide (C—O—C) and other C=O or C—O containing chemical species. Using Hummers method for GO production results in a structure that contains all mentioned functional groups. There is also a DFT study which has investigated the energy loss spectra of model structures of GO with such compositions [35].

To avoid some difficulties in achieving POGs and RGOs using Hummers method, Hossain et al. [33] recently suggested an alternative approach for GO production using atomic oxygen plasma in

* Corresponding author.
E-mail addresses: m_seifi2000@yahoo.com, seifi@guilan.ac.ir (M. Seifi).

ultrahigh vacuum (UHV) condition. According to their report the UHV oxidation leads to functionalization of graphene only with epoxide groups (C—O—C) which is completely reversible at 260 °C and preserve the ideal honeycomb structure of the surface. In the present work, we aim to investigate the optical spectrum of such GO and POG structures.

Reduced GO (maximum 7–8% oxygen) is highly transparent in the visible spectrum. Therefore, it has been widely investigated for transparent conductor applications as a possible successor for indium tin oxide (ITO) in solar cells and light-emitting diodes [39]. Reduced GO also shows a strong absorption in the UV region, with absorption peaks shifting toward the visible region as the oxidation level increased [40]. Moreover, near-infrared and visible fluorescence has been observed for RGO and POG structures which make them attractive for several applications such as biological applications [39]. Therefore, in this study, we plan to carry out the effect of O modification (with different concentrations) on the optical properties of graphene. Optical measurement technique (for example, absorption measurement) can also be employed to monitor reduction (or oxidation) process as a contact-free method.

To calculate the optical response of POG structures, at first, we perform a through DFT study on six different POGs with O/C ratios of 2%, 4%, 6%, 8%, 12%, 25% and 50% to find the most stable configuration (ground state) of each case. In the second step, for each case, the complex dielectric function is derived within the random phase approximation (RPA) in the linear response using the converged systems of Kohn–Sham eigenstates and eigenvalues. Using the calculated dielectric function, other optical parameters such as absorption coefficient, optical conductivity, loss function, reflectivity and the refraction index are calculated for both in-plane (p) and perpendicular (s) polarizations of the electric field of the incident light. The calculations are performed in the infrared (IR), visible (VS) and ultraviolet (UV) regions and show different characteristic features depending on the degree of oxidation. Our results show that the effect of oxidation on the optical parameters is significant. Moreover, it should be noted that in the infrared (low energy) region, only the electronic contributions are considered and vibrational contributions are not taken into account.

The rest of this paper is organized as follows: In the Section 2, we introduce our model and computational methods, and then the most favorable POG structures with different O/C ratios are presented in Section 3. The electronic structure of double side oxygen functionalized graphene systems is argued in Section 4. In Section 5, the optical parameters of the systems are calculated. The conclusions are presented in Section 6.

2. Computational methods

Oxygen functionalized graphene sheets with different O coverages are modeled with the 5×5 rhombohedral supercells including 50 C atoms with one or more O functional (epoxy) groups (Fig. 1). In the case of fully oxidized surface (with O/C ratio of 50%), a rectangular unit cell of graphene with 8 C atoms and 4 O adsorbates is used (see Fig. 2). In the perpendicular direction to the surface, Graphene sheets are separated by a distance of 20 Å to minimize the inter layer interactions.

All the structures are optimized via DFT calculations using Quantum ESPRESSO [22] package. We use the ultrasoft pseudopotentials [23] for carbon and oxygen atoms and Perdew–Burke–Ernzerhof (PBE) [24] generalized gradient approximation (GGA) for the exchange–correlation potential in the optimization process. The self-consistent calculations are performed using a kinetic energy cutoff of 30 Ry for the wave functions and of 300 Ry for the charge densities. The Brillouin zone is sampled using a $10 \times 10 \times 1$ Monkhorst–Pack [25] grid and Methfessel–Paxton

[26] smearing of 0.02 Ry. The optimization process terminates when total forces on each atom is reduced to the 0.001 a.u. The convergence criterion between subsequent iterations is set to 10^{-7} Ry.

In the second step, the full potential linearized augmented plane wave [27] code WIEN2K [28] is employed to calculate optical properties of the optimized structures. We again use the PBE functional for the exchange–correlation energy. To perform optical calculation, we use a dense k-point sampling of $(25 \times 25 \times 1)$ in the irreducible part of the Brillouin zone for all 5×5 supercells. The Brillouin zone integration makes use of the tetrahedron method [29] and only interband transitions are taken into account. The converged Kohn–Sham [30] eigenvalues and eigenstates are obtained for $R_{mt} \times K_{max} = 7$, where R_{mt} is the smallest atomic radii and K_{max} is the plane wave cut-off. Finally, we use these converged eigenvalues and eigenstates to obtain the complex dielectric function that is used to calculate all the optical parameters in the linear response.

Our test calculations show that oxygen adsorption on graphene plane does not lead to a magnetic structure; therefore, it is not essential to take spin polarizations into account in the calculations.

3. Graphene oxide structures

According to insights from Experimental studies, oxygen adatoms are not uniformly dispersed on the graphene surface and GO structures contain separated segments of oxidized and clean graphene [31,32]. Our DFT calculations also indicate a strong tendency of O adatoms to aggregate and form close-packed structures on graphene plane. These results are achieved when we identify the most stable configuration for each O/C ratio. Therefore, *for each O/C ratio* we first calculate O adsorption energies for different possible configurations (at least 6–8 different configurations for each O/C ratio are examined in this study) and then by comparing these adsorption energies, the most stable configuration is identified. The adsorption energy (E_{ads}) is defined as follows:

$$E_{ads} = E_{tot}(\text{graphene} + \text{O}) - E_G - E_O \tag{1}$$

where E_{tot} is the total energy of the graphene sheet with the adsorbates, E_G is the energy of graphene sheet and E_O is the energy of an isolated O atom.

The most stable configurations of the partially oxidized graphene with O/C ratios of 2%, 4%, 6%, 8%, 12%, 25% are presented in Fig. 1 and the case of fully oxidized surface (O/C = 50%) is depicted in Fig. 2. The corresponding structural data and adsorption energies are also summarized in Table 1. Our results are also in accordance with the results of previous DFT study on Binding of atomic oxygen on graphene [16].

4. Electronic structure

As predicted in the previous studies [34,35], our DFT calculations (GGA functional) indicate that all graphene structures with oxygen adsorption have a nonzero band gap, but the band gap values are insignificant for O/C ratios less than 8%. However, for O coverages higher than 12%, the band gap value considerably increases by the O/C ratio. For our POG structures, the calculated band gaps are summarized in Table 1. Note that the use of PBE exchange correlation functional in calculations may underestimate the band gaps. On the other hand, the use of hybrid functionals for large and ambitious computational studies, results in difficult and time-consuming calculations.

In the case of fully oxidized graphene (double side oxidation, O/C = 50%) a band gap of 3.9 eV has been calculated. Previous DFT studies also reported the band gap values of 4.8 eV (PBE functional)