

STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF GRAPHENE AND SOME GRAPHENE DERIVATIVES BASED ON ORTHORHOMBIC UNIT CELL BY DENSITY FUNCTIONAL THEORY

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Received: 12 September 2021; Accepted for publication: 10 December 2021

Abstract. Pristine graphene and graphene derivatives have been investigated with the density functional theory (DFT). The calculations consist of structural optimization, density of states (DOS), projected density of states (PDOS) based on orthorhombic 4-atom unit cell. The obtained results are in good agreement with the experimental data. The highest deviations from the experiment are 0.35 % and 0.28 % for the lattice constant and bond length, respectively. In addition, the results of DOS, and PDOS have shed light on electronic properties of graphene. The functionalization of graphene leads to distortion of graphene sheet. New states around the Fermi level of graphene derivatives are mainly composed of $2p$ orbitals of carbon and oxygen atoms. Besides, structural and electronic properties of graphene and derivatives obtained from the 4-atom orthorhombic unit cell are in line with those from the traditional hexagonal 2-atom unit cell in the previous works. This result proved the reliability of the constructed orthorhombic 4-atom unit cell of graphene.

Keywords: graphene, graphene derivatives, hexagonal unit cell, orthorhombic unit.

Classification numbers: 2.5.2.

1. INTRODUCTION

Since the first successful synthesis in 2004 due to mechanical exfoliation, the keyword ‘graphene’ becomes popular on the headline of hundreds of papers. The reasons for considerable scientific interest are unique and novel characteristics of graphene. Graphene is the thinnest material and one of the strongest materials ever discovered. It has high thermal conductivity [1], good electrical conductivity [2], high transparency [3], superior carrier mobility at room temperature [4], and high surface area. Besides, it possesses unconventional quantum Hall effect [5] and behaves as massless Dirac fermions near the Fermi surface [6]. These features have promoted investigation for application of graphene.

Along with experimental researches, there are a lot of theoretical studies on graphene and its compounds. However, the theoretical investigations mainly consider graphene based on a hexagonal two-atom unit cell. To illustrate, most studies on chemical modification of graphene applied the hexagonal two-atom unit cell [7 - 17]. In addition, studies of doping graphene, adsorption on graphene were also constructed from the hexagonal two-atom unit cell [18, 19]. In particular, computational models of heterogeneous graphene/semiconductor composites have also been derived from the hexagonal two-atom unit cell. The utilization of hexagonal two-atom unit cell in the hybrid systems leads to certain limitations. To illustrate, Run Long *et al.* investigated the graphene/TiO₂ composites [20]. They chose the most stable surface of rutile-TiO₂, (110) surface, for their calculations. However, the authors still utilized graphene constructed from a hexagonal unit cell. On the other hand, the rutile-TiO₂ (110) unit cell is rectangular. Therefore, the two kinds of different unit cells caused lattice mismatch as the hybrid graphene/TiO₂ systems were built. The same situation occurred in the research of Aijun Du and his co-workers [21]. Fortunately, graphene could be constructed from an orthorhombic 4-atom unit cell due to reflection symmetry through O_x and O_y axes of hexagonal lattice that graphene possesses. However, only a small number of papers based on the orthorhombic 4-atom unit cell have been published to date and the publications only considered pristine graphene [22 - 23]. To the best of our knowledge, so far there have been no studies on graphene derivatives containing epoxy and hydroxyl groups based on the orthorhombic 4-atom unit cell. Therefore, in the present work, we constructed the orthorhombic 4-atom unit cell of graphene, from which calculations on graphene and its derivatives were performed. The results of structural and electronic properties of graphene based on the orthorhombic 4-atom unit cell agreed well with the available experiments [24]. In addition, the calculations of the graphene derivatives based the orthorhombic 4-atom unit cell were in line with the published studies based on the hexagonal 2-atom unit cell.

2. COMPUTATIONAL METHOD

All calculations have been implemented with the Vienna Ab initio Simulation Package (VASP) [25]. The package was performed according to the density functional theory (DFT) [26, 27] with generalized gradient approximation (GGA) for the exchange and correlation in Perdew-Burke-Ernzerhof (PBE) [28-30]. The projector augmented wave (PAW) approximation [31] was applied to treat electron-core interactions.

Benchmark tests indicated that good convergence of binding energy and lattice parameters was achieved with $12 \times 6 \times 1$ and $6 \times 6 \times 1$ Monkhorst - Pack grids [32] for the sampling of the Brillouin zones of orthorhombic 4-atom and hexagonal 2-atom unit cells, respectively. The Monkhorst - Pack k grids of $36 \times 18 \times 1$ and $36 \times 36 \times 1$ were employed for corresponding calculation of density of state (DOS). Dispersion interactions were taken into account due to the optPBE-vdW [33].

Besides, according to the benchmark results, an energy cutoff of 450 eV was chosen. The positions of nuclei were relaxed until the Hellman - Heynman forces on each nucleus were less than 0.01 eV/Å. The spin polarized calculations were applied for graphene derivatives and isolated functional groups. A supercell 6×3 (containing 72 carbon atoms) built from the orthorhombic 4-atom unit cell was employed. The vacuum height was set to 12 Å to eliminate interaction between adjacent images.

In the present paper, the binding energy is defined as

$$E_{bind} = E_{G-f} - E_g - E_f \quad (1)$$

where E_{G-f} is the total energy of a graphene derivative, E_g is the energy of graphene surface, and E_f is the energy of isolated fragment. The fragment could be oxygen atom or hydroxyl group (-OH group).

3. RESULTS AND DISCUSSION

3.1. Pristine graphene

3.1.1. Structural properties

Slab corresponding to the orthorhombic 4-atom unit cell was constructed. In order to compare with the results obtained from traditional hexagonal unit cell, we also created a slab of the hexagonal 2-atom unit cell. Two slabs were labeled as orthorhombic and hexagonal unit cells, respectively (Figure 1). Structural optimizations of these unit cells are presented in Table 1.

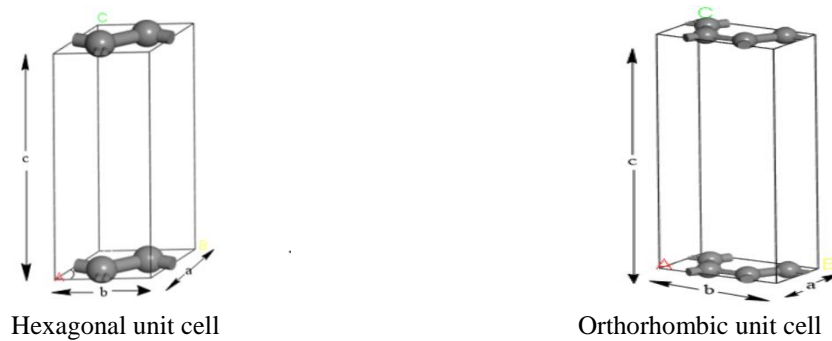


Figure 1. Two types of unit cells of graphene.

Table 1. Some geometrical parameters of optimized structures.

Slab	Parameters	Calculation	Experiment [24] (and induced from experiment)	Deviation (%)
Hexagonal unit cell	$a = b$ (Å)	2.472	2.463	0.37
	$r(CC)$ (Å)	1.427	1.422	0.35
Orthorhombic unit cell	a (Å)	2.470	2.463	0.28
	b (Å)	4.281	4.266	0.35
	$r(CC)$ (Å)	1.426	1.422	0.28

Generally, the results on both hexagonal and orthorhombic unit cells are in good agreement with the experiment [24]. The highest deviation of 0.37 % is witnessed at the lattice constant of the hexagonal unit cell. The calculated lattice constant is received at a value of $a = 2.472$ Å. In comparison with some other investigations, the result is quite good. For example, the calculation of V. M. Karpan *et al.* within the local density approximation (LDA) of density functional theory gave a lattice constant of $a = 2.45$ Å [34] corresponding to a deviation of 0.53 % from the experiment. Moreover, the value of $a = 2.45$ Å was also reported in the work of Jun Nakamura and his co-workers [9]. They utilized a local (spin) density functional given by Perdew and Wang for the exchange - correlation energy functional. Furthermore, Weiliang Wang *et al.*

reported a lattice constant of $a = 2.47 \text{ \AA}$ [11], which is consistent with our result. Besides, for the orthorhombic unit cell, the lattice constants are $a = 2.470 \text{ \AA}$, $b = 4.281 \text{ \AA}$. The values only deviate 0.28 % and 0.35 % from the experimental values, respectively. In addition, the bond lengths of the C-C bonds for two types of unit cells are quite close to the experiment [24]. The C-C bond distance is 1.427 \AA for the hexagonal unit cell while a length of 1.426 \AA is observed at the orthorhombic unit cell. Therefore, it can be confirmed that the calculation method which we have chosen is reliable.

3.1.2. Electronic properties

The density of states (DOS) was investigated for the relaxed geometries of hexagonal and orthorhombic unit cells. The total DOS values are depicted in Figure 2.

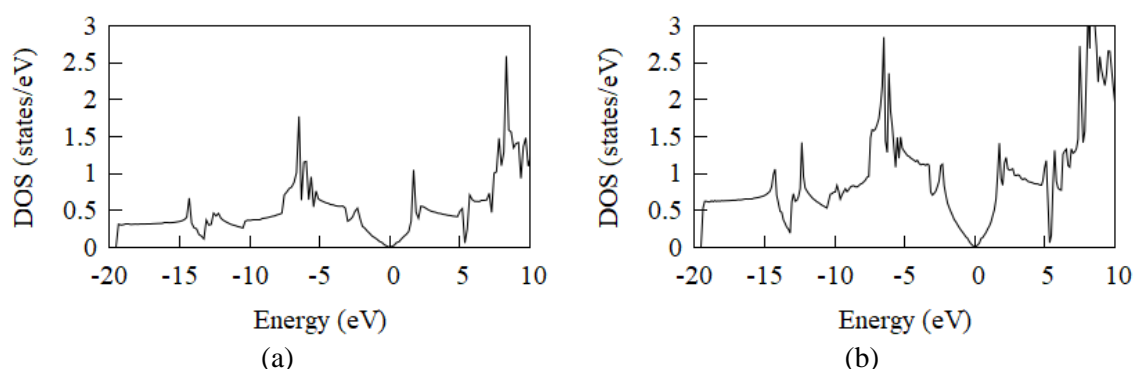


Figure 2. Electronic density of states of hexagonal (a) and orthorhombic (b) unit cells.

It can be seen that DOS variations are the same for both hexagonal and orthorhombic unit cell. Besides, Figure 2 also indicates that the energy gap of graphene is zero. Here, the energy gap is defined as the energy difference between the lowest unoccupied orbital and the highest occupied orbital when the Fermi level is set to zero eV. The result is completely consistent with the experiment. The zero - gap leads to good electrical conductivity of graphene.

For more detail, PDOS graph shows that the valence and conductor bands around the Fermi level are composed mainly of $2p_z$ states of carbon atoms (Figure 3).

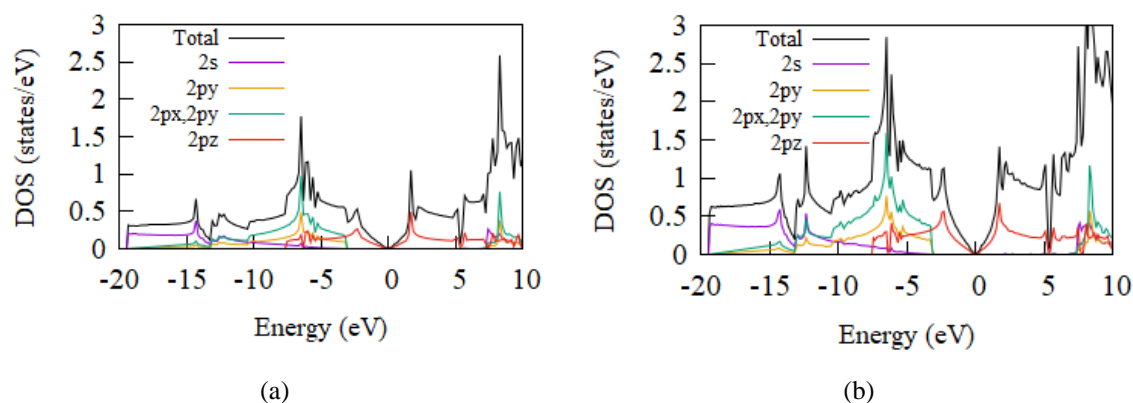


Figure 3. Projected density of states of hexagonal (a) and orthorhombic (b) unit cells.

These valence and conductor bands are just π and π^* bands. Since each $2p_z$ orbital of a carbon atom has one electron, the valence band is completely filled and the conduction band is empty. On the other hand, it is known that the states near the Fermi level are responsible for electronic properties of a material. In other words, the electronic properties of graphene are principally decided by $2p_z$ orbitals. Meanwhile, from PDOS, it can be seen that the $2p_x$, $2p_y$ and $2s$ of carbon atoms contribute to deep lying valence bands of graphene electronic structure. The deep valence bands represent strong in-plane covalent bonds (σ bonds). The σ skeleton results in excellent mechanical properties of graphene.

3.2. Graphene derivatives

3.2.1. Structural properties

We have considered two graphene derivatives. The first one contains one -OH group on the graphene surface. The second one is composed of one epoxy on graphene sheet. The two derivatives were symbolized as GOH and GO, respectively. The results obtained from structural relaxation are shown in Figure 4 and Table 2.

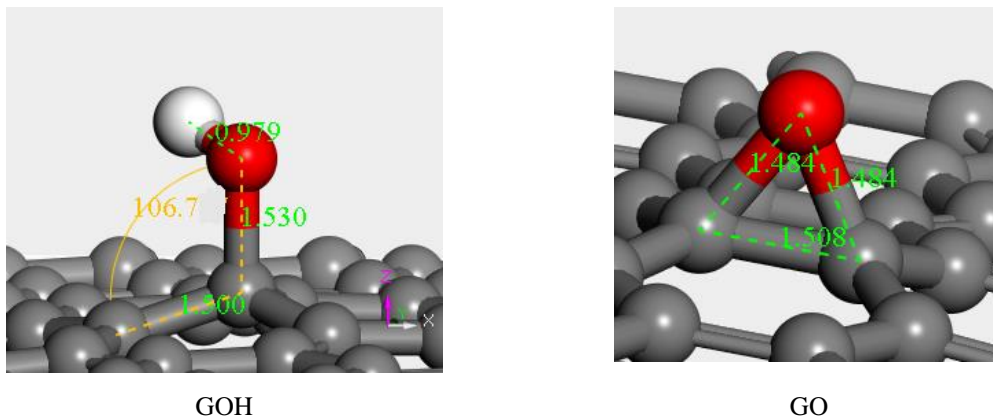


Figure 4. Relaxed structures of GOH and GO derivatives.

From Figure 4, it can be seen that the formation of either epoxy or -OH group on the graphene sheet leads to the distortion of the carbon framework. To specify, for the GOH derivative, an upward movement of the carbon atom connected to the oxygen atom was observed. Besides, the C-C bonds around the carbon atom expand and take on a value of 1.500 Å, which is in line with the previous work based on hexagonal unit cell [35]. In addition, the bond angle C-C-O (Figure 4a) is 106.7°. This value is very close to the sp^3 -hybridized bond angle, 104.5°. Thereby, the carbon bonding to oxygen atom is in distorted sp^3 hybridization. The same trend is witnessed in the GO derivative. The expansion of the C-C bond in the epoxy group is about 1.508 Å. The result is consistent with the studies of Yan *et al.* (1.48Å) [35] and Li *et al.* [36] (1.58Å), of course, all these previous studies were based on the hexagonal unit cell.

Furthermore, the C-O bond in the GOH derivative almost localized in the vertical direction of the graphene sheet, with a bond length of 1.530 Å. For comparison, the oxygen atom in the epoxy group lies at the bridging site of graphene to form an isosceles triangle. The C-O bond in the epoxy group is around 1.484 Å. Unlike the GOH derivative, the formation of C-O bond in three-membered ring creates great strain in the GO derivative. This is a consequence of changes in two carbon atoms, from planar sp^2 -hybridized to distorted sp^3 -hybridized structure.

Besides, Table 2 indicates that the formation of OH group and epoxy group on the graphene surface is exothermic. The binding energy between the OH group and graphene is -1.01 eV. Meanwhile, -2.4 eV is released when the epoxy group is generated on the graphene plane. The results are in good agreement with previous works [36, 37] which reported energy levels of 2.4 eV and 2.1 eV, respectively.

Table 2. Energy of structures after relaxation.

	Graphene	GOH	GO	O	OH
Energy (eV)	-562.18	-569.00	-564.39	0.19	-5.81
E_{bind} (eV)		-1.01	-2.40		

3.2.2. Electronic properties

The results of DOS, PDOS on the relaxed structures of GOH and GO derivatives are shown in Figure 5. As above analysis of PDOS of pristine graphene, we already know that the $2p$ orbitals of carbon atoms mainly contribute to the states around the Fermi level. Thereby, we only considered the $2p$ orbitals of carbon atoms for further study (Figure 5).

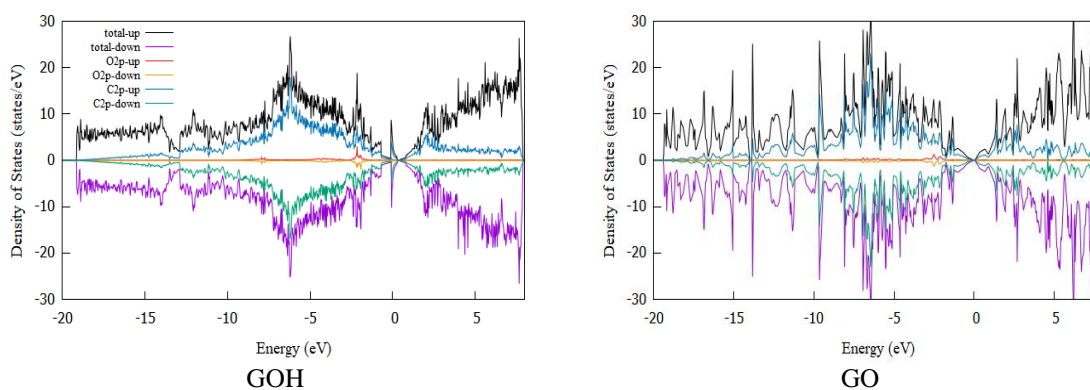


Figure 5. PDOS of GOH and GO.

(In Figure 5, the symbols of “up” and “down” mean spin up and spin down, respectively)

In comparison with pristine graphene, the DOS images of GOH and GO derivatives have the emergence of new peaks around the Fermi level. The result is attributed to the reduction in graphene symmetry when OH, epoxy groups bond on the graphene sheet. In addition, the analysis of PDOS indicates that the states near the Fermi level is mainly composed of $2p$ orbitals of carbon atoms. The $2p$ orbitals of oxygen atom also contribute to the states. Besides, for the small ratio of O/C (about 1/72), no band gap appeared in both GOH and GO derivatives. The result is in agreement with previous work based on the hexagonal unit cell [35-37].

4. CONCLUSIONS

In the present work, the structure and electric properties of graphene and its derivatives were studied based on the orthorhombic 4-atom unit cell. For the purpose of comparison, calculations on traditional hexagonal 2-atom unit cell were performed. The results for pristine graphene are consistent with the experimental data. The deviation of the lattice parameters from

the experiment ranges from 0.28 % to 0.35 %. Meanwhile, the deviation of bond length is about 0.28 %. In addition, for the two kinds of unit cells, the result of DOS exhibited zero - band gap, which is consistent with the experiment. The calculated PDOS results provided a better understanding of the contribution of orbitals, in particular, the $2p_z$ states to the electronic properties of graphene. Furthermore, the results of graphene derivatives based on the orthorhombic 4-atom unit are in good agreement with previous works based on the hexagonal 2-atom unit cell. It is confirmed that the constructed 4-atom orthorhombic unit cell is satisfying to represent graphene and pave the way for the study of graphene and graphene derivatives.

Acknowledgements. We thank the National Foundation for Science and Technology Development (Nafosted), Viet Nam, which has sponsored this work under the project number of 104.06-2017.343.

CRedit authorship contribution statement. All authors contributed to the conceptualization and realization of the study. Tran Thi Thoa and Vu Chi Tuan carried out the computations. Pham Tho Hoan solved technical problems. Tran Thi Thoa wrote the first draft and Hoang Van Hung edited it. Supervision was done by Nguyen Thi Minh Hue and revision was done by her with the help of Tran Thi Thoa. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest. There are no conflicts to declare.

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