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## The Role of the Oxygen Impurity on the Electronic Properties of Monolayer Graphene: A Density-Functional Study

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# The Role of the Oxygen Impurity on the Electronic Properties of Monolayer Graphene: A Density-Functional Study

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**Abstract.** Oxidation during the fabrication of a two-dimensional carbon-based system (graphene) can not be avoided so that will affect the electronic properties of the system. In this study, we investigate the effect of the oxygen impurity on the electronic properties of monolayer graphene using density functional theory calculations. The calculations were performed using the  $(3 \times 3)$  supercell model and were validated by the  $(1 \times 1)$  supercell calculations. We find that by increasing the oxygen concentration from 6%, 11%, 17%, 33% and 50%, the band gap enhanced from 0.1 to 2.48 eV. An analysis using the partial density-of-states projected to the atoms confirmed that strong hybridizations between  $O - P_y$  and  $C - P_z$  orbitals are responsible for inducing the enhancement of the bandgap. Therefore, we conclude that oxygen atoms are highly sensitive to changes in the electronic properties of monolayer graphene.

## 1. INTRODUCTION

During the last year, technological development is very advanced in terms of searching for new material such as carbon-based materials known as graphene. Graphene is two-dimensional of carbon atoms arranged in a hexagonal crystal and that has a single-atoms thickness[1,2]. Monolayer graphene has extraordinary properties such as high electron mobility in the ambient condition about  $20 \text{ m}^2/\text{Vs}$ [3], incredible mechanical strength with strain strength up to 130 Gpa[4] and thermal conductivity above  $2000 \text{ Wm}^{-1}\text{K}^{-1}$ [5]. In the pristine graphene, a linear dispersion appears around Fermi level known as the Dirac cone[2]. Moreover, the Fermi velocity up to  $v_F \approx 1.0 \times 10^8 \text{ m/s}$  depending on the Fermi momentum as confirmed by data analysis of Shubnikov-de Haas oscillations (SdHO) on magnetoresistances[6].

Due to zero band-gap in the pristine graphene, it is important to induce opening band gap, which is expected to be useful for the electronic device. There are many methods to provide opening band gap in monolayer graphene, one of them is using atomic covalent functionalization such as hydrogen[7], flourine[8] and oxygen[9,10] or molecule[11] either above or below the graphene surface. However, the used of oxygen for graphene functionalization is more promising. On the other hand, introducing oxygen is expected to cause symmetry breaking on the electronic properties[9].

In present work, we used a first-principle density functional theory (DFT) calculation to clarify the electronic properties of graphene with oxygen-functionalization.

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## 2. COMPUTATIONAL METHODS

We performed first-principle electronic structure calculation on the monolayer graphene based on the density functional theory (DFT) within generalized gradient approximation (GGA)[12] using the OpenMX code[13]. Norm-conserving pseudopotentials[14] is used and the wave function is expanded by the linear combination of pseudo-atomic orbitals (LCPOs) generated using a confinement scheme[15,16]. The orbitals are specified by  $C6.0 - s^2p^2d^1$  and  $O7.0 - s^2p^2d^1$  which means that the cutoff radii are 6.0 and 7.0 bohr for the *C* and *O* atoms, respectively, in the confinement scheme[15,16]. For the *C* dan *O* atoms, two primitive orbitals expand the *s* and *p* orbitals, and one primitive orbital expands the *d* orbital.

The monolayer graphene is modelled as a periodic slab with a large vacuum layer (25Å) in order to avoid interaction between adjacent layers. We used  $3 \times 3$  supercell consisting of 18 *C* atoms. We introduced the oxygen atoms with concentrations are varied for 0% – 50%. A  $12 \times 12 \times 1$  *k*-point grid and energy cutoff 250 Ry are used. The geometries were fully relaxed until the force acting each atom was less than 2 meV/Å. We find that the optimized lattice constant of pristine graphene is 2.47 Å, which is good agreement with recently calculated reported data[10].

We calculated the adsorption energy defined as follows[10]:

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

Where  $E_{\text{tot}}$  is total energy of graphene with various oxygen concentration,  $E_G$  is the energy of pristine graphene,  $N$  is the number of *O* atoms and  $E_O$  is the energy of an isolated *O* atom.

## 3. RESULT AND DISCUSSION

First, we examine the structural and energetic stability of graphene-oxygen functionalization. Table 1 shows calculated the result of structural optimisation and adsorption energy. In the pristine graphene, we find that  $d_{c-c} = 1.42$  Å which is consistent with the previous result[10]. Furthermore, oxygen-functionalization graphene will cause an increase of total energy.

**Table 1.** Summary of the structural optimisation.  $d_{c-c}$  (Å) denotes to the distance between of two *C* atoms which are bonded.  $d_{c-o}$  (Å) denotes to the distance between of *C* atom and *O* atom which are bonded.  $E_{\text{ads}}$  (eV/O) is oxygen adsorption energy for the most stable configuration, and  $E_{\text{tot}}$  (eV) is total energy a system.

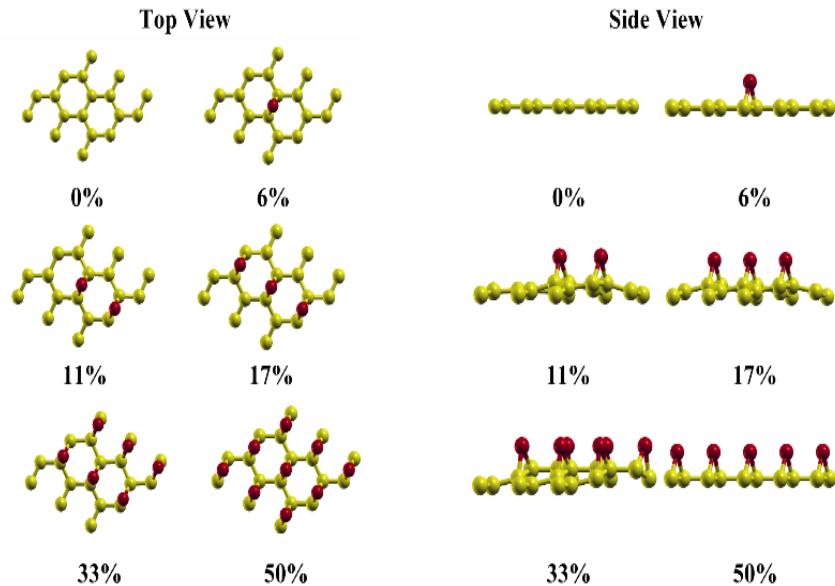
O/C(%)	0%	6%	11%	17%	33%	50%
$d_{c-c}$ (Å)	1.42	1.42	1.39	1.37	1.35	1.41
$d_{c-o}$ (Å)	-	1.42	1.45	1.45	1.48	1.44
$E_{\text{ads}}$ (eV/O)	-	-2.19	-2.02	-1.94	-2.36	-1.90
$E_{\text{tot}}$ (eV)	-286154.91	-330182.93	-374156.53	-418157.34	-550377.45	-682053.34

Figure 1 shows the relaxed geometry of the oxygen-functionalization graphene, we find buckling structures at 11%, 17% and 33% concentrations. These buckling structures occur due to the symmetry breaking induced by the presence of the *O* atoms.

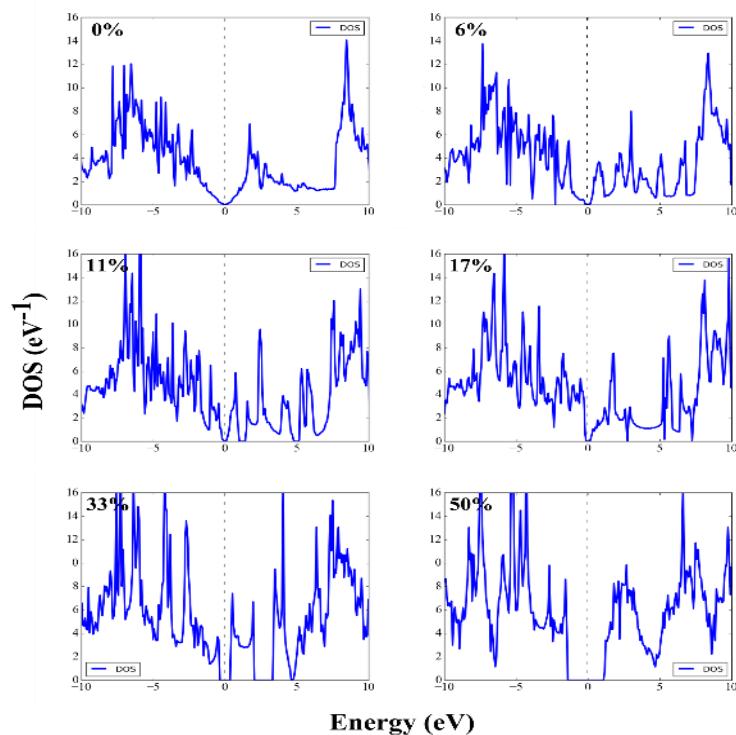
Next, we investigate the effect of oxygen-functionalization on the electronic properties graphene. As shown in table 2, the opening band gap is visible by introducing oxygen atoms, which is in a good agreement with previous results[10].

**Table 2.** Summary of band gaps energy of graphene with the different oxygen concentration.

O/C(%)	0%	6%	11%	17%	33%	50%
$E_g$ (eV)	0	0.1	0.19	0.23	0.73	2.48

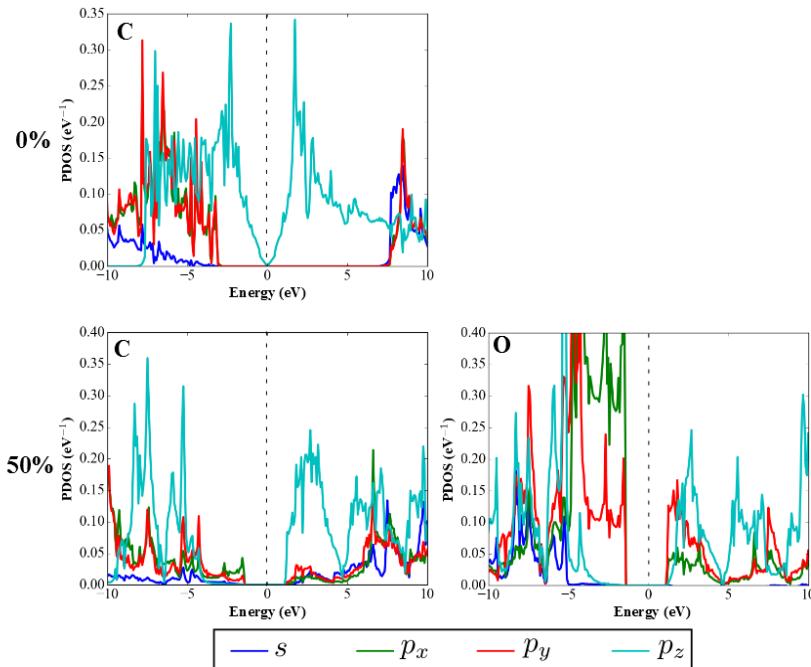


**Figure 1.** Structure optimization result for monolayer graphene systems with  $3 \times 3$  supercell with various oxygen concentration (O/C) is 0%, 6%, 11%, 17%, 33% and 50%.



**Figure 2.** A Density of states (DOS) of monolayer graphene with the different oxygen concentration.

To clarify the origin of the opening the band gap, we consider the partial density of states (PDOS) projected the atomic orbitals as shown in figure 3.



**Figure 3.** PDOS for C and O atoms with 0% and 50% oxygen concentration.

Figure 3 shows the PDOS of monolayer graphene with 0% oxygen concentration. The  $p_z$  orbital of the C atom dominates the band energy in the area around the Fermi level. Taking the system with 50% concentration, we find that strong hybridization between the  $C - p$  and  $O - p$  orbitals play an important role in the opening band gap. Here, the valence band maximum (VBM) is originated from the contribution of the  $O - p_z$  and  $O - p_y$  orbitals, while the conduction band minimum (CBM) predominantly by  $C - p_z$  and  $O - p_y$  so that the energy level in the valence band and the conduction shifting from the Fermi level and causing the bandgap in the systems.

#### 4. CONCLUSION

In conclusion, we have successfully calculated the structure electronic properties of oxygen-functionalization of graphene using first-principle DFT calculation. We found that enhancement of the band gap is visible by increasing the oxygen concentrations. An analysis using the partial density-of-states projected to the atoms confirmed that strong hybridizations between  $O - P_y$  and  $C - P_z$  orbitals are responsible for inducing the enhancement of the bandgap.

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