ELECTRONIC PROPERTIES OF O-DOPED POROUS GRAPHENE AND BIPHENYLENE CARBON: A DENSITY FUNCTIONAL THEORY STUDY

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We have used density functional theory to study the electronic properties of O-doped porous graphene and O-doped biphenylene carbon. The porous graphene is an insulator, while the biphenylene carbon shows semiconducting property. It was found that oxygen doping has a considerable effect on the electronic properties of porous graphene and biphenylene carbon sheets. These sheets become n-type semiconductors in the presence of oxygen impurity. The energy band gap was decreased due to the presence of oxygen impurity.

Key words: Porous graphene; Biphenylene carbon; Oxygen impurity; Electronic band structure; Density of states; Density functional theory.

1. INTRODUCTION

Recent advances in the field of nanotechnology have led to synthesis and characterization of two-dimensional nanostructures such as graphene [1]. Graphene is a monolayer of sp^2 bonded carbon atoms arranged in a honeycomb lattice. The p_z orbitals of carbon atoms are half filled in graphene, which results in the Dirac like electronic structure with semimetallic feature [2, 3]. Because of the unique structure and electronic properties of graphene, it is introduced as a promising material for nanoscale electronics. The gapless semiconducting property of graphene imposes serious limitations to its use in some electronic applications. To proper a band gap, many physical and chemical approaches such as cutting, etching and functionalization have been discussed [4-6]. One of the most interesting approaches has been trying to obtain intrinsically hydrogenated structures such as porous graphene (PG). In recent years, PG has been synthesized successfully [7]. Nevertheless, PG is not an ideal structure due to its large band gap and flat (low mobility) electronic bands [8]. Recently, another two-dimensional carbon allotrope named biphenylene carbon (BPC) is obtained from selective dehydrogenation of PG [8]. BPC presents an intrinsic good band gap and well-delocalized frontier orbitals [8, 9].

Since it is almost impossible to work with impurity-free materials, it is essential to understand how impurities change the electronic properties of graphene based materials [10]. The present studies show impurity efficiently modulates the electronic structures of graphene [11-13]. Despite this result, role of dopant atoms in modulating the electronic properties of PG and BPC has not been reported yet. Hence, we have studied the effect of oxygen impurity on electronic properties of

PG and PBC using density functional theory (DFT) in the present work.

2. COMPUTATIONAL DETAILS

DFT calculations are performed using the OpenMX3.7 [14]. The OpenMX (Open source package for Material eXplore) is a software package for nanoscale material simulations based of DFT, norm-conserving, pseudopotentials, and pseudo-atomic localized basis functions. The methods and algorithms used in OpenMX and their implementation were carefully designed for the realization of large scale ab initio electronic structure calculations on parallel computers based on the MPI or MPI/OpenMP hybrid parallelism. The efficient implementation of DFT enables us to investigate electronic, magnetic, and geometrical structures of a wide variety of materials such as biological molecules, carbon-based materials, magnetic materials, and nanoscale conductors [14].

The Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) is used [15]. The plane wave cutoff energy is set to be 150 Ry. The electronic band structures are calculated using 51 k-points along each high symmetry lines. A 2×2 supercell is considered and periodic boundary conditions are employed. A vacuum region of 20 Å is introduced between different sheets in neighboring periodic replicas. All geometries are fully relaxed until the residual force is less than 0.01 eV/Å on each atom.

We have calculated the cohesive energy, E_{coh}, to quantify the stability and formation ability of different structures. The cohesive energy is defined as

$$E_{coh} = \frac{E_{tot} - \sum n_x E_x}{\sum n_x} \qquad (1)$$

where E_{tot} is total energy of sheet, E_x and n_x are total energy and number of type x atom (x=C, H, O).
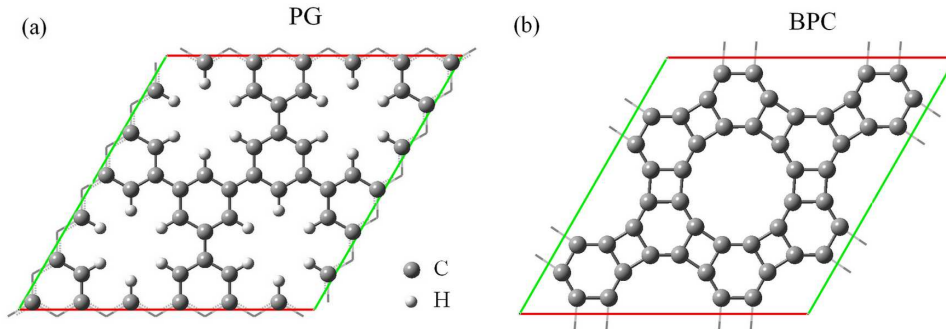
3. RESULTS AND DISCUSSIONS

Fig. 1 - Atomic structures of PG and BPC.

First, we have studied the structure and electronic properties of PG and BPC. The optimized structure of PG and PBC are presented in Fig. 1. In PG, the bonds of C atoms have two types, i.e., C-C bonds in the C hexagons and the C-C bonds link the different hexagons. Here, the bond lengths in the rings and intrarings are 1.40 and 1.50 Å, respectively. In BPC, the bond lengths in 4-membered and 12-membered rings are 1.48 and 1.36 Å, respectively. The obtained geometries are in good agreement with theoretical [8] and experimental [16] reported data. The cohesive energy is calculated to investigate stability of PG and PBC. The cohesive energy of PG and BPC are -6.7 and -7.5 eV, respectively (Table 1). As expected PG and BPC are stable in thermodynamics and they may be synthesized in ambient temperature [8]. The larger cohesive energy of BPC than PG indicates that BPC is more stable than PG. This result agrees with previous report [8].

The electronic band structures and density of states (DOS) of PG are shown in Fig. 2a. A large band gap is observed between the conduction and valence bands, and DOS is zero around the Fermi level (The Fermi level is set at 0 eV). It means PG is an insulator with a large band gap of 2.2 eV at the K-point, which is in good agreement with previous estimation of 2.35 [9], 2.34 [17], and 3.3 eV [8].

In Fig. 2b, the electronic band structure and DOS of BPC are presented. As seen, DOS is zero at the Fermi level (0 eV) and band gap is 0.4 eV at the K-point. Hence, BPC is a semiconductor. The semiconducting property of BPC was reported in Ref. [8]. The energy band gaps of PG and BPC are listed in Table 1.

Table 1
The cohesive energy (E_{coh}) and energy band gap (E_g).

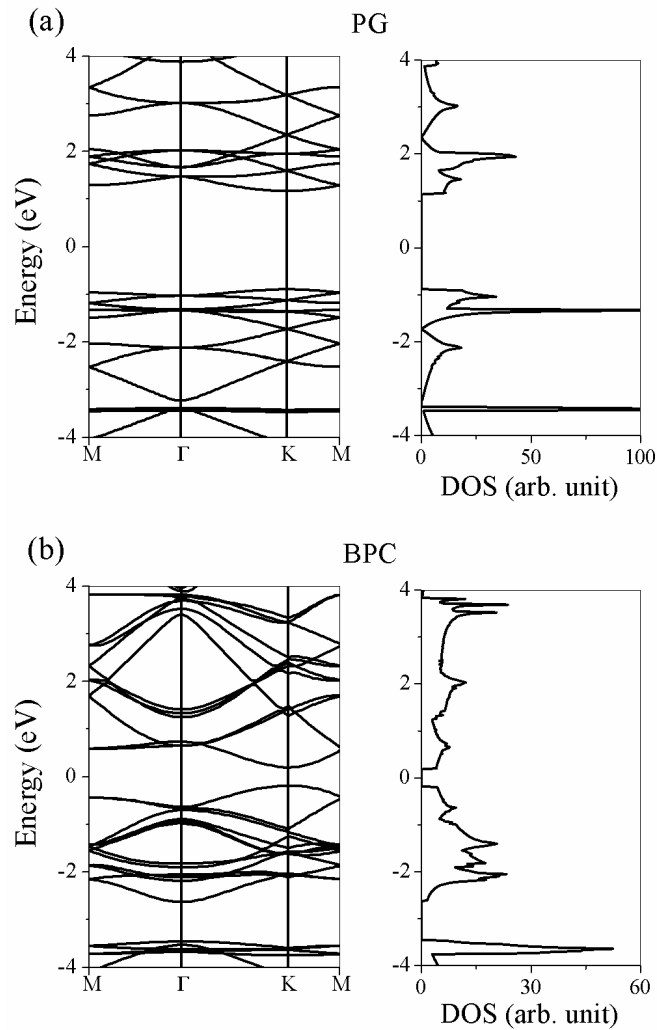| structure		E_{coh} (eV)	E_g (eV)
PG		-6.7	2.2
BPC		-7.5	0.4
O-doped PG	I	-6.7	2.04
	II	-6.6	0.86
	III	-6.6	0.61
O-doped BPC		-7.3	0.23

Fig. 2 - Electronic band structures and DOS of PG and BPC.

We have modeled O-doped PG and BPC sheets by one oxygen atom substituting one carbon or hydrogen atom in the sheets. As shown in Fig. 3, three different configurations of O-doped PG and one model of O-doped BPC. The values of cohesive energy show stability of O-doped PG and BPC.

The electronic band structure and DOS of O-doped PG and BPC are presented in Fig. 4. As a result of oxygen doping, occupied states and sharp DOS peaks below the Fermi level are created. Hence, O-doped PG and PBC become n-type semiconductors. This can be explained by the fact that oxygen has more electron than carbon atom so called donor. On account of having these extra electrons for the purpose of conduction, O-doped PG and BPC become n-type semiconductors.
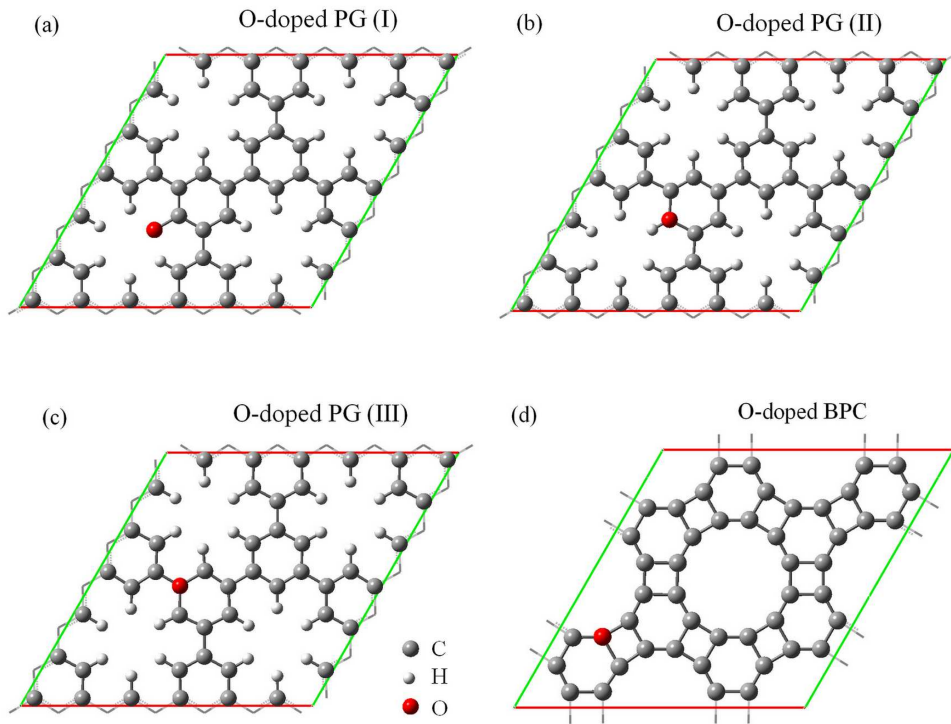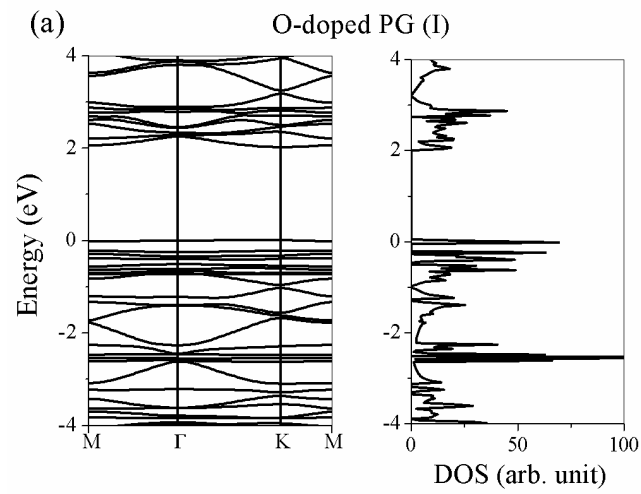
(a) O-doped PG (I)   (b) O-doped PG (II)

(c) O-doped PG (III)   (d) O-doped BPC

C
H
O

Fig. 3 - Atomic structures of different configurations of O-doped PG and BPC.

(a) O-doped PG (I)

(b) O-doped PG (II)
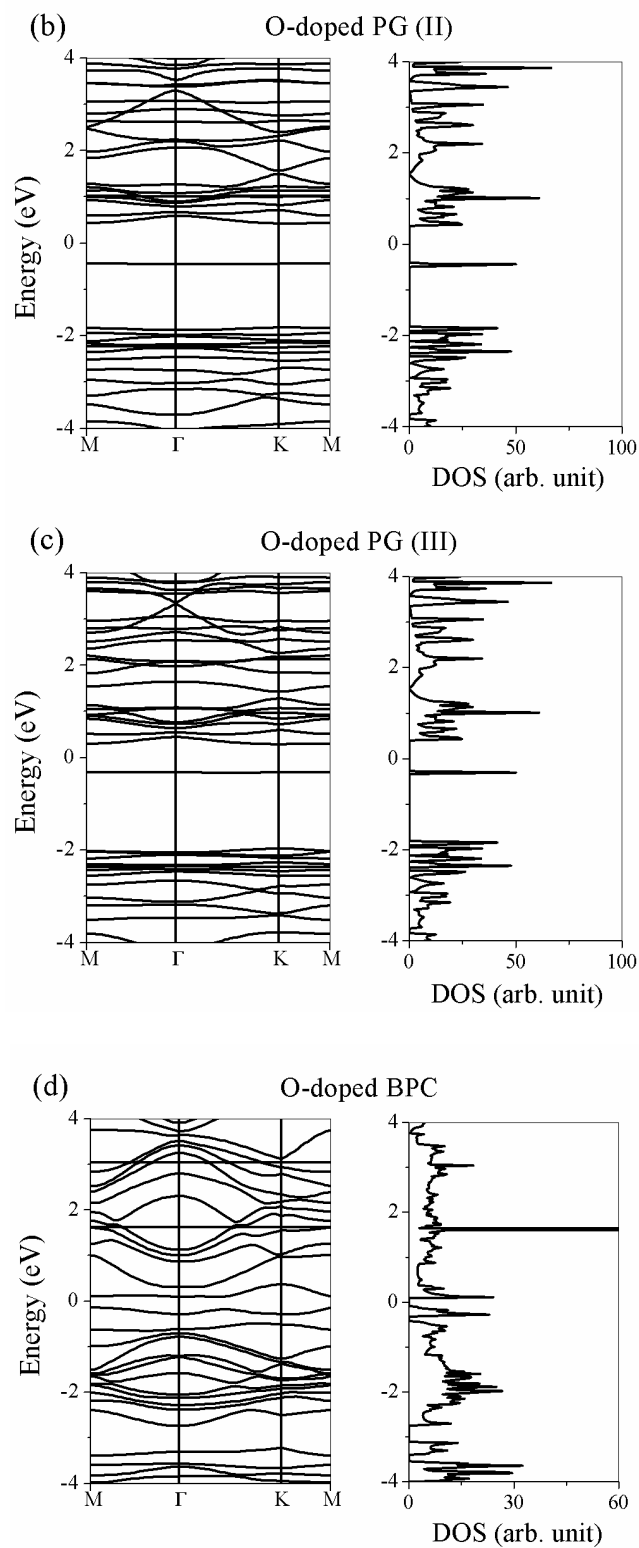

(c) O-doped PG (III)

(d) O-doped BPC

Fig. 4 - Electronic band structures and DOS of O-doped PG and BPC.

The changes especially near the Fermi level are expected to cause changes in the energy band gap and corresponding electronic properties. The energy band gaps of different configurations are listed in Table 1. The results indicate that oxygen impurity causes a decrease in energy band gap of PG and BPC.

To clarify the changes induced by oxygen impurity, partial DOS (pDOS) is calculated. For instance, the pDOS of O-doped PG (III) is shown in Fig. 5. The pDOS shows the DOS peak below the Fermi level are mainly formed by oxygen atom.
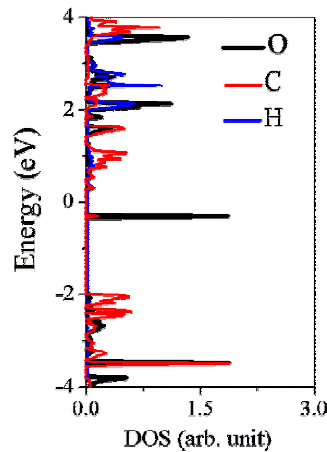

Fig. 5 - pDOS of O-doped PG (III).

4. CONCLUSIONS

The effect of oxygen impurity on the electronic properties of PG and BPC was studied using DFT. The cohesive energy, electronic band structures, DOS, and pDOS of different configurations of O-doped PG and BPC were calculated. The cohesive energy indicates stability of the considered structures. The PG and BPC show insulating and semiconducting properties, respectively. The oxygen impurity has a considerable effect on the energy band gap and consequently electrical conductivity of PG and BPC. They become n-type semiconductors in the presence of oxygen impurity.

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