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Influence of oxygen impurities on the electronic properties of graphene nanoflakes

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ABSTRACT

Controlled chemical doping with oxygen impurities is a promising approach for the electronic band engineering of graphene nanoflakes (GNFs). Based on the first-principles of the density functional theory (DFT) calculations, we investigated the effect of various consternations of substitutional impurities from oxygen atoms on the electronic properties of GNFs. Our results show that the electronic properties of GNFs do not only depend on the oxygen impurity concentrations, but also depend on the geometrical pattern of oxygen impurities in the GNFs. Additionally, we also found interesting electronic properties of GNFs structure, which significantly contribute to that oxygen dopants cause a decreased energy gap. So, our results suggest that substitutional impurities are the best viable option for enhancement of desired electronic properties of GNFs.

1. Introduction

The name of a single layer of graphite is called graphene, which consists of sp^2 hybridized carbon atoms. These atoms are arranged in a honeycomb lattice [1,2]. Graphene, a two-dimensional sheet has no band gap and small density of state (DOS) at the fermi level, which making graphene a semi-metal. Then, graphene has limitation in electronic applications [3]. Several methods have been proposed to present a band gap such as chemical doping and cut graphene into nanoribbons or nanoflakes [4–6]. GNFs is the name given to the zero-dimensional (0D) form of graphene. This is amazing given that preliminary studies indicated GNFs has a range of properties which vary from those of 2-D and 1-D graphene, and offer great potential for a set of electronic and magnetic applications.

In fact, the properties of GNFs are very useful for future electronics spintronics devices since these materials will need to be at the nanometer scale to increase the performance with minimum size. According to the creating methods of GNFs, this material is widely used in modern nanotechnology when GNFs is reasonable, reproducible, predictable, and stable [7]. This material is also considered a one picture from graphene related carbon materials (GRCMs), which has been extensively studied by theoreticians due to they have a broad area of applications. For instance, they use in battery electrodes, catalytic support, capacitors, gas storage, electrodes for fuel cells, and biomedical applications [8,9]. There are different studied to control on the electronic band gap. Depending on the size, the electronic band gap is decreased by increasing the size of graphene cluster [10].

This study aims at gaining insight into the effects of six concentrations of oxygen impurities in various locations on the electronic properties of GNFs. The studies electronic properties of GNFs principally DOS based on the first-principles of the DFT calculations. Our system contains from 24 carbon and 12 hydrogen atoms in the edge of GNFs. We studied six concentrations of oxygen impurities in various locations.

2. Computational details

In this work, all the structure optimizations, the GNFs with and without various dopants analysis, the DOS, and calculations of energies were done by using DFT [11,12] as it is implemented in the Gaussian 09 program package [13–15] at the level of B3LYP/6–31G basis set for the full geometry optimizations of GNFs with and without different constructions of oxygen impurities. All calculations are started by relaxation structures of all our systems. Before dopants, all geometrical structures were fully optimized and all the atoms were relaxed when GNFs included various concentrations of oxygen impurities. By using the above mentioned level of theory, the electronic properties of GNFs are investigated theoretically with various constructions of oxygen impurities in various locations. Moreover, DOS, LUMO, HOMO, and band gap are also calculated.

3. Results and discussions

First of all, a pure graphene nanoflakes (PGNFs) was fully

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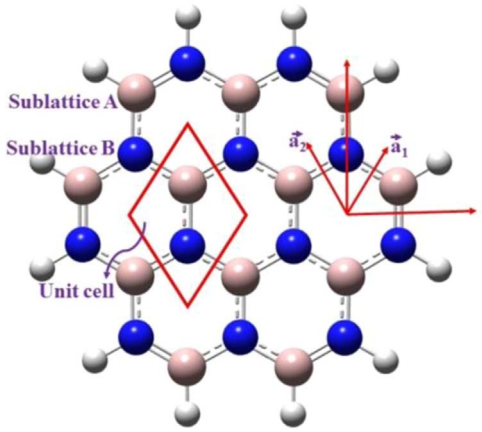

Fig. 1. The periodic lattice of GNF consisting of the unit cell of two carbon atoms in real space with the basis vectors a_1 and a_2. This system contains from 24 carbon and 12 hydrogen atoms in the edge of GNFs.

optimized, including their lattice constant, which was found to be 2.43 Å somewhat less than the experimental value of 2.46 Å. In addition, we found the C-C bond length of PGNFs is 1.43 Å which is in agreement with previous results [16]. Fig. 1 shows the unit cell and lattice constants a_1 and a_2 are expressed in cartesian coordinates $a_1=\frac{a_0}{2}(3, \sqrt{3})$ and $a_2=\frac{a_0}{2}(3, -3)$ where a_0 is an interatomic distance which has been found to be close to 1.43 Å.

Then, we calculated the DOS of PGNFs, which is presented in Fig. 2. We found that the electronic DOS and the electronic band gap is 4.02 eV of PGNFs are in agreement with the reference [17].

Subsequently, we discuss how the electronic properties of GNFs are affected by various concentrations of oxygen impurities in different locations. We considered $(n + 1)$ dopant of oxygen impurities in GNFs, where n is a positive integer number.

Our calculation started with single oxygen impurity. By substituting

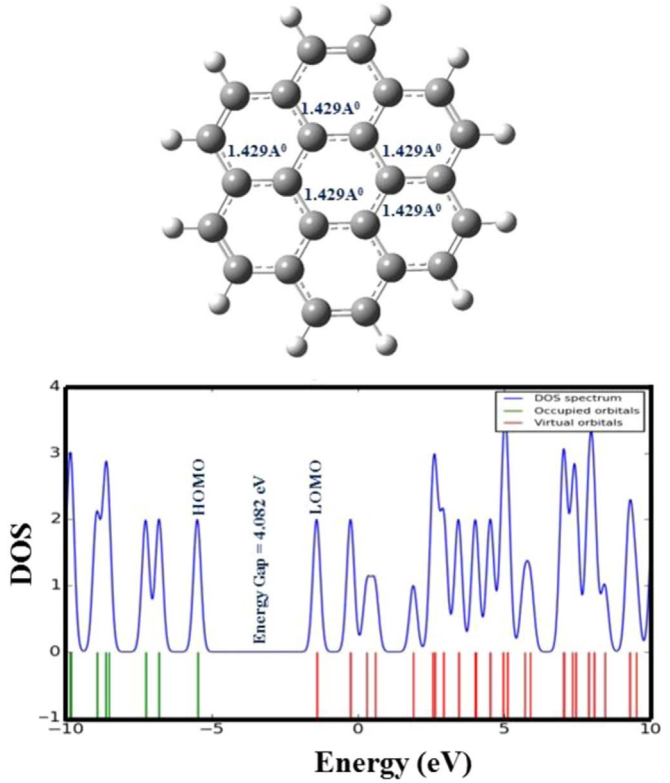

Fig. 2. Optimized geometry and DOS of PGNFs.

one carbon atom with one oxygen impurity in the center of GNFs structure. We observed that a bond length is found to expand to 1.5 Å approximately between C-O atoms, but it's decreased from 1.42 to 1.39 Å approximately between C-C atoms. Moreover, the energy gap is possible to calculate by using the above method. By breaking the symmetry of two carbon sub-lattices because of introduction of oxygen impurity, we observed that an energy gap is reduced from 4.082 eV to 2.372 and 2.049 eV as shown in Fig. 3(a) and (b), respectively. This interesting result of the smallest electronic gap for the single oxygen impurity doped in GNF due to the larger extent of orbital delocalization at the peripheral rings.

After finding an interesting result of changing the energy gap of GNFs with single oxygen impurity, we carried out our calculations with increased number of oxygen impurities dopant and also taking into account different sites of doping for the same concentration. It has been found that GNFs of same atomic concentrations doped GNFs can reduce the electronic band gap. We present the optimized structure as well as the electronic DOS structure of various GNFs of obtained by doping increased number of oxygen doped impurities in Figs. 4–7.

The realizations of structural properties show that the retraction of C-C bond length and longer C-O bond in case of oxygen impurity attend in structure due to having various sizes (Covalent radius of C and O are 76 and 73 pm, respectively), which effected on the bond length. Moreover, these results in defects of the lattice when the impurities are placed at adjacent positions. These results regarding bond length alternation are in general agreement with earlier calculations of doping [17].

Likewise, we found out that DOS with various concentrations of oxygen impurities has the same shape (levels are packed and shaper) to DOS of PGNFs, but with less density of the diagram as a result of GNFs' fewer electrons. By comparing the DOS diagram of PGNF with DOS diagram of O-GNFs, we found out that they have the same shaper, but the gap of DOS for O-GNFs is smaller (2.05 eV blue shift) see Fig. 3(b). As a consequence, the electronic DOS is decreased due to the number of concentrations are increased, which make the DOS shape approach infinite DOS diagram shape of GNFs as shown in Figs. 4 and 5.

By changing the location of the oxygen impurities with the same concentrations, we also observed that the DOS diagrams are affected. For instance, by increasing the distance between two oxygen impurities, the density of diagram is changed. The gap between the valence and conduction bands (energy gap) is reduced as shown in Fig. 6. These results are very important in various applications because it changes the GNFs from insulator to semiconductor. Additionally, substituting 5C atoms with 5O impurities in the center's hexagonal of GNFs also alters the DOS shape. These substitutional impurities increases the energy gap value compared with a previous study, see Fig. 7(a). To confirm the result, we replaced one hexagonal of C atoms with one hexagonal of oxygen impurities, see Fig. 7(b). We observed the same outcome as we explained in Fig. 7(a). In brief, the electronic band gap is reduced by increasing the distance between the oxygen impurities, see Table 1.

We calculated the total energies of GNFs with and without oxygen impurities, where such data would be of great importance of assessment of stability of doped GNFs and for selection of the most stable structures. Table 1 shows that the total energy is decreased by increasing the concentrations of oxygen impurities compared with origin case. Total energy also altered by using the same concentrations of oxygen impurities in different locations. All these impurities make the structures unstable due to decrease in the total energy of these structures. That means the GNFs becomes more reactive in the presence of oxygen impurities.

4. Conclusion

Effect of oxygen impurities on electronic properties of GNFs is analyzed by using DFT/B3LYP with the 6–31G basis set. We studied