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Hydrogen Peroxide Adsorption on Graphene with Stone-Wales Defect

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Abstract

To explore the possibility of using graphene based biosensor, adsorption of hydrogen peroxide on graphene has been investigated using density functional theory. The electronic properties of defect free and defective graphene in the presence of different number of hydrogen peroxide have been studied. The graphene with the most stable configuration defect named as SW defect is considered. The high adsorption energies indicate chemisorption of hydrogen peroxide on graphene. It is found that defect free graphene exhibits semimetallic behavior, while graphene with Stone-Wales defect shows semiconducting property. The charge is transferred from hydrogen peroxide to graphene. At low concentration of this donor molecule, defect free and defective graphene become n-type semiconductors. The energy band gap is decreased and metallic behavior is observed in graphene by increasing the number of hydrogen peroxide. The sensitivity of the electronic property of graphene to the presence of hydrogen peroxide suggests that these nanostructures are good choice to design biosensor for hydrogen peroxide detection.

1. Introduction

Hydrogen peroxide, an incompletely reduced metabolite of oxygen, is generated as a by-product of a wide range of biological processes [1]. It has a diverse array of physiological and pathological effects within living cells depending on the extent, timing, and location of its production. Characterization of cellular functions of hydrogen peroxide and provision of an opportunity for early diagnosis of progressive disease depend on detection of hydrogen peroxide and measurement of its concentration selectively in the presence of other oxygen metabolites. To detect hydrogen peroxide in biological processes, several sensitive methods have been developed [2, 3]. Among different techniques, the electrochemical ones have the advantage of being simple, having low cost and huge sensibility and selectivity [4].

The recent advances in nanotechnology have enable researchers to design and fabricate biosensors using nanostructures. Recently, biosensors based on graphene, graphyne and carbon nanotubes have attracted great attention due to unique structural and electronic properties of these carbon based nanostructures [5-9]. For instance, graphene and carbon nanotubes have been used to detect small molecules such as NO, NO_2, CO, CO_2, H_2O and biomolecules including DNA and proteins [5, 6]. In addition, high sensitivity of graphyne and carbon nanotubes to the presence of hydrogen peroxide has been reported [7-9]. The results indicate the optical sensitivity of carbon nanotubes to hydrogen peroxide even at low concentration [7]. It is also found that hydrogen peroxide has considerable effect on the electronic properties of semiconducting carbon nanotubes and gamma type graphyne [8, 9]. The sensitivity of optical and electrical properties of carbon nanotubes and graphyne to hydrogen peroxide open a new insight into developing biosensors. Intrigued by these results, we have exploited possibility of using graphene for hydrogen peroxide detection in the present work.

In reality, graphene usually suffers from various types of defects in the atomic structures during its growth [10, 11]. As electronic, chemical, thermal and mechanical properties of graphene are extensively sensitive to lattice imperfections [12, 13], considering the effect of defects is crucial. The Stone-Wales (SW) defect is one of the most common types of topological defects in graphene. It is formed by rotating a carbon-carbon bond in hexagonal network by $90°$ to convert four hexagonal rings to two pentagons and two heptagons. It is denoted in short as 5-7-7-5 defect due to the presence of pairs of five and seven atom rings [11]. The recent studies show that the presence of SW defect modifies the electronic, magnetic and elastic properties of graphene [14-18]. In recent years, adsorption of different gases and molecules on graphene with SW defect has been compared with adsorption on defect free graphene. For instance, adsorption of formaldehyde on SW defected graphene has been studied and suggested that adsorption on defective graphene was stronger than perfect one [19]. It is also found that atomic and electronic structures are very different in two cases, and defective graphene is more sensitive than perfect graphene [20, 21]. Adsorption of hydrogen peroxide on defective graphene functionalized with carboxyl groups has been also investigated [4]. The results indicate that functionalization increases the adsorption energy of hydrogen peroxide and improves the reduction reaction due to a favorable change in the properties of the defective layer. For comparison, results of these recent studies are listed in Table 1.

In the present work, we have studied the electronic properties of defect free and defective graphene in the presence of different number of hydrogen peroxide.

2. Computational details

The simulations are performed based on the density functional theory (DFT) as implemented in OpenMX 3.6 code [22]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) method is used to take into account the exchange correlation energy. The cutoff energy is set as 150 Ry. All atomic coordinates are fully relaxed until the force on each atom converges to 0.01 eV/Å. The k-point is set as 51 points along each high symmetry line in the Brillouin zone. The charge transfer between hydrogen peroxide and graphene is estimated by Mulliken population.

Table 1. The results of some recent studies

Results	Method	Year
CNTs are optically sensitive to hydrogen peroxide [7].	experiment	2007
Defective graphene functionalized with carboxyl groups is favorable for hydrogen peroxide detection [4].	DFT	2010
Graphene with SW defect is more sensitive than perfect graphene to formaldehyde [19].	DFT	2011
CNTs are electrically sensitive to hydrogen peroxide [8].	DFT	2013
Graphyne is electrically sensitive to hydrogen peroxide [9].	DFT	2013
Electrical sensitivity of SW defective and perfect graphene to different number of hydrogen peroxide is studied.	DFT	present work

In our simulations, a 5×5 supercell of graphene consists of 50 carbon atoms is considered (Fig. 1(a)). Three-dimensional periodic boundary conditions are applied to the supercell. The supercell of graphene is placed inside a simulation box of 12.3×12.3×15 Å^3. A vacuum above graphene sheet is assumed large enough to avoid interaction between two adjacent graphene sheets. To construct defective graphene, one SW defect is considered in one supercell as shown in Fig. 1(b). The optimized bond lengths of defective graphene are presented in Fig. 1(b).

3. Results and discussion

To evaluate interaction between hydrogen peroxide and graphene sheet, adsorption energy (E_{ads}) is calculated by

$$E_{ads} = E_{graphene+H2O2} - (E_{graphene} + E_{H2O2}) \qquad (1)$$

where $E_{graphene+H2O2}$ denotes the total energy of graphene with adsorbed hydrogen peroxide, $E_{graphene}$ and E_{H2O2} are the energies of graphene and hydrogen peroxide molecule, respectively.
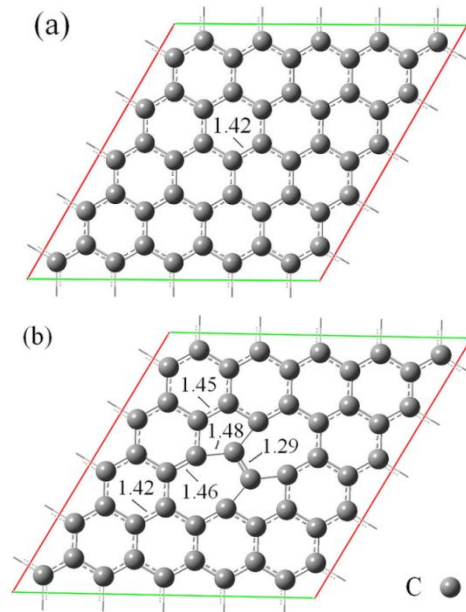

Fig. 1. Geometrical structures of (a) defect free and (b) defective graphene.

We have considered all possible adsorption sites for hydrogen peroxide adsorption on graphene sheet. At these sites, hydrogen peroxide is placed parallel and perpendicular to graphene sheet. The nearest distance between oxygen atom of hydrogen peroxide and carbon atom of graphene is varied from 2 to 4 Å at each adsorption configurations. It is found that adsorption energy of the configurations with hydrogen peroxide perpendicular to the graphene sheet is lower than the configurations with parallel hydrogen peroxide. For these configurations, the nearest distance between oxygen atom of hydrogen peroxide and carbon atom of graphene is about 2.6 Å. The most

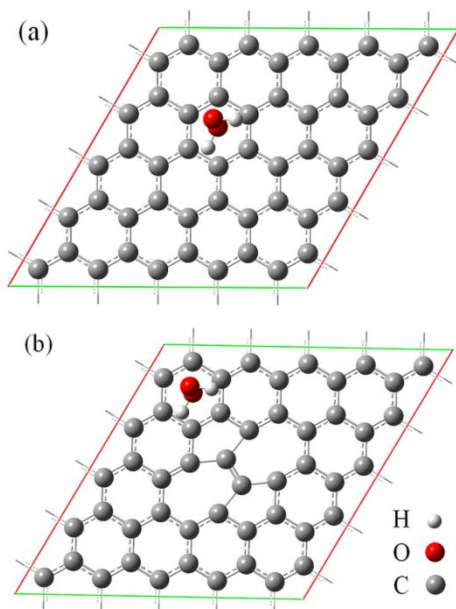stable adsorption configurations with the lowest adsorption energies are shown in Fig. 2.

Fig. 2. Most stable adsorption configurations of hydrogen peroxide on (a) defect free and (b) defective graphene.

The adsorption energies of hydrogen peroxide adsorbed on defect free and defective graphene are -1.28 eV and -1.81 eV, respectively. These high adsorption energies indicate chemisorption of hydrogen peroxide on defect free and defective graphene. Comparison of the adsorption energies shows that interaction between hydrogen peroxide and graphene is enhanced in the presence of SW defect.

3.1. Hydrogen peroxide adsorption on defect free graphene

The electronic band structure and density of states (DOS) of defect free graphene are presented in Fig. 3(a). As shown, valence and conduction bands are crossed at K point and DOS is zero at the Fermi level. (The Fermi level is set at 0 eV.) It means the defect free graphene is a semimetal in good agreement with previous studies [14, 23]. To clarify the effect of hydrogen peroxide on the electronic property, the electronic band structure and DOS of the defect free graphene in the presence of one hydrogen peroxide molecule per supercell are shown in Fig. 3(b). Adsorption of one hydrogen peroxide molecule leads to an occupied state and a sharp DOS peak below the Fermi level. It means the defect free graphene becomes n-type semiconductor in the presence of one hydrogen peroxide per supercell. The energy band gap between the highest occupied and the lowest unoccupied state is 0.08 eV.

The charge transfer between molecule and graphene are studied by Mulliken population analysis during the adsorption process. It is found that 0.37e charge is transferred from hydrogen peroxide to defect free graphene. Therefore, hydrogen peroxide as a donor molecule changes the defect free graphene with semimetallic property to n-type semiconductor.

To better understand the effect of hydrogen peroxide on the electronic properties of graphene, partial DOS (pDOS) of hydrogen peroxide adsorbed on defect free graphene is shown in Fig. 4(a). It is observed that DOS peaks near the Fermi energy are formed by the oxygen atom of hydrogen peroxide. The pDOS indicates that the sharp DOS peak below the Fermi level mainly comes from the contribution of hydrogen peroxide molecule.
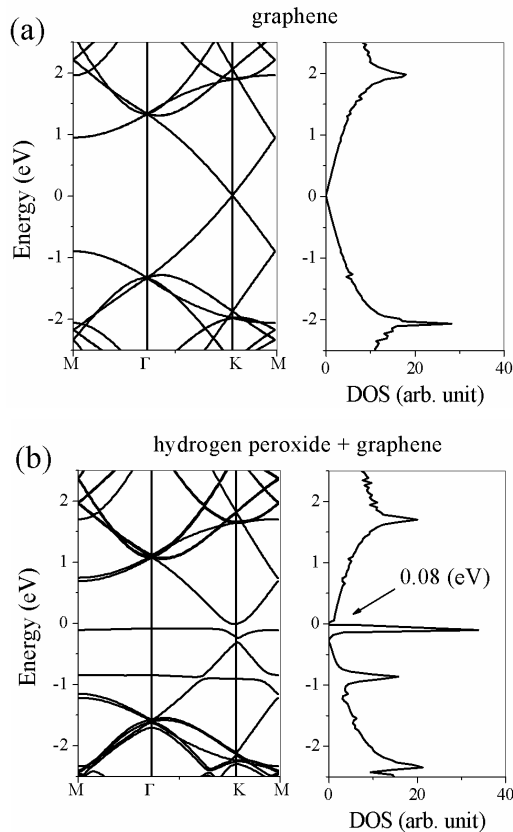
Fig. 3. Electronic band structures and DOS of defect free graphene (a) without and (b) with one hydrogen peroxide per supercell.

3.2. Hydrogen peroxide adsorption on defective graphene

The electronic band structure and DOS of defective graphene are shown in Fig. 5(a). The presence of SW defect opens a small band gap of 0.25 eV at K point. Hence, graphene with SW defect is a semiconductor. It means the electronic property of graphene is modified by introducing SW defect. This result is in agreement with previous investigations [4, 14, 24, 25].
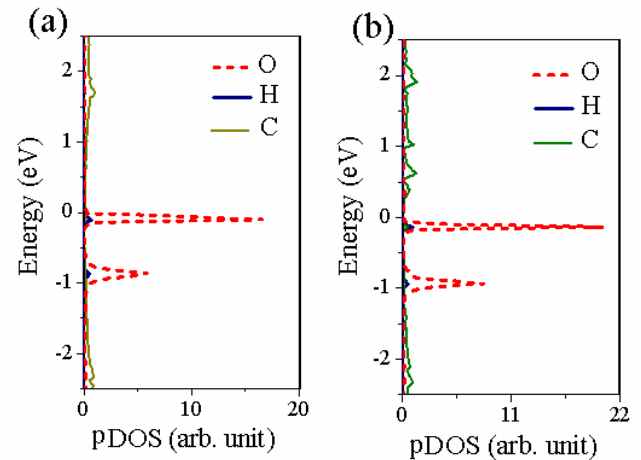

Fig. 4. pDOS of (a) defect free and (b) defective graphene with one hydrogen peroxide per supercell.

Now, we have studied effect of hydrogen peroxide on the electronic properties of defective graphene. As shown in Fig. 5(b), adsorption of one hydrogen peroxide on defective graphene leads to an occupied state and a sharp DOS peak below the Fermi level. Hence, graphene with SW defect becomes n-type semiconductor in the presence of one hydrogen peroxide per supercell.

The Mulliken population analysis clarify that charge of 0.35e is transferred from hydrogen peroxide to defective graphene. It means concentration of electrons and consequently electrical conductivity of defective graphene are increased by hydrogen peroxide adsorption.

In Fig. 4(b), pDOS for adsorption system of hydrogen peroxide and defective graphene is presented. As shown, a sharp DOS peak below the Fermi energy is formed by oxygen atom of hydrogen peroxide. It means the peak of DOS near the Fermi level mainly comes from contribution of hydrogen peroxide molecule.

The electronic property of defective graphene in the presence of different number of hydrogen peroxide is also studied. The energy band gap as a

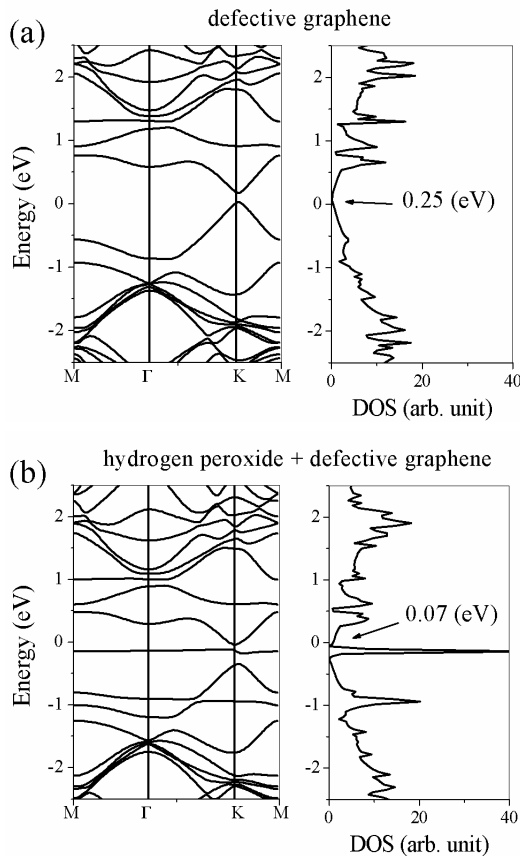function of the number of adsorbed hydrogen peroxide is shown in Fig. 6.

Fig. 5. Electronic band structures and DOS of defective graphene (a) without and (b) with one hydrogen peroxide per supercell.

The energy band gap reduction and consequently conductivity enhancement are observed by increasing the number of hydrogen peroxide per supercell. The energy band gap reaches zero and defective graphene becomes metal when the number of hydrogen peroxide is more than seventeen per supercell. The results indicate the electronic property of defective graphene is sensitive to the concentration of hydrogen peroxide.
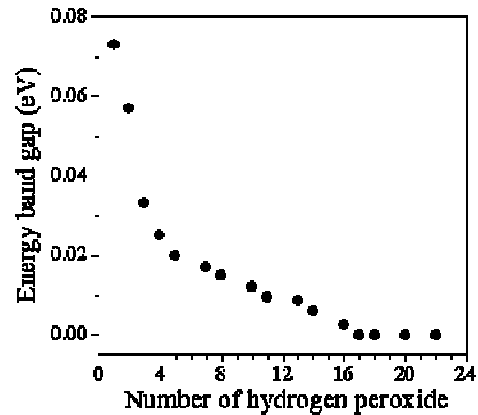

Fig. 6. Energy band gap of defective graphene via number of hydrogen peroxide per supercell.

For instance, the electronic band structures and DOSs of defective graphene in the presence of two and eighteen hydrogen peroxide per supercell are shown in Fig. 7. As shown in Fig. 7a, two occupied states and two sharp DOS peaks below the Fermi level are created by adsorption of two hydrogen peroxide molecules per supercell. It means the number of occupied states and peaks of DOS below the Fermi level depend on the number of hydrogen peroxide. As shown in Fig. 7b, the valence and conduction bands are crossed at the Fermi level, and DOS is non zero at the Fermi level. It means defective graphene with eighteen hydrogen peroxide molecules per supercell has a metallic property.

4. Conclusion

We have used DFT to study adsorption of hydrogen peroxide on defect free and defective graphene. The graphene with the most stable configuration defect named as SW defect is considered. A detailed investigation was performed on the adsorption energy, adsorption structure,

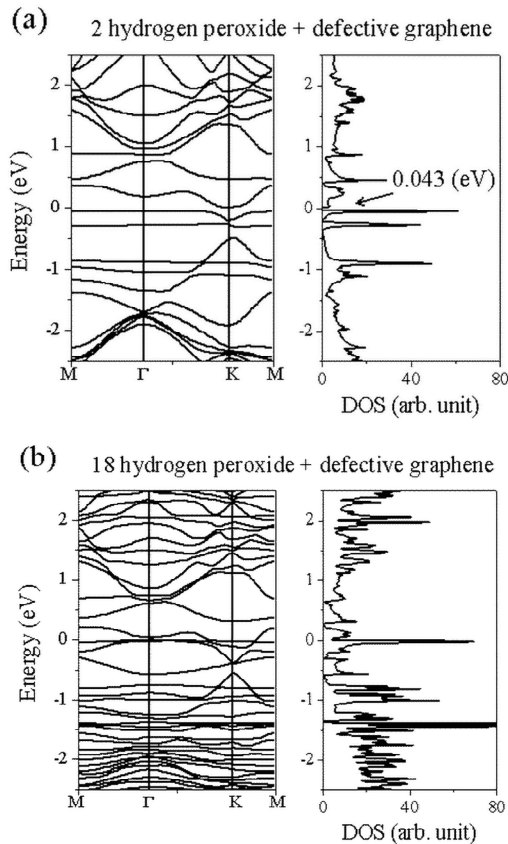charge transfer, electronic band structure, and DOS.

Fig. 7. Electronic band structures and DOSs of defective graphene in the presence of (a) two and (b) eighteen hydrogen peroxide per supercell.

The high adsorption energies show that hydrogen peroxide is chemically adsorbed on perfect and defective graphene sheets. The presence of SW defect in graphene enhanced the adsorption of hydrogen peroxide, which exhibited larger binding energy than that of defect free graphene. The results indicate that defect free and defective graphene has semimetallic and semiconducting properties, respectively. In the presence of hydrogen peroxide, defect free and defective graphene become n-type semiconductors. It is also found that the energy band gap is changed by number of hydrogen peroxide. The sensitivity of the electronic property of graphene indicates that detection of hydrogen peroxide and measurement of the concentration of this molecule are possible by graphene based biosensors.

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