



Effect of hydrogenation on the band gap of graphene nano-flakes

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ABSTRACT

The effects of hydrogenation on the band gap of graphene have been investigated by means of density functional theory method. It is generally considered that the band gap increases with increasing coverage of hydrogen atom on the graphene. However, the present study shows that the band gap decreases first with increasing hydrogen coverage and reaches the lowest value at finite coverage ($\gamma = 0.3$). Next, the band gap increases to that of insulator with coverage from 0.3 to 1.0. This specific feature of the band gap is reasonably explained by broken symmetry model and the decrease of pi-conjugation. The electronic states of hydrogenated graphene are discussed.

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1. Introduction

During the last decade, the graphene-based molecular devices were widely used as energy-related material, sensor, field-effect transistor, and biomedical application, due to their excellent electrical, mechanical, and thermal properties [1,2]. As well as pure graphene, functionalized graphenes were synthesized and characterized by several groups [3–6]. The tuning of graphene-based molecular devices to obtain the higher performance molecular devices is now an important field.

Recently, Elias et al. have investigated hydrogenated graphene by exposing to hydrogen plasma [7]. They found that a highly conductive graphene is converted from semimetal to insulator after the hydrogenation. Raman spectroscopy revealed that the hydrogenation breaks the π -bonding system of graphene surface after the formation of sp^3 carbon–hydrogen bonds. Transmission electron microscopy study indicates that the original hexagonal bonding arrangement is retained, whereas the lattice constant is significantly reduced. The hydrogenation is reversible through annealing, thereby restoring the conductivity and structure of graphene. This reversibility also creates the possibility of using such materials for hydrogen storage. Thus, the addition of hydrogen atom can be used to tune the electronic properties of graphene-based molecular devices [8].

From a theoretical point of view, density functional theory (DFT) calculations of hydrogenated graphene have been carried out by several groups [9–14]. Sofo et al. proposed that full hydrogenation of graphene forms a stable two dimensional (2D) hydrocarbon named *graphane* [10]. By means of the DFT computations, they also predicted that *graphane* has a wide band gap. Gao et al. calculated the band gap as a

function of coverage in the range of 66–100% [11]. They found that the band gap increases gradually up to 8 eV.

Casolo *et al.* investigated the adsorption of hydrogen atom to a 5×5 surface unit cell of graphene using DFT method [14]. The binding energy per hydrogen atom was calculated to be 0.8–1.9 eV. It suggested that the change of hybrid orbital from sp^2 to sp^3 is important due to the hydrogen atom adsorption to graphene.

Thus, the binding energy of hydrogen atom on the surface of graphene is quite well understood. However, the coverage dependence of band gap was only investigated in the range of 0.7–1.0 coverage (i.e., higher coverage regions). Therefore, the relation between the band gap and coverage in a wider coverage range remains unclear.

In the present study, the DFT method was applied to the hydrogen atom interacting with a graphene flake. The dependence of band gap on hydrogen coverage was investigated in detail in order to elucidate the effects of hydrogen addition on the electronic structures of graphene nano-flakes. In a previous paper [15], we conducted a preliminary investigation on the effects of hydrogen addition on the electronic states of graphene surface. We found that hydrogen addition causes a lowering of band gap of graphene flake in case of low coverage regions. However, the calculation was carried out at the semi-empirical PM3 molecular orbital level. In the present study, accurate DFT calculation was performed for the hydrogen added graphene to elucidate the origin of specific band gap property.

The paper is organized as follows: in Section 2, we present the method of calculations. In Section 3, the structures and electronic states of hydrogenated graphene with 19 benzene rings are reported. Subsequently, we give the results of larger graphene with 37 benzene rings to elucidate the size-dependence of the band gap. In Section 4, we discuss the specific band gap properties of hydrogenations.

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2. Method of calculation

Graphene nano-flakes composed of 19 and 37 benzene rings ($n = 19$ and 37) were used as models (denoted by GR(19) and GR(37), respectively). The edge carbon of graphene was terminated by a hydrogen atom. In case of hydrogenation of GR(19), even hydrogen atoms (from $m = 2$ to 54) were bonded to the surface carbon atoms, where m means the number of hydrogen atoms added to the surface. This addition causes a change of coverage from zero to 1.0.

The hydrogen atoms were first added to the carbon atoms at central region of GR(19), and then the additions were expanded to the edge region. Two hydrogen atoms were added to carbon atoms on the surface and reverse side. In case of GR(37), a similar hydrogenation was performed up to the maximum hydrogen atoms ($m = 96$).

The structures and electronic states of normal and hydrogenated graphenes were calculated by means of DFT method at the B3LYP/6-31G(d) level using Gaussian 03 program package [16]. The excitation energy and band gap were calculated by means of time dependent (TD) DFT method. The electronic states of all molecules were obtained by natural population analysis (NPA) and natural bond orbital (NBO) methods at the B3LYP/6-31G(d) level. The levels of theory calculated for GR(19) and GR(37) were B3LYP/6-31G(d) and 3-21G(d), respectively. These levels give a reasonable electronic state of the graphene as shown in previous calculations [17–20].

3. Results

A. Structures of hydrogenated graphene flakes

The structure of GR(19) optimized at the B3LYP/6-31G(d) level is

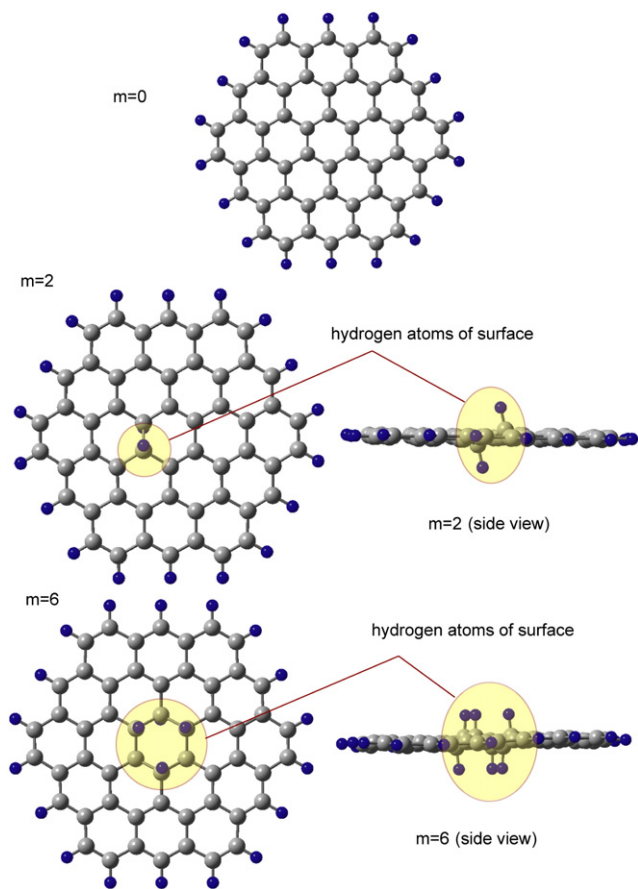


Fig. 1. Optimized structure of pure graphene GR(19) ($m = 0$), and hydrogen added graphene flakes ($m = 2$ and 6) obtained at the B3LYP/6-31G(d) level. Hydrogen atom is bound to central carbon atoms. Notation of m means number of hydrogen atoms added to the graphene. The structures were fully optimized at the B3LYP/6-31G(d) level.

illustrated in Fig. 1 ($m = 0$). The optimized structure of GR(19) ($m = 0$) showed a purely planar form. The C–C bond distance was calculated to be 1.420 Å around the center of graphene.

Next, two hydrogen atoms were added to the carbon atoms around the central region of GR(19), and then the structure was fully optimized. The optimized structure is illustrated in Fig. 1 ($m = 2$). The C₁–H bond distance between added hydrogen atom and carbon was calculated to be $r(\text{C}_1\text{–H}) = 1.111$ Å, where C₁ means the carbon atom added by a hydrogen atom. The structure around the C₁–H bond has a pyramidal form, and the carbon atom was 0.39 Å higher than the graphene plane. The C–C bond length was 1.522 Å around the C₁–H bond, which is 0.10 Å longer than that of $m = 0$.

The electronic states of carbon atoms at the binding site (denoted by C₁ and C₂) were changed by the addition of hydrogen atoms. To elucidate the change of electronic state of the carbon atoms, the NBO analysis was carried out for $m = 0$ and 2. The NBO of the C₁–C₂ bond of free graphene ($m = 0$) is expressed by

$$\sigma_{\text{C-C}} = 0.707(sp^{1.99})_{\text{C}_1} + 0.707(sp^{1.99})_{\text{C}_2} \quad (1)$$

where, C₁ and C₂ mean carbon atoms in the binding and neighbor sites, respectively. After the addition of the hydrogen atoms, the NBO for $m = 2$ was expressed by

$$\sigma_{\text{C-C}} = 0.707(sp^{2.80})_{\text{C}_1} + 0.707(sp^{2.80})_{\text{C}_2} \quad (2)$$

The coefficient of sp orbital for $m = 0$ (1.99) was close to 2.00, indicating that the orbitals of the carbon atoms are close to a sp^2 orbital before the addition. After the addition of hydrogen atoms, the coefficient is changed from 1.99 to 2.80. The result indicates that the binding nature is changed from sp^2 to sp^3 -like orbitals after the addition of hydrogen atoms. This feature is the same as reported in previous works [7,21].

The structure for $m = 6$ is also given in Fig. 1 (lower). The C–H bond length was 1.016 Å, and the structure of the six-membered ring added by hydrogen atoms takes an armchair form, which is close to the structure of cyclohexane molecule. The C–C bond length was 1.526 Å around the binding site, which is slightly elongated from that of $m = 2$.

The structures of middle and high coverage graphenes ($m = 24$ and 54) are illustrated in Fig. 2. In case of $m = 24$, all carbon atoms in bulk surface are covered with the hydrogen atoms. However, the π orbitals in the edge region still remain. In $m = 54$, there is no

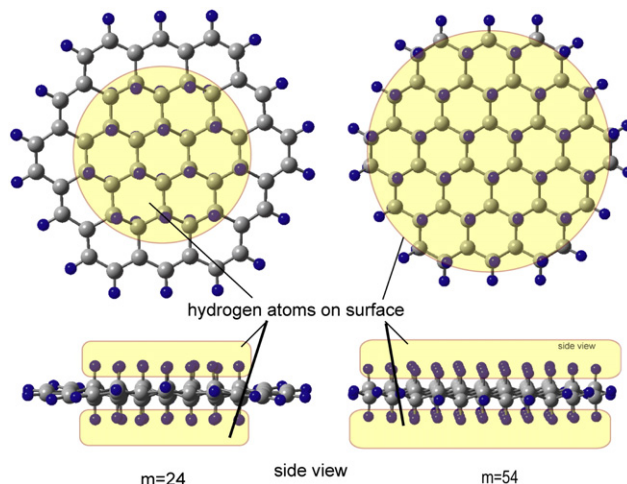


Fig. 2. Optimized structure of hydrogen added graphene flakes GR(19) ($m = 24$ and 54) with higher coverage. The structures were fully optimized at the B3LYP/6-31G(d) level.

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