Short communication

Density functional theory (DFT) study on the effects of Li+ doping on electronic states of graphene

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ABSTRACT

The electronic structures of a lithium ion (Li+) doped-graphene at the ground and low-lying excited states have been investigated by means of density functional theory (DFT) method. A graphene composed of 19 benzene rings was used as a model of graphene, while the edge carbon atom was terminated by hydrogen atom (expressed by $C_{54}H_{18}$). The geometry optimization showed that the Li+ ion binds to a hexagonal site where six carbon atoms interact equivalently to the Li+ ion. When the Li+ ion interacts with the graphene surface, the electronic configuration of the Li+ ion is changed from $(1s)^2(2s)^0$ to $(1s)^2(2s)^{0.01}(2p)^0(3p)^{0.02}$, suggesting that the sp-hybridization of lithium ion is important in the adsorption to the graphene surface. The band gap of graphene is slightly red-shifted by the doping of Li+ ion due to the interaction with the sp-hybrid orbital. The effects of Li+ on both the ground and excited electronic states of graphene were discussed on the basis of theoretical results.

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1. Introduction

The interactions of alkali ion with carbon materials such as graphene and C_{60} are important in the development of new molecular devices. It is known that the electronic states of graphene are drastically changed by doping of the alkali metal and ions. Also, the doping to graphene increases a capacity of molecular hydrogen as a H_2-storage. Especially, in the case of Li+ doped graphene [1–4], the interaction is much important in the field of secondary rechargeable batteries. A theoretical maximum capacity of normal graphite material for lithium ion (LiC_6) is 372 mAh g^{-1}. If the carbon material is changed from graphite to graphene, it has been expected that the capacity increases up to 500–1100 mAh g^{-1}. The characteristics are originated from non-layer structure where Li atom and ion are stored in both surface and edge regions of the graphene.

The interaction between Li+ and graphene has been investigated theoretically by several groups using lithium-small carbon cluster models. Marquez et al. calculated the binding energy of Li+ and hydrogen terminated graphene ($C_{32}H_{18}$) using density functional theory (DFT) method and indicated that the Li+ ion is preferentially bound outside the graphene (i.e., the edge region) [5]. On the basis of semi-empirical molecular orbital (MO) calculations using a C_{96}

planer carbon cluster and Li+, Nakadaira et al. suggested that the adsorption to the edge site is more stable than that of bulk [6]. The tight binding calculations showed that flat band composed of side edge carbon atoms is located near Fermi level [7]. Ab initio calculations for the interaction of lithium atom with graphite model clusters indicated that charge transfer from the Li atom to graphite cluster is important in the large cluster size [8,9].

Ishikawa et al. investigated the interaction of Li atom with polycyclic hydrocarbon molecules (pyrene, anthracene, and phenanthrene) [10]. The binding energies for several sites are calculated using the B3LYP/6-31G(d)//HF/6-31G* level. More recently, Suzuki et al. investigated the storage state of the Li+ ion with a $C_{54}H_{18}$ cluster using the semi-empirical PM3 method [11]. Thus, the electronic structures at the ground states of Li+-graphene system have been extensively studied. However, the information about excited states is still unclear.

In the present study, we applied density functional theory (DFT) [12–15] to a lithium–graphene interaction system to shed light on doping effects on the electronic structures of graphene from quantum mechanical point of view. In particular, we focus our attention on both ground and low-lying excited states of Li+ doped-graphene.

2. Method of calculations

As a model of graphene, a graphene composed of 19 benzene rings ($C_{54}H_{18}$), was examined in the present study. The graphene

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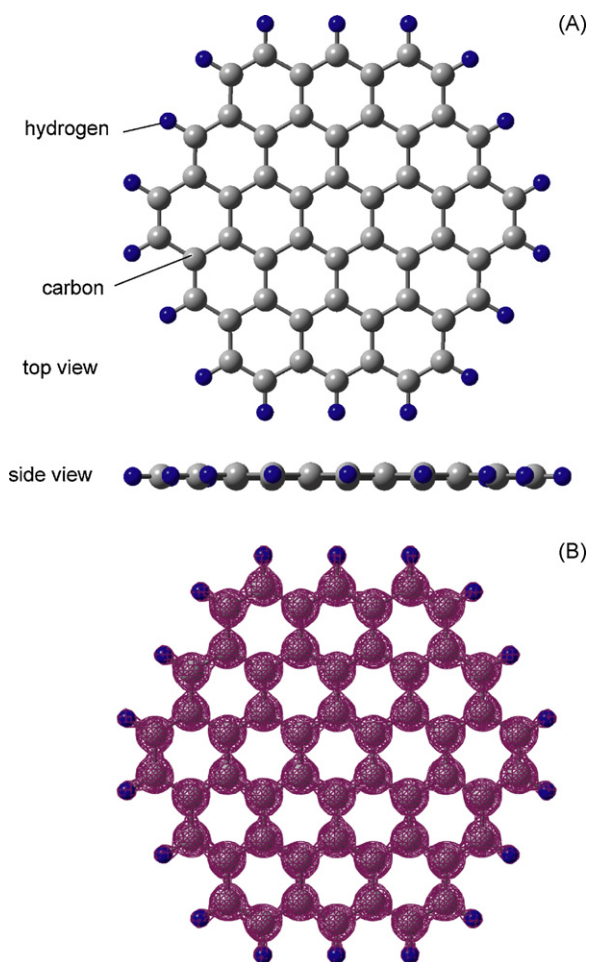 E-mail address: hiroto@eng.hokudai.ac.jp (H. Tachikawa).

Fig. 1. Structure of graphene (normal graphene) used in the present study. (A) Optimized structure of normal graphene obtained at the B3LYP/6-31G(d) level. Edge region of graphene is terminated by hydrogen atom. (B) Electrostatic potential of normal graphene.

used in the present study (denoted by H-graphene) is illustrated in Fig. 1. The edge carbon atom of graphene was terminated by hydrogen atom. First, the structure of the graphene was fully optimized at the B3LYP/6-31G(d) level of theory, and then the excitation energies and electronic structure at the excited states were obtained by the time-dependent (TD)DFT calculation.

For the lithium-doped graphene (denoted by Li$^+$-graphene), it was assumed that lithium ion interacts with the central region of the graphene. The structure of Li$^+$-graphene was fully optimized. All DFT calculations were carried out using Gaussian 03 program package [16].

3. Results

3.1. Structures of the graphene

The structure of the graphene ($C_{54}H_{18}$) was fully optimized at the B3LYP/6-31G(d) level of theory. The optimized structure is given in Fig. 1(A). The C–C bond and C–H bond lengths are calculated to be 1.420 and 1.088 Å, respectively.

The electrostatic potential is illustrated in Fig. 1(B). The positive charge is distributed on the carbon and hydrogen atoms, indicating that the lithium ion cannot bind directly with a carbon atom, but the ion may interact with hexagonal site composed of six carbon atoms.

The molecular orbitals (MO's) of the graphene ($n = 19$) are illustrated in Fig. 2 together with the orbital energies around highest occupied (HO)MO and lowest unoccupied (LU)MO calculated at the B3LYP/6-31G(d) level. Both HOMO and LUMO are doubly degenerated in energy. The orbitals from HOMO-2 to LUMO+3 are widely delocalized over the graphene surface.

To elucidate the electronic states of graphene at the ground and low-lying excited states, MO's and weights of configuration state functions (CSF's) are analyzed in detail. The excitation energies and CSF's are given in Table 1. The main configurations for the first excitation are ϕ(HOMO → LUMO+1) and ϕ(HOMO-1 → LUMO), while the coefficients of CSF's are 0.515 and −0.515, respectively. Here, ϕ(HOMO → LUMO) means a CSF where one electron is excited from HOMO to LUMO. It should be noted that HOMO and HOMO-1 are doubly degenerated, while LUMO, LUMO+1 are also doubly degenerated. These results indicate that the low-lying excited states of graphene are composed of the HOMO–LUMO excitations.

3.2. Electronic structure of Li$^+$ doped graphene

To elucidate the effects of lithium doping on the electronic structures of graphene, the similar calculation was carried out for the Li$^+$ doped graphene. The structure of the Li$^+$ adsorbed graphene (Li$^+C_{54}H_{18}$) was fully optimized at the B3LYP/6-31G(d) level of theory. The geometry of Li$^+$ doped graphene was optimized at the B3LYP/6-31G(d) level. The optimized structure is illustrated in Fig. 3. The lithium ion is trapped in a hexagonal site where six carbon atoms bind equivalently to the lithium ion. The Li$^+$ ion is located at $h = 1.812$ Å from the graphene surface. The C–C bond length around the Li$^+$ ion is calculated to be 1.429 Å, which is slightly elongated by the Li$^+$ doping. The natural charge of Li$^+$ is changed from +1.0 to +0.97, indicating that only 3% of positive charge is transferred from Li$^+$ ion to the graphene surface. The electron configuration of Li$^+$ is calculated to be $(1s)^2(2s)^{0.01}(2p)^0(3p)^{0.02}$. This result indicates that the electron donation from 2p-orbital of carbon atom to sp-orbital of Li$^+$ is important in the binding of Li$^+$ to the graphene.

The excitation energies of Li$^+$ doped graphene are given in Table 2. It was found that the first and second excitation ener-

Table 1

Excitation energies (E_{ex} in eV) and configuration state functions (CSFs) of the graphene (H-graphene with $n = 19$) calculated at the TD-DFT(B3LYP)/6-31G(d) level. Ten states were solved.

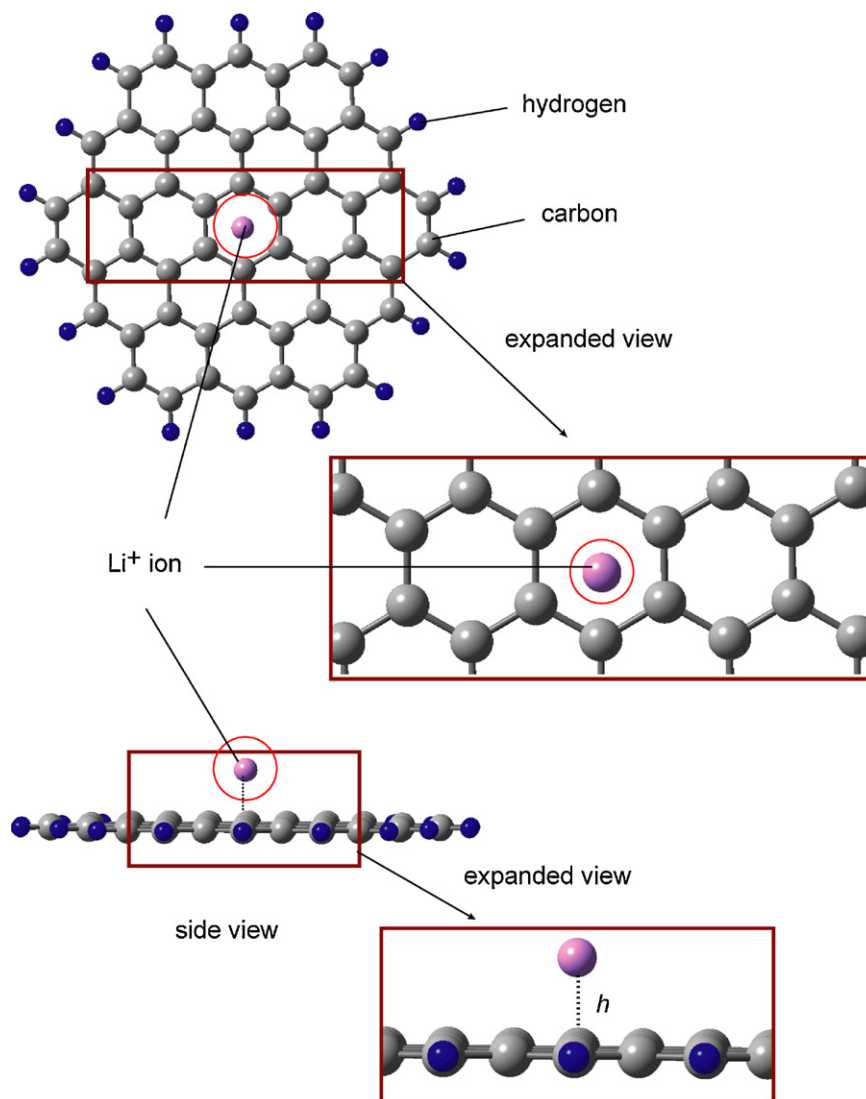| State	CSF and CI vectors	E_{ex} (eV)
S_1	0.515ϕ (HOMO → LUMO+1) − 0.515ϕ (HOMO-1 → LUMO)	2.24
S_2	0.492ϕ (HOMO-1 → LUMO+1) + 0.492ϕ (HOMO → LUMO)	2.39
S_3	0.426ϕ (HOMO-1 → LUMO) − 0.426ϕ (HOMO → LUMO+1)	2.91
S_4	0.426ϕ (HOMO-1 → LUMO+1) − 0.426ϕ (HOMO → LUMO)	2.91
S_5	0.401ϕ (HOMO-1 → LUMO+3) − 0.406ϕ (HOMO → LUMO+2)	3.12
S_6	0.403ϕ (HOMO-1 → LUMO+2) − 0.403ϕ (HOMO → LUMO+3)	3.12

Fig. 2. Structure of lithium doped-graphene (Li$^+$-graphene) optimized at the B3LYP/6-31G(d) level.

gies of the Li$^+$ graphene were calculated to be 2.21 and 2.34 eV, respectively, indicating that the excitation energies are slightly red-shifted by the doping (the excitation energies of normal graphene are 2.24 and 2.39 eV).

To elucidate the electronic feature in the Li$^+$ doped-graphene, MO's and weights of CSF's at the excited states are analyzed in detail. The special distributions of MO's and orbital energies around HOMO and LUMO are given in Fig. 4. It was found that HOMO, HOMO-1, LUMO, and LUMO+1 are widely delocalized on graphene surface. On the other hand, only HOMO-2 is localized in the edge region of graphene.

The coefficients of CSFs in the Li$^+$ graphene are summarized in Table 2. The first excited state was composed of two CSF's, ϕ(HOMO → LUMO+1) and ϕ(HOMO-1 → LUMO), while the coefficients of CSF's for former and latter were calculated to be 0.513 and 0.553, respectively. The second excited state is mainly composed of ϕ(HOMO-1 → LUMO+1) and ϕ(HOMO → LUMO) with the coefficient of 0.496 and −0.496. The orbital pictures of first and second excitations are the same as those of normal graphene. This result indicates that the excited states of graphene are slightly perturbed by the lithium doping, while the nature of the electronic structure is hardly changed.

Table 2
Excitation energies (E_{ex} in eV) and configuration state functions (CSFs) of Li$^+$-graphene with n = 19 calculated at the TD-DFT(B3LYP)/6-31G(d) level. Ten states were solved.

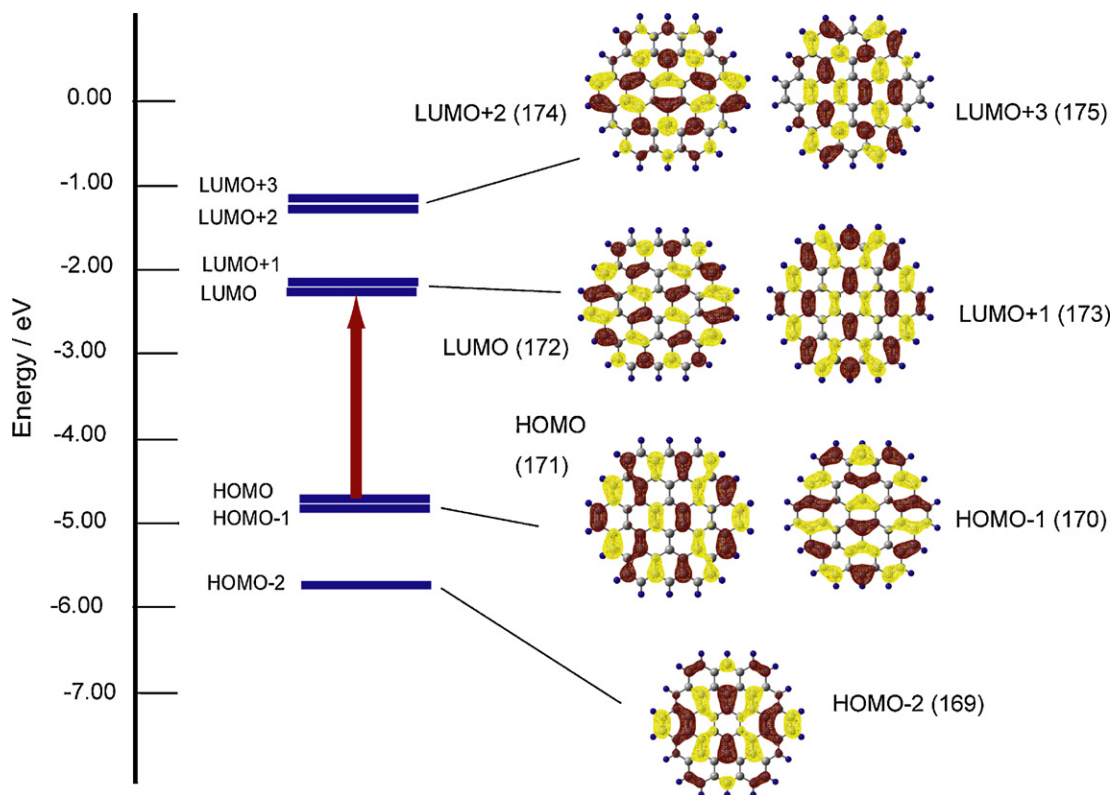| State	CSF and CI vectors	E_{ex} (eV)
S$_1$	0.513ϕ (HOMO → LUMO+1) + 0.553ϕ (HOMO-1 → LUMO)	2.21
S$_2$	0.496ϕ (HOMO-1 → LUMO+1) − 496ϕ (HOMO → LUMO)	2.34
S$_3$	0.425ϕ (HOMO-1 → LUMO+1) + 0.425ϕ (HOMO–LUMO)	2.79
S$_4$	0.425ϕ (HOMO-1 → LUMO) − 0.425ϕ (HOMO → LUMO+1)	2.79
S$_5$	0.498ϕ (HOMO → LUMO+3) − 0.482ϕ (HOMO-1 → LUMO+2)	3.01
S$_6$	0.482ϕ (HOMO-1 → LUMO+2) − 0.466ϕ (HOMO → LUMO+3)	3.01

Fig. 3. Molecular orbital energies of the normal graphene calculated at the B3LYP/6-31G(d) level. Isosurface indicates the special distributions of molecular orbitals. Arrow indicates a main configuration of first electronic excitation. Orbital numbers are given in parenthesis.
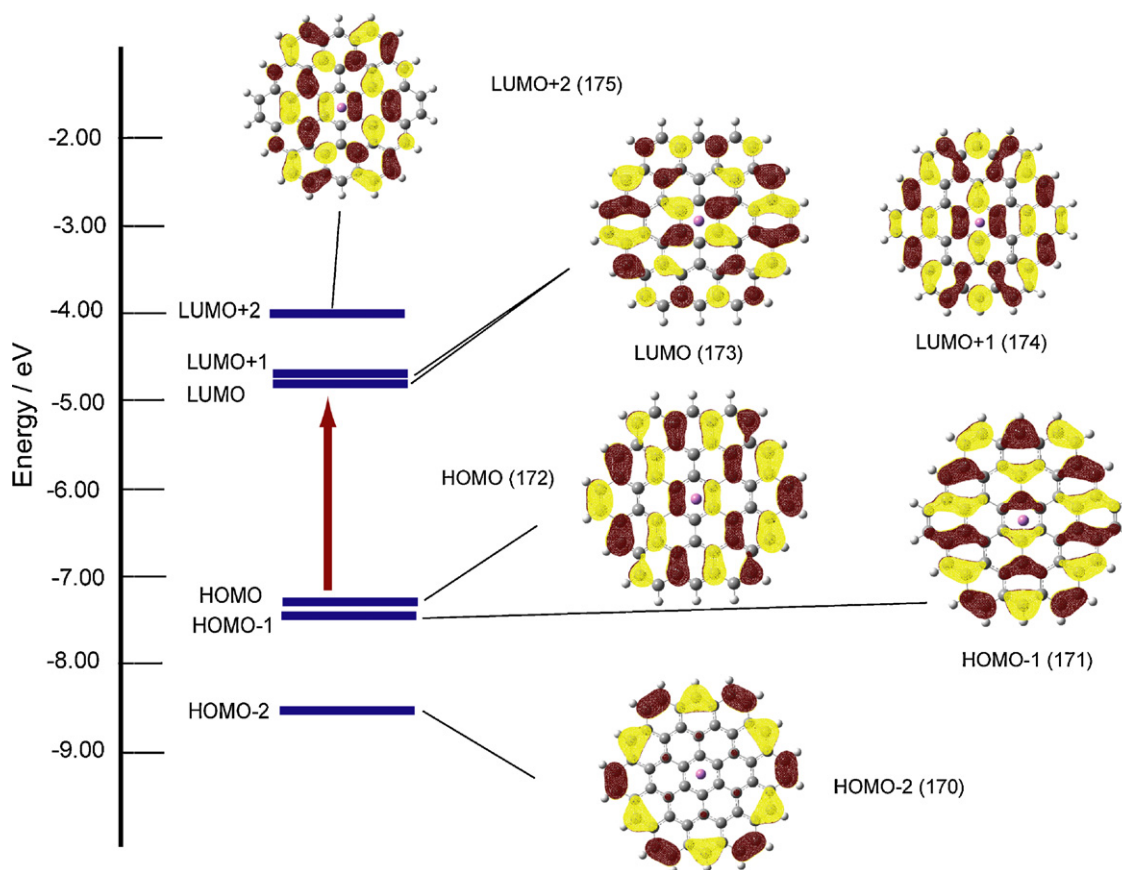

Fig. 4. Molecular orbital energies of Li$^+$ doped-graphene calculated at the B3LYP/6-31G(d) level. Isosurface indicates the special distributions of molecular orbitals. Arrows indicate main configurations of first electronic excitation. Orbital numbers are given in parenthesis.

When Li$^+$ ion interacts with the graphene, p-orbital of Li$^+$ contaminates to HOMO-1 orbital, as shown in Fig. 4, HOMO-1 (171). This orbital contamination causes the spectrum shift. However, the magnitude of contamination is significantly small, so that the shift is small.

4. Summary

In the present study, the electronic structures of Li$^+$ doped graphene have been investigated by means of DFT calculation. A free Li$^+$ ion has an electronic configuration of $(1s)^2(2s)^0$. When the ion interacts with the graphene surface, the electronic configuration is changed to $(1s)^2(2s)^{0.01}(2p)^0(3p)^{0.02}$. This result indicates that the sp-hybridization of lithium ion is important in the adsorption to the graphene surface. The band gap of graphene is slightly red-shifted by the doping of Li$^+$ ion due to the interaction with the sp-hybrid orbital.

Acknowledgments

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