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Structures and electronic states of halogen-terminated graphene nano-flakes

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ABSTRACT

Halogen-functionalized graphenes are utilized as electronic devices and energy materials. In the present paper, the effects of halogen-termination of graphene edge on the structures and electronic states of graphene flakes have been investigated by means of density functional theory (DFT) method. It was found that the ionization potential (*Ip*) and electron affinity of graphene (*EA*) are blue-shifted by the halogen termination, while the excitation energy is red-shifted. The drastic change showed a possibility as electronic devices such as field-effect transistors. The change of electronic states caused by the halogen termination of graphene edge was discussed on the basis of the theoretical results.

1. Introduction

Graphene has received worldwide research interest due to its unique physical and chemical properties. Surface-modified graphenes are known as functionalized graphenes, and the electronic states of graphene are variously changed by the functional group added to the surface [1–3]. Especially, the graphene has a high carrier mobility [4]. Hence, these characters have been applied to the electronic devices such as field-effect transistors. The edge-modified graphene is also one of the functionalized graphenes. However, the effect of edge-modification on the electronic states of graphene is scarcely known.

In the present paper, the effects of halogen-termination of graphene edge on the structures and electronic states of graphene were investigated by means of density functional theory (DFT) method. We focus our attention mainly on the effects to the ionization potential (Ip), electron affinity of graphene (EA), and excitation energies of graphene.

Fluorine-modifies graphenes have received much attention because the electronic structure is drastically changed by the fluorination. Fluorination of graphene proceeds easily by a chemical reaction and a mechanistic treatment [5–18]. Robinson et al. [10] reported that a reaction of graphene with XeF_2 leads to partial or full fluorination of graphene and showed that the properties of graphene, such as the band gap, can vary considerably as a function of the degree of fluorination. The reaction of graphene surface with F was found to significantly depend on reaction conditions; only 25% coverage was observed when a single graphene surface is exposed to XeF_2, but full (100%) coverage emerged when both surfaces were allowed to react with XeF_2.

Delabarre et al. used fluorinated graphite as the cathode in primary lithium batteries [19]. The higher capacity values were achieved for low temperature fluorinated graphite. Halogenation of carbon materials is possible to open new materials chemistry. However, the effects of halogen substitution of edge region of graphene on the electronic structure of the graphene are not clearly understood.

In the present paper, the effects of halogenations of graphene edge have been investigated by means of density functional theory (DFT) method. The Cl and Br were examined as halogen in the edge region. In previous papers [20–22], we investigated fluorine atom-substituted graphene flakes using the DFT method. The effects of halogen atom on the UV and near IR band were investigated theoretically. The UV band was red-shifted by the F substitution. In this work, the similar technique was applied to the halogen atom-substituted graphene nano-flakes (denoted by X–GR, where X = F, Cl, and Br).

The halogenated polycyclic aromatic hydrocarbons are one of

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the representative environmental cancer-causing materials and are known to be formed at the time of organic incomplete combustion easily [23]. Hence, to elucidate the electronic states of halogenated graphene is important from environmental problem.

2. Method of calculation

In the present calculation, X–GRs (X = F, Cl, and Br) were examined together with the normal hydrogen terminated graphene (denoted by H–GR). The sizes of halogen terminated-graphene used in the present study were chosen as n = 7, 14, 19, 29 and 37, where n means number of benzene ring in each graphene. The geometry of the X–GR was fully optimized at the B3LYP/6-31G(d) level. The structures of X–GR are illustrated in Fig. 1. The carbon atoms in the edge region are terminated by halogen atoms.

Atomic charges of carbon and fluorine atoms of X–GR were calculated by means of natural population analysis (NPA). All structures and electronic states of X–GR were calculated by means of DFT method at the B3LYP/6-31G(d) level using Gaussian 09 program package [24]. 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. These levels give a reasonable electronic state of the graphene as shown in previous calculations [25–29].

3. Results

3.1. Structures of X–graphene (X–GR)

The optimized structures of hydrogen terminated graphene for n = 37 are illustrated in Fig. 1. Hereafter, the hydrogen and normal hydrogen terminated graphenes are expressed as X–GR and H–GR, respectively. It was found that the structures of H–GR and F–GR are

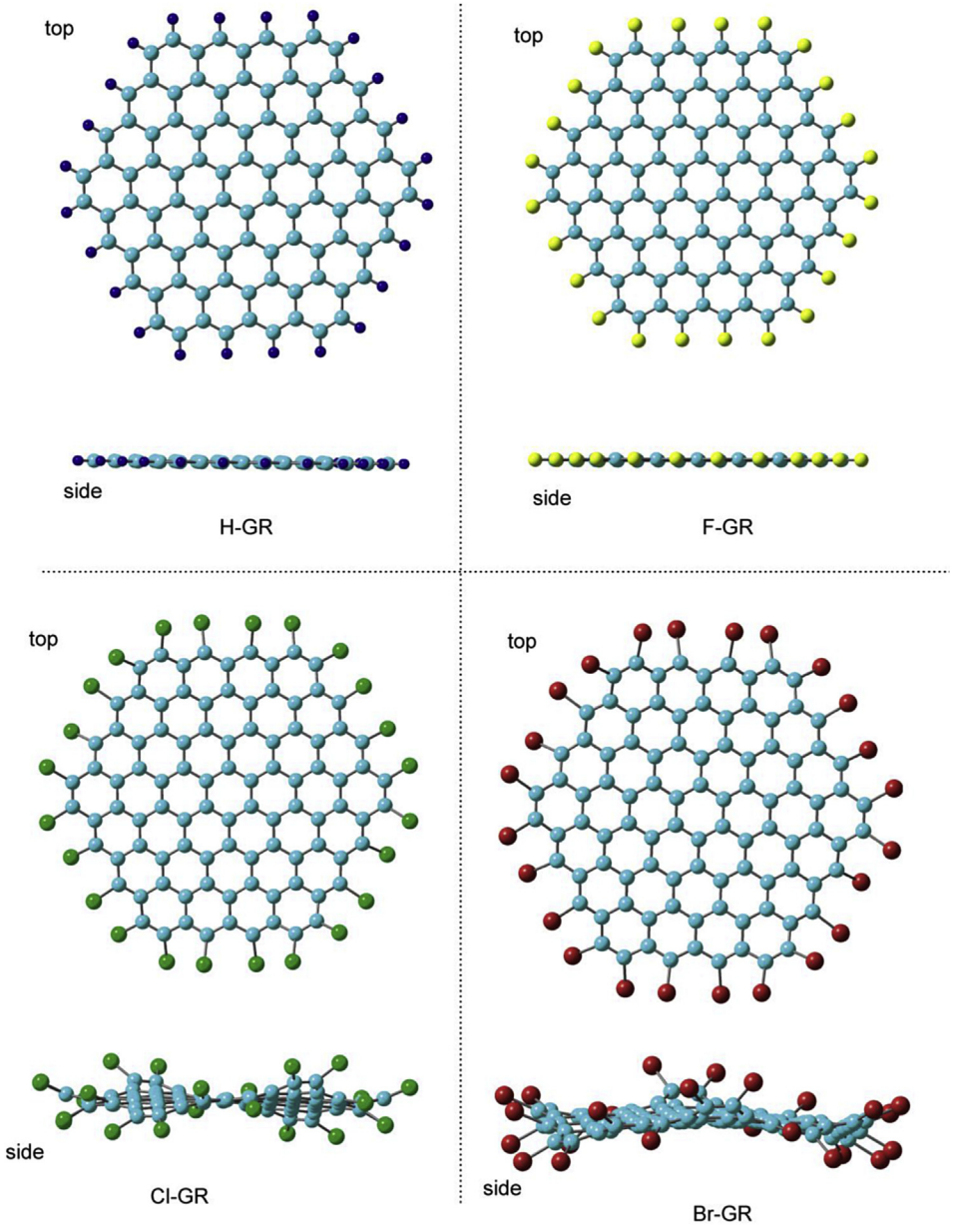

Fig. 1. Optimized structures of halogen terminated graphene (X–GR) with n = 37 calculated at the B3LYP/6-31G(d) level.