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Structural stability and aromaticity of pristine and doped graphene nanoflakes

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We have quantitatively investigated the relationship between the aromaticity and structural stability of graphene nanoflakes (GNFs) using first-principles calculations. The aromaticity of each six-membered ring of GNFs is evaluated with the nucleus-independent chemical shifts (NICS). We have found that for armchair-edge GNFs, the degree of stability, that is, the edge formation energy, is proportional to the average NICS for all six-membered rings. Even for nitrogen- and boron-doped GNFs, the average NICS strongly correlates with the doping formation energy. Our results indicate that NICS is a good measure not only for the aromaticity but also for the structural stability of pristine/doped nanographene systems.

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1. Introduction

Graphene, a two-dimensional material form of carbon atoms arranged in a honeycomb lattice, has attracted great attention because of its exceptional electronic and thermal properties.1–10 Graphene nanoribbons (GNRs), a one-dimensional strip of graphene, and graphene nanoflakes (GNFs) have also received considerable attention as a promising candidate of next-generation materials for many applications.11–21 Such nanocarbon materials are fabricated by several methods, e.g., a solution plasma technique.22,23 Since GNFs are zero-dimensional materials, one of the key factors that determine their physical properties is their boundary characteristics, that is, shape and edges. It is known, both theoretically and experimentally, that the electronic and optical properties of GNFs vary depending on their size and shape of edges.24,25 Kim et al. have successfully fabricated GNFs with various sizes up to 40 nm and have reported that the photoluminescence property of GNFs depends on their size.26 The shape of GNF edges also varies with their size. Relatively large scale GNFs of hexagonal shape can be fabricated on metal surfaces using a C60 precursor.27 Although GNFs can be fabricated by several experimental techniques,28 it is difficult to precisely control their size and edge shape. Furthermore, it is not fully understood how their size and edge shape affect their stability.

To functionalize graphene-based materials, it is important to modulate the electronic properties of graphene. One of the most common approaches to altering the electronic properties is heteroatom doping. It has been reported that nitrogen/boron-doped graphene can be synthesized by chemical vapor deposition techniques.29,30 The stability of doping into graphene systems has been extensively studied from the theoretical viewpoint.31,32 It has been known that nitrogen/boron-doped graphene with a uniform doping configuration is stabilized under a certain condition, which can be understood through the symmetry of the doping configuration and its electronic structure.33 For GNRs, the edge shape is relevant to the stability of heteroatom doping. In particular, the edge-localized states on zigzag edges play a crucial role on the doping stability.34–36 For nitrogen doping, a valence electron of the nitrogen atom occupies an unoccupied edge state, while the other four valence electrons form three sp2-σ bondings and a π-conjugated network with neighboring carbon atoms. For boron-doped systems, vice versa, the occupied edge state on zigzag edges localizes on the boron atom to form π-conjugated rings. In other words, a “hole” induced by the boron atom doping occupies the edge states. The stabilization mechanism of heteroatom doping can be understood by charge transfer between dopants and the edge states.37 Hence, the charge redistribution with doping dominates the doping stability as well as the edge shape.

The stability and reactivity of polycyclic aromatic hydrocarbons (PAHs) have been discussed by considering aromaticity.37–39 The well-known Hückel’s rule describes the stability of PAHs with (4n + 2) π electrons that are delocalized around six-membered rings.37,40 More advanced understanding of aromaticity was developed by Clar on the basis of the resonance of π electrons.39,41 The Clar formula describes the method of determining which six-membered rings of PAHs are aromatic in accordance with the resonance of the so-called Kekulé structure. The PAHs with Clar sextets become stable owing to the resonance energy of π electrons.

In recent decades, several theoretical methods have been developed to evaluate the aromaticity of the six-membered rings of PAHs within the framework of the molecular orbital theory. One of the most reliable measures for ring aromaticity is the nucleus-independent chemical shifts (NICS), developed by Schleyer et al.42 NICS is based on the magnetic shielding of external magnetic fields, which is induced by the existence of ring currents within cyclic structures of a molecule. In fact, for many polycyclic chemical compounds including PAHs, it has been reported that the aromatic rings in terms of NICS correspond to Clar’s π-sextets.43–45

Aromaticity is also relevant to chemical reactivity and stability of molecules. Aihara has developed the framework for evaluating the resonance energy of each six-membered ring of PAHs.46 Using the resonance energy-based method, the pattern of resonant rings illustrates the spatial map of aromatic rings in the Clar structure.47,49 Indeed, the energetic analyses based on the resonance energy have revealed that the Clar structure is relevant to the aromatic stability of cyclic compounds. In addition, the relationship between the aromaticity in terms of the Clar structure and structural stability has been discussed by investigating the electronic structures of relatively large GNFs using density functional theory (DFT) calculations.50 For such GNFs, the electronic structures of the highest occupied molecular orbital (HOMO) and lowest
unoccupied molecular orbital (LUMO) play a significant role in determining structural stability as well as the energy gap between HOMO and LUMO.

Among these previous studies, however, the quantitative understanding of the relationship between aromaticity and structural stability is limited. Furthermore, the aromaticity of doped graphene systems has not been discussed thus far. In the present paper, we discuss the structural stability of pristine GNFs and doped GNFs in view of aromaticity. In particular, we focus on the relationship between NICS and the formation energy. For doped GNFs, we investigate the local electronic structure around dopant atoms and how the change in charge distributions by doping affects NICS.

2. Calculation models and methods

We calculated the stability and aromaticity of the following models: (i) hexagonal GNFs (h-GNFs), (ii) triangular GNFs (t-GNFs), (iii) rhombic GNFs (r-GNFs), and (iv) nitrogen/boron-doped hexagonal GNFs. As shown in Fig. 1, we consider h-GNFs with both zigzag (ZZ) and armchair (AC) edges. The chemical formulae for zigzag-edge h-GNFs (ZZGNFs), t-GNFs, and r-GNFs are \(C_{6n}\)H\(_{2n}\), C\(_{3n}\)H\(_{2n+1}\)H\(_{n}\), and C\(_{6n}\)H\(_{2(n+1)}\), respectively. Armchair-edge h-GNFs are classified into two types, namely, AC1 and AC2, whose chemical formulae are C\(_{18n}n\)H\(_{18n+6}\) and C\(_{18n}n\)H\(_{30n+12}\), respectively. Note that AC1-type GNFs (AC1GNFs) have one carbon atom on each vertex of the envelope hexagon, while AC2-type GNFs (AC2GNFs) have two carbon atoms (see Fig. 1). For t-GNFs and r-GNFs, we only considered those with armchair edges. The point groups of h-GNFs, t-GNFs, and r-GNFs are \(D_{6h}\), \(D_{3h}\), and \(D_{3d}\), respectively.

The chemical compositions of the models employed in the present study are listed in Table I.

We also considered the doped GNFs where one carbon atom is substituted by a nitrogen or boron atom. Figure 2 shows the calculation models of the heteroatom-doped GNFs.

Nitrogen and boron atoms are preferably doped at the zigzag edges of graphene because of the existence of the so-called edge states. Our doped GNFs consist of h-GNFs with zigzag edges and the dopant atom is placed in the middle of the edge. We calculated several doping sites by changing the distance from the edge (see Fig. 2).

The structural stability of non-doped GNFs was evaluated on the basis of the edge formation energy \(E_{edge}\) defined as

\[
E_{edge} = \frac{1}{n_{H}} (E_{GNF} - n_{C}E_{C} - n_{H}\mu_{H}),
\]

where \(E_{GNF}\) is the total energy of GNFs and \(E_{C}\) is the total energy per atom of pristine graphene. \(n_{C}\) and \(n_{H}\) are the numbers of C and H atoms, respectively. \(\mu_{H}\) is the chemical potential of a hydrogen atom, which is given as

\[
\mu_{H} = \frac{1}{6} (E_{benzene} - 6E_{C}),
\]

where \(E_{benzene}\) is the total energy of benzene. As for the stability of the doped GNFs, we calculated the formation energy for substitutional doping.
where $E_{N(B)}$ is the total energy of the N(B)-doped GNFs and $\mu_{N(B)}$ is the chemical potential of N(B).

For DFT calculations, we used the Gaussian09 program package$^{[34]}$ employing the local spin density approximation with the VWN functional$^{[52]}$ and the 6-31G basis set in the package. We also used the 6-31G(d,p) basis set for doped systems and found no qualitative changes of results (see the online supplementary data at http://stacks.iop.org/JJAP/57/0102BA/mmedia). Structural optimization with respect to ionic positions was performed until each component of the interatomic force becomes less than 0.0003 Ha/Bohr.

The aromaticity of a given ring was evaluated using the NICS(1) value which was NICS at point 1 Å above the center of the ring. Note that a significantly negative NICS indicates the aromaticity of the ring and rings with positive NICS values are antiaromatic. All doped systems kept the structure planar during the optimization and no buckled structures of dopants were observed.

3. Results and discussion

3.1 Stability and aromaticity of non-doped GNFs

Figure 3 shows the edge formation energies of h-GNFs as a function of the number of carbon atoms at the edges. For ZZGNFs, the formation energy per edge atom increases with increasing GNF size. The formation energies of ACGNFs saturate for large GNFs. Note that there is a distinct difference in stability between AC1 and AC2, where AC2GNFs are more stable than AC1GNFs. In contrast to that of ACGNFs, the edge of ZZGNFs becomes unstable as the GNF size increases. This is due to the existence of the edge-localized state: similarly to the GNRs with zigzag edges,$^{[17]}$ the states localized at the zigzag edges make the system unstable. In fact, the HOMOs of ZZGNFs have large amplitudes at the edges (see Fig. 4). Such localization of HOMOs becomes prominent as the size of the edge increases. The edge states apparently emerge at the edges of ZZGNFs that are larger than C$_{96}$H$_{24}$. Accordingly, the formation energies of ZZGNFs deviate from the trends of those of ACGNFs at C$_{96}$H$_{24}$ (see Fig. 3). Thus, the instability of ZZGNFs is attributed to the evolution of the edge state.

We presume that the edge formation energies of ZZGNFs also saturate for larger sizes. If the size of edges is sufficiently large, the edge states dominate the edge stability and the effects of flake corners become negligible. As a result, the stability of large GNFs is attributed only to the difference in edge type. For GNRs, the formation energy per edge atom of the zigzag edge is 0.2 eV larger than that of the armchair edge.$^{[17]}$ The saturated formation energy of ZZGNFs is estimated to be 0.275 eV and the edge size $n_{edge}$ required for saturation is about 250.

For the stability of ACGNFs, the AC2-type GNFs are more stable than the AC1-type GNFs at any edge size. This observation is somewhat counterintuitive: At the vertices of the envelope hexagon of AC1GNFs, the corner consists of one carbon atom, while there are two carbon atoms at those of AC2GNFs. We here define that the pure AC-type carbon atom on edges is a carbon atom bonded with a hydrogen atom for which only one of the neighboring carbon atoms is also bonded with a hydrogen atom and the second neighboring carbon atoms have no bonds with hydrogen atoms. One can verify that the corner carbon atoms do not satisfy this definition and thus AC1GNFs (AC2GNFs) have one (two) impure AC-type carbon atom(s). The ratio of the number of pure AC atoms to that of edge atoms is defined as the purity of the AC edge.

The AC purities of AC1 and AC2 GNFs are listed in Table I. The purity of AC1GNFs is greater than that of AC2GNFs. In view of the AC purity, one may expect that AC2GNFs are more likely to have the edge properties of ZZGNFs than those of AC1GNFs. Consequently, AC2GNFs are expected to be unstable than AC1GNFs, since zigzag edges are energetically unstable. However, this is not the case for the observed trend of the edge formation energies, indicating that the stability of ACGNFs is not necessarily dominated by the edge type.

We investigate the difference in stability between AC1GNFs and AC2GNFs in view of the aromaticity. Figure 5 depicts the color maps of NICS values for each six-membered ring. For AC1GNFs, the six-membered ring at the flake center has the largest negative NICS and the NICS values of the neighboring rings are close to zero. The second neighboring rings of the center ring have small NICS values. The rings with large NICS values can be distinguished as
Clar’s π-sextets and this spatial arrangement corresponds to the Clar structure as shown in Fig. 1(b). On the other hand, for AC2GNFs, the NICS of the center ring is small and those of the neighboring rings are large. This pattern for AC2 again coincides with the Clar structure [see Fig. 1(c)]. Such coincidence has also been discussed in the literature.\textsuperscript{44,45} We emphasize that this correspondence between the patterns of NICS values and the Clar structure is also found for all t-GNFs and r-GNFs [see Figs. 1(d) and 1(e) and the online supplementary data at http://stacks.iop.org/JJAP/57/0102BA/mmedia].

Although the relationship between the aromaticity in terms of NICS calculations and the Clar structure has been discussed thus far, a quantitative relationship has not been fully understood. To this end, we relate the stability to the aromaticity by means of NICS values averaged over all six-membered rings of a GNF. Figure 6 shows the relationship between the edge formation energy and the average NICS. In addition to ACGNFs, we calculated those for t-GNFs and r-GNFs. As clearly seen, the edge formation energy is proportional to the average NICS. The slope is almost the same for each type of GNF and the intercept depends on the type. The average NICS has one-to-one correspondence with the formation energy regardless of the GNF size. This means that the stability of the GNF edge is dominated by the
degree of aromaticity over all the rings of GNFs. Therefore, it is concluded that NICS is a good measure of both the aromaticity and structural stability of GNFs.

### 3.2 Doped GNFs

As shown in the previous sections, the NICS values successfully predict the Clar structure, that is, the local aromaticity of GNFs, thus becomes a good measure of the stability of GNFs. However, one cannot apply the Clar structure to heteroatom-doped systems, since the types of bonding between dopant and neighboring carbon atoms are not always uniquely determined. Here, we examine the relationship between the aromaticity and structural stability of nitrogen- and boron-doped GNFs. Since nitrogen and boron atoms are preferably doped at zigzag edges,\textsuperscript{36} we have considered doped ZZGNFs. The stability of doped GNFs is discussed by using the formation energy for doping. Figure 7(a) shows the doping formation energies as a function of the distance between a doping site and the edge. For both nitrogen and boron doping, the formation energy increases with the distance from the edge. Furthermore, the formation energies of C\textsubscript{149}XH\textsubscript{30} (X = N, B) are smaller than those of C\textsubscript{53}XH\textsubscript{18} for the same doping configuration. These results are associated with the emergence of the edge state at the zigzag edge: As discussed in the previous sections, the HOMOs for C\textsubscript{150}H\textsubscript{30} are clearly localized at the zigzag edges. Such formation of the edge state contributes to the stabilization of heteroatom doping, for the nitrogen and boron doping in GNRs, as discussed in the literature.\textsuperscript{34–36,53}

The charge redistribution caused by the localization/delocalization of the edge state affects the aromaticity of the rings around the dopant atom. To elucidate the aromaticity of the doped systems, we show the NICS patterns of the nitrogen-doped ZZGNFs in Fig. 8. The NICS values of the rings around the nitrogen atom are positive, indicating that these rings are antiaromatic. As for the doping sites distant from the edge, there are several antiaromatic rings around the dopant. The rings that are distant from the dopant remain aromatic. This observation clearly indicates that the charge redistribution caused by the localization/delocalization of the edge state affects the aromaticity of the rings around the dopant atom.

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**Fig. 7.** (Color online) (a) Dope formation energies for the nitrogen- and boron-doped GNFs as a function of the distance between the dopant and the edge. (b) $E_{\text{dope}}$ versus the average NICS values. The black line is a line of the least square fitting. The correlation coefficient for the data is 0.8415. The doping energies for C\textsubscript{53}NH\textsubscript{18}, C\textsubscript{53}BH\textsubscript{18}, C\textsubscript{149}NH\textsubscript{30}, and C\textsubscript{149}BH\textsubscript{30} are indicated by open squares, open triangles, filled squares, and filled triangles, respectively.

**Fig. 8.** (Color online) Color maps of the NICS values of C\textsubscript{149}NH\textsubscript{30} where the dopant positions are 1, 2, 3, 4, and 5 for (a), (b), (c), (d), and (e), respectively.
regeneration around the dopant makes the neighboring rings antiaromatic. Note that for, site-1 doping, as shown in Fig. 8(a), only the six-membered ring containing the nitrogen atom becomes antiaromatic and the others are hardly affected by the doping [see the NICS patterns of non-doped ZZGNFs in Fig. 5(c) in the online supplementary data at http://stacks.iop.org/JJAP/57/0102BA/mmedia]. This accords with the fact that the charge regeneration is limited to occur at the edge, if the N or B atom is doped only at the edge.30 Since it is known that the distribution of the dopant charge is closely related to the stability of the doped systems,36 the aromaticity should also be related to the stability. In fact, for the doped ZZGNFs, the doping stability strongly correlates with NICS. Figure 7(b) shows the relationship between the doping formation energy and the average NICS. As clearly seen in this figure, these two measures correlate with each other as in the case of the non-doped GNFs. It should be addressed that NICS is a good measure not only for the aromaticity but also for the stability of π-conjugated systems even containing nitrogen and boron atoms.

4. Conclusions

We have examined the stabilities of pristine GNFs and doped GNFs and related them to their aromaticity by considering NICS. The stability of non-doped GNFs is dominated by the following factors: (i) The formation of zigzag edges make GNFs unstable because of the existence of edge states. (ii) The average NICS strongly correlates with structural stability regardless of the shape of GNFs. For both nitrogen- and boron-doped GNFs, the dopant atom is preferably doped near zigzag edges. This is because the electron-hole from the nitrogen/boron atom migrates to the unoccupied/occupied edge states. Even for doped GNFs, the average NICS positively correlates with the doping formation energy, whereas the six-membered rings around the dopant become antiaromatic.

The Clar formula is useful for describing the resonance structure of PAHs in terms of aromaticity. As for doped systems, however, it is not always valid to predict the aromatic rings using the Clar formula, since the number of π electrons for dopants and neighboring carbon atoms is not necessarily predictable unlike in the case of non-doped carbon systems. In spite of the lack of the Clar structure, for nitrogen- and boron-doped ZZGNF systems, NICS is certainly a good measure of structural stability. It has been clarified that aromaticity is relevant to stability not only for pristine GNFs but also for doped GNFs, where the Clar formula is necessarily applicable.
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