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Kyoko Nakada [a], Susumu Okada [b] & Masatsura Igami [b]

[a] College of Science and Engineering, Aoyama Gakuin University, Atsugi, 243-0123, Japan

[b] Institute of Materials Science, University of Tsukuba, Tsukuba, 305-8573, Japan

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First-Principles Study on the π Electronic Structure of Nanographite

KYOKO NAKADA[a], SUSUMU OKADA[b] and MASATSURA IGAMI[b]

[a]*College of Science and Engineering, Aoyama Gakuin University, Atsugi 243–0123, Japan and* [b]*Institute of Materials Science, University of Tsukuba, Tsukuba 305–8573, Japan*

We studied electronic structure of one-dimensional nanographite ribbons with a pair of zigzag edges by performing first-principles calculations within the local density approximation. The edge state of zigzag ribbons, which was predicted by the previous tight-binding calculations, was well reproduced by the present first-principles scheme. Nearly flat bands of the edge state were seen in zigzag ribbons which are condensed in a manner of AB-stacking as in bulk graphite. We took account of dangling bonds at edge sites and confirmed that the dangling-bond state near the Fermi level does not affect the nearly flat dispersion of the edge state. We also examined electronic structure of zigzag ribbons made up of an odd number of C-C chains and discussed the possibility of lattice distortion.

Keywords: Edge State; Nanographite; π Electronic State; Zigzag Edge; Localized State; First-Principles Calculation

INTRODUCTION

Amorphous carbons have been used in a variety of electrochemical systems such as a medium for high-capacity lithium ion batteries. The functionality of those materials, however, has not yet been fully understood because of their highly disordered structure as an assembly of tiny graphite fragments. We have focused our interest on the minute graphite fragment on a nanometer scale which we term nanographite.

By using one-dimensional graphite ribbons as a model structure, we found that zigzag ribbons (Figure 1(a)) with a nanometer width exhibit a pair of almost flat bands at the Fermi level.[1] As shown in Figure 1(b), the nearly flat bands yield a sharp peak in the density of states where the charge

density is strongly localized on edge sites. This localized state, which we term the edge state, stems from the topology of the π electron networks having a zigzag edge and is characterized by a non-bonding orbital (NBO).

The theoretical studies which we made are now followed by some experimental works to make real nanographites.[2] The progress of the experimental studies requires theoretical analyses on more realistic levels which is the aim of the present work.

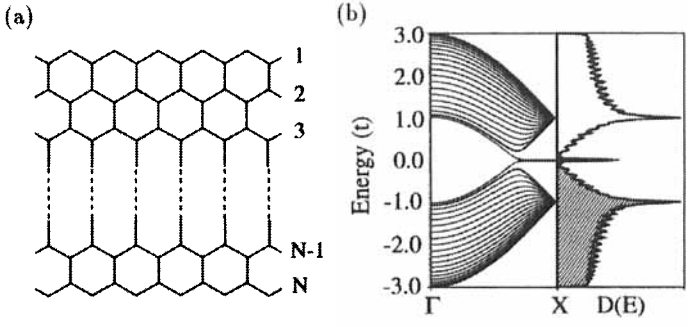

FIGURE 1 (a) Skeleton of a zigzag ribbon where all the edge sites are assumed to be terminated by H atoms. The ribbon width N means the number of zigzag C-C chains. (b) Energy band structure and density of states for a zigzag ribbon ($N = 20$). The energy unit is scaled by the nearest-neighbor hopping integral t. The wave vector in the first Brillouin zone (BZ) is $k = 0$ at Γ and $k = \pi/a$ at X.

METHOD OF CALCULATION

We performed energy band calculations and atomic geometry optimizations within the local density approximation (LDA) by using pseudopotentials and planewave basis sets. The exchange correlation energy of many-body electrons are treated as a functional form of the charge density,[3] which was fitted to the numerical results of the homogeneous electron gas.[4] To express effects of C 1s core electrons on valence electrons, the norm-conserving nonlocal pseudopotentials are generated by using a scheme of soft core radius.[5] The planewave basis sets are expanded up to 40Ry for multilayered ribbons and to 50Ry for otherwise.

SINGLE AND MULTILAYERED ZIGZAG RIBBONS

Figure 2(a) shows the energy band structure of a zigzag ribbon with $N = 10$.[6] The π band profile near the Fermi energy keeps the two feature of the edge state which we pointed out within the framework of the tight-binding model, *i.e.*, (1) a pair of π bands exhibit a nearly flat dispersion within the region of $2\pi/3 < k \leq \pi$ and (2) charge density in the flat band region is mostly localized on the edge sites. As shown in Figure 2(b), the edge state survives in a AB-stacked layer of zigzag ribbons.[6] Since edge sites in adjacent layers do not face directly, interlayer interactions between π electrons at edge sites are not fatal to the edge state.

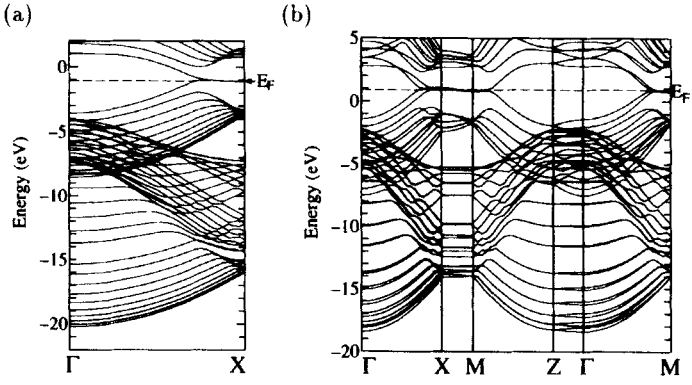

FIGURE 2 (a) Energy band structure of a H-terminated zigzag ribbon ($N = 10$). (b) Energy band structure of AB-stacked zigzag ribbons ($N = 6$) Γ-X and Z-M lines correspond to the ribbon axis while Γ-Z and X-M lines correspond to the stacking direction.

EFFECT OF DANGLING BONDS

Up to the present stage, the edge sites are all assumed to be terminated by H atoms. This, however, is not necessarily the case of actual nanographite materials. We therefore examined electronic structure of zigzag ribbons having bare dangling bonds at edge sites.

Figure 3(a) shows the band structure of a zigzag ribbon ($N = 6$) having no H-termination. The first BZ is folded into halves when it is compared with the one in Figures 1(b) and 2(a), because the ribbon period is doubled

to allow interactions between adjacent dangling bonds. As is seen in Figure 3(b), however, there is no remarkable dimerization or lattice distortion in the ribbon. The calculated dangling-bond state denoted by the arrow is doubly degenerate and has a narrow dispersion around the Fermi level. The energy dispersion of the dangling-bond state overlaps with the one of the edge state which also appears near the Fermi energy. Nevertheless, the dispersion relation and the wavefunction distribution of the edge state remain almost unchanged. Being originally a π electronic state, the edge state of zigzag ribbons cannot be affected by any σ dangling bonds at edge sites. We therefore say that the edge state can be formed in actual nanographite materials which may contain some dangling bonds at edge sites.

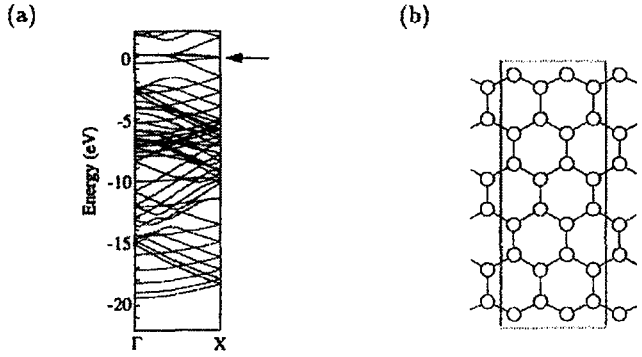

FIGURE 3 (a) The energy band structure of a zigzag ribbon ($N=6$) with no H-termination. The arrow indicates the dangling-bond state which is doubly degenerate throughout the first BZ. (b) The optimized structure of the zigzag ribbon ($N=6$) with no H-termination. The unit cell is indicated by the rectangle.

POSSIBILITY OF LATTICE DISTORTION

Since the metallic electronic structure of zigzag ribbons originates from the doubly degenerate bands of the edge state, there was a question whether a gap will open or not in reality. Taking account of electron-phonon interactions between the nearest neighbor sites, we previously showed that zigzag ribbons have no lattice distortion to open a gap, while a chain of *trans*-polyacetylene has a lattice distortion with a resultant gap.[7] This is because of the wavefunction distribution of the edge state as an NBO. Since

the amplitude of the NBO vanishes at every other site of a ribbon, the edge state itself is not responsible for the lattice distortions via electron-phonon interactions between the nearest neighbor sites.

There is, however, another possibility of a lattice distortion, especially for ribbons with an odd N. As we showed previously,[8] the site geometry of zigzag ribbons with an odd N may allow a lattice distortion along the zigzag C-C chains, if the long-range Coulomb interaction is not screened out and survives sufficiently enough to reach the ribbon width. We therefore studied electronic structure of zigzag ribbons made up of an odd number of zigzag chains within the framework of LDA.

Figure 4(a) shows the optimized structure of a zigzag ribbon ($N=7$). For the ribbons with an odd N, we could not obtain stable structures having a lattice distortion along the zigzag chains. The stable structure which we found exhibits a slight lattice distortion that the bonds in the zigzag chain shrink a little while the rung bonds between the chains expand a little. This bond alternation texture consists quite well with what we obtained within the model Hamiltonian taking account of the nearest-neighbor electron-phonon interactions. The energy band dispersion for the ribbon is shown in Figure 4(b) where the edge state of the undistorted ribbon is reproduced.

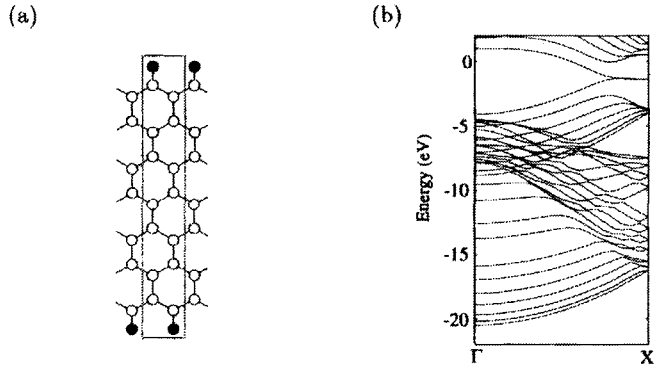

FIGURE 4 (a) The optimized structure of a zigzag ribbon ($N=7$) where H atoms are indicated by filled circles. (b) The energy band structure of a zigzag ribbon ($N=7$).

The present result indicates that electronic structure of zigzag ribbons is essentially governed by the nearest-neighbor hoppings and by the nearest-neighbor electron-phonon interactions at most, even for the ribbons with an odd N. It is also suggested that long-range Coulomb interactions are

almost screened out so that they cannot reach the ribbon width. We should mention, however, that the present result may be due to the limitation of LDA. This will be clarified elsewhere.

CONCLUSION

We showed that the edge state which we predicted previously is well reproduced for single- and AB stacked- zigzag ribbons within the framework of LDA. It was found that dangling bonds at edge sites do not destroy the edge state. We also showed that the lattice distortion to open a gap will not occur even for the ribbons having an odd number of zigzag chains. The present results strongly support the possibility that the edge state may be seen in actual nanographite materials which are now in preparation.

Acknowledgments

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