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Localized π Electronic Edge State in Nanographite

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Graphite fragments on a nanometer scale can present a distinctive edge state depending on the edge shape. By examining the electronic band structure of graphite ribbons within the Pariser-Parr-Pople model, we study the effect of the electron-electron interaction on the edge state. Depending on the ribbon width N, the long-range Coulomb interaction affects the edge state of narrow ribbons. The characteristics of the edge state, however, still persist in zigzag ribbons of a few nanometer width. Recent experimental approaches to synthesize nanographite are also introduced.

Keywords: Edge State, Graphite Ribbon, π Electronic State, Zigzag, Armchair, Electron-Electron Interaction, Nanographite

INTRODUCTION

Porous carbons have drawn increasing attention because of the large potential for application. where an alternative medium for lithium ion batteries may be most expected. They are considered to be assembly of graphite fragments on a nanometer scale, which we call "nanographite". The highly disordered structure of porous carbons has long prevented precise analysis of their functionality; The electronic and magnetic properties of interest are simply referred to the dangling bonds or impurities, while the π electronic structure is undoubtedly considered to be that of bulk graphite. In the constituent nanographite of porous carbons, however, the *itinerant* π electrons are confined into a region of nanometer dimensions. A number

of edge sites having hydrogen termination may affect the π electronic state of nanographite. Studying the π electronic structure of nanographite, we show the nanometer size effect and edge shape dependence of graphite systems, which distinguish nanographite both from bulk graphite and from small aromatic molecules as the end materials of π electron system.

EDGE STATE IN GRAPHITE RIBBON

A graphite sheet can be cut along a straight line to exhibit two prototype edge shapes, i.e., the armchair and zigzag edges. We utilized graphite ribbon model having armchair (zigzag) edges, where the ribbon width N shows the system size (Fig. 1). The band structure of wide armchair (zigzag) ribbons can be predicted by projecting that of a graphite sheet onto the armchair (zigzag) axis. Zigzag ribbons, however, unexpectedly show a pair of center bands which are almost flat in $2\pi/3 \leq k \leq \pi$. These bands thereby give a sharp peak in the density of states (DOS) near the Fermi level, where the charge density is strongly localized on the edge sites. We derived an analytic expression for this edge state as a non-bonding orbital (NBO),[1] and found that the edge state is most effective when the system is of a nanoscale length.

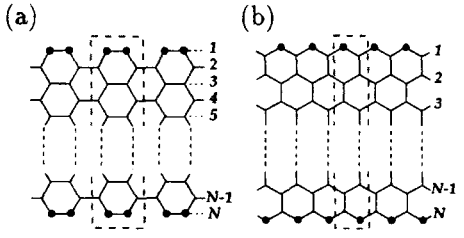

Fig. 1. Graphite ribbon with (a) armchair and (b) zigzag edges. The edge sites are indicated by solid circles.

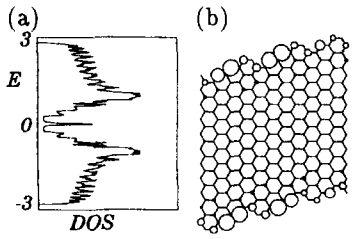

Fig. 2. (a) DOS of a general graphite ribbon. (b) Charge density distribution near the Fermi level.

We also extended the graphite ribbons to have edges of general shape, which is defined as a mixture of zigzag and armchair sites.[2] It was found that only four or five zigzag sites per sequence are enough to exhibit the edge state as a distinguishable DOS peak at the Fermi level (Fig. 2). Those

graphite ribbons having much less zigzag sites still show the characteristic charge density distribution, which is mostly localized on the edge sites in the vicinity of the resultant gap. We, therefore, cannot neglect the singular π electronic state in nanographite which may constitute the carbon materials of interest such as porous carbons.

EFFECT OF LONG-RANGE COULOMB INTERACTION

The distinctive edge state of zigzag ribbons can be featured by the partly flat bands at the Fermi level. Strong Fermi instability may naturally be expected making a gap enough to destroy the localized electronic state. Our study of the lattice distortion in graphite ribbons taking account of the nearest-neighbor electron-phonon interaction indicates, however, zigzag ribbons make no in-plane distortion which spoils the edge state.[3] This is because the nature of the edge state is intrinsically expressed by a pair of NBOs which degenerate at the Fermi level. Since the NBOs have no component of the wave function at one of the two sublattices, the edge state is not responsible for the Peierls distortion under the nearest-neighbor electron-phonon coupling.

The long-range electron-electron interaction, which may cause another instability at the Fermi level, is then brought into focus. Here we study whether and how the long-range Coulomb interaction affects the characteristics of the edge state. The band calculation for zigzag ribbons based on the Pariser-Parr-Pople (PPP) model[4] is performed. The π electronic state is described in the SCF scheme taking account of the long-range Coulomb repulsion as well as the nearest-neighbor electron-phonon coupling, by employing the variable-β,γ approximation.

Within the PPP model, zigzag ribbons with a small N show a direct gap at $k=\pi$ (Fig. 3(a)). The gap stems from the nonlocal exchange term through the interelectron Coulomb repulsion, whose contribution is governed by each bond order between i-th and j-th sites ($i \neq j$). The bond order distribution for zigzag ribbon with $N=4$ is depicted in Fig. 3(b). Each radius indicates the magnitude of the bond order between there and the arrowed site, showing its sign by shading. We find out that the main contributor to the gap is the long-range Coulomb interaction between the

pair of edge sites, each sitting on the opposite edge to the other. Reflecting the localized charge density distribution of the edge state, the bond order distribution between the arrowed site and the opposite edge site exhibits a long trail over a distance, which results in the wide gap at $k=\pi$.

The long-range Coulomb repulsion also makes a gap for zigzag ribbons with an odd N. In contrast to the even-N ribbons, however, the bond order distribution of the odd-N ribbons shows a symmetry breaking, indicating a slight bond alternation along the translational axis (Fig. 3(c)). This is because of the network geometry; The arrowed site in Fig. 3(c) has no opposite edge site on the mirror plane passing through itself. For every edge site on the opposite edge, another edge site symmetrical with the mirror plane always makes a pair. At $k=\pi$ the exchange repulsion terms from these pairing sites inevitably cancel out, since these two sites are the lattice constant times an odd number away from each other. The ribbons with an odd N virtually give a zero gap at $k=\pi$, if a restriction to keep the D_{2h} symmetry is imposed. Being stable than in the symmetrical form, zigzag ribbons having an odd N make a lattice distortion along the translational axis, to which the interelectron repulsion between the edge sites gives rise.

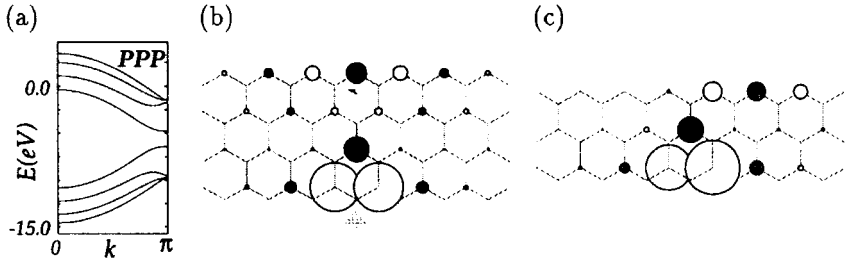

Fig. 3. (a) Band structure of zigzag ribbon with $N=4$. Bond order distribution for zigzag ribbon with $N=4$ (b) and $N=3$ (b). Each radius indicates the magnitude of the bond order between there and the arrowed site, showing its sign by shading.

The electron-electron interaction in narrow ribbons results in the direct gap at $k=\pi$, showing skeleton with or without bond alternation depending on N. The gap, however, becomes smaller and smaller with increasing N. In Fig. 4(a) the gap width is plotted versus N, where the ribbon

with N=8 already presents a gap below 1 eV. It also has the almost flat bands around k=π (Fig. 4(b)), where the charge density distribution is exceedingly localized on the edge sites. We thus conclude that the wider ribbons on a nanometer scale are expected to have the peculiar electronic state near the Fermi level, enough to exhibit the characteristics of the edge state.

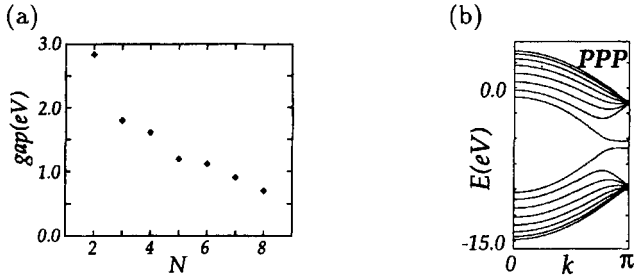

Fig.4 (a) Gap width at k=π vs. ribbon width N of zigzag ribbons. (b) Band structure of zigzag ribbon with N=8.

DISCUSSION

We showed that the edge state of nanographite do not collapse under the long-range Coulomb interaction. This increases the interest in porous carbons, whose electronic structure, however, is not fit to be examined because of the highly disordered structure. Preparation of nanographite materials having controlled size and structure is therefore anticipated.

In concert with the theoretical prospect of the special edge state, experimental studies to synthesize nanographite are now in progress. One such approach is to form nanographite from diamond powder of a nanometer dimension by heat treatment.[5] A sort of nanographite having size of ~8 nm in plane and 5-6 stacked layers is already obtained, where some anomalies in ESR spectra, magnetic susceptibility and so on are extensively examined.

Another interesting approach[6] is based on the recent technique to form monolayer graphite on various solid surfaces. It is known that a graphite sheet tears easily at step edges made incidentally on the substrate. It may then be possible to form graphite in ribbon shape of a specific width, if we

prepare terraced substrates by making so-called vicinal surfaces. Though one cannot neglect the interaction between the formed graphite and substrate, this work is said to be a most promising approach to nanographite.

The most serious difficulty in these approaches is to control the edge shape of the formed nanographite, which we should leave to chance at present. However, some STM observations of minute graphite grown on a substrate provide an evidence for the existence of zigzag edges.[7] It is therefore expected that nanographite ribbons having controlled dimension and zigzag edges can be prepared in the near future. The distinctive edge state, whose characteristics bear the electron-phonon and electron-electron interactions, may then be observed, as anomalies in the electronic properties of nanographite. We believe that such studies may reveal the functionality of porous carbons.

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