Electronic structures of peanut-shaped fullerene tubes

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Received 27 October 2006; received in revised form 13 January 2007; accepted 15 January 2007

Available online 18 April 2007

Abstract

We have investigated electronic structures of the peanut-shaped polymerized fullerene with so-called P55, P56 and P66 tubular linkage structures. The stable atomic configurations in these one-dimensional or two-dimensionally bundled tubes are searched out by a tight-binding calculation, and then their electronic structures are evaluated by using an ab initio density functional calculation. The electronic structures change drastically depending on the bonding interaction between the tubes. The P66 tube can show metallic conduction when it is bundled two-dimensionally.

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Keywords: Fullerene polymer; Peanut-shaped; Electron transport; Metallic conduction; Ab initio calculation

1. Introduction

Recent continuous development in the semiconductor device industry relies on the successive progress of the miniaturization technology, which enables atomic-scale control in fabricating device nanostructures. As the minimum feature size of the device structure decreases within nanoscale level, in contrast, characteristic phenomena in such nanoscale devices come to appear in their electron transport properties as quantum mechanical effects. For example, while the source-drain junction length in metal-oxide-semiconductor (MOS) structure approaches within a nanometer region, the problems of the leakage current and the short channel effect in nanometer size MOS field effect transistor have become hot topics that must be solved in the very near future.

Concerned about these problems on silicon-based nanodevices, trials of using other alternative materials as semiconductor nanodevices have been studied extensively in organic molecules, carbon nanotubes, fullerenes, and so on. Above all, fullerenes have attracted much attention recently since the metallic conduction (with resistivity ~7Ω cm) was reported in the fullerene film polymerized by electron-beam (EB) irradiation [1].

On the theoretical side, Esfarjani et al. [2] studied the electronic structures of P55, P56, and P66 dimer structures by tight-binding calculation and found that the energy difference between the highest occupied molecular orbital and the lowest unoccupied one of P66(P55) dimer is the smallest(largest). Later, Tsukamoto et al. [3] implemented first-principles calculations of the electronic structures of one-dimensional (1D) P55 and P56 tubes, and reported that the band gaps are about 1 eV or more. In addition, Ueda et al. [4] showed that the P66-linked tube has a gap of 0.54 eV when it is bundled in 2D, while it becomes semi-metallic when it is bundled in 3D. However, some of their calculation are limited due to the usage of orthorhombic unit cell for the bundling of the tubes, in particular two-dimensional (2D) case. The analysis of the interaction between the 2D bundled tubes and its effect on the electronic structures should be investigated in relation to the metallic phase. Moreover, it is of scientific interest to clarify how the formation of the tubular linkage in the network of fullerenes affects their electronic structure.

Here, following the previous theoretical studies [2–4], we examine the electronic structures of P55, P56 and P66 fullerene tubes by optimizing the atomic configurations together with the shape of the monoclinic unit cells. Fig. 1 shows the computational models. The P55 tube has six hexagons and six heptagons in the linkage structure. The P66 tube has six pentagons and six octagons. The P56 tube...
is a hybrid between P55 and P66, with three pentagons, three hexagons, three heptagons and three octagons in the linkage structure. The periodic unit length of the P56 tube is twice as that of the P55 and P66 tubes, containing 120 carbon atoms in the unit cell. Each of the tubes has a threefold rotation axis along the tube.

We have performed the detailed investigation for the metallic phase throughout the 1D and 2D bundled tubes. Since it is tedious and computationally demanding task to determine the stable atomic configurations and the lattice parameters especially for the 2D bundled tubes, the empirical tight-binding calculation parameterized by Xu et al. [5] has been performed for the optimization of lattice and atomic positions. This tight-binding method is known to successfully predict the ground-state geometry of fullerene dimers [2], and is in good agreement with experiments, e.g., fullerene impact on diamond surface [6]. Using the geometry obtained by the tight-binding calculation, the electronic structure has been elucidated from an \textit{ab initio} calculation based on the density functional theory and the real-space finite-difference (RSFD) approach [7]. Unlike the first-principles calculations using the plane wave basis, this RSFD method can evaluate the electronic structure of 1D and 2D systems accurately, because the boundary condition is not constrained to be periodic. For the calculation of 1D tubes, an isolated boundary condition is imposed in the direction perpendicular to the tube, while a periodic boundary condition is imposed in the direction parallel to the tube axis. The ion cores are represented by the norm-conserving pseudopotentials [8] and the exchange–correlation interaction is treated within local density approximation [9].

All the results of this work are summarized in Table 1. From the next section we will discuss these results in detail.

2. Electronic structure of 1D tubes

As shown in Table 1, the P55 tube is most stabilized among the three 1D tubes, while its energy gap is as wide as the isolated fullerene. Therefore, we can exclude the possibility of the metallic conduction as for the P55 tube. The P66 or P56 tube has an energy gap of 1 eV or more. The P66 tube has the narrower gap than the P56 tube, thus the P66 tube will have a larger possibility for the metallic phase if it is bundled in 2D. However, the P66 tube is energetically metastable as compared with the isolated fullerene.

The band structures of the P66 and P56 tubes are shown in Fig. 2. The P56 tube has a direct band gap at \(X\) point \((= \frac{1}{2} G_1)\). For the P66 tube, the conduction band minimum (CBM) lies between \(I\) and \(X\) point. Both have the flat valence and conduction bands.

3. Electronic structure of 2D bundled tubes

For the P66 tubes bundled two-dimensionally, we have searched out three metastable configurations (shown in Figs. 3–5) as a function of the distance between the tubes. Let us start from the situation when the tube is far from the others. It can be stabilized through a weak interaction

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
 & Tight-binding calculation & & & & Ab \textit{initio} calculation & \\
 & Total energy & Periodic length & Distance between tubes & Gap (eV) & Gap (eV) & Structures shown \\
& per C\text{60} (eV) & of the tube & tubes \(D\) (\AA) & & & \\
\hline
P55 & 1D & -2.88 & 8.63 & - & - & 1.56 & 0.96 & Fig. 1(a) \\
P66 & 1D & 1.87 & 8.75 & - & - & 1.02 & 0.96 & Fig. 1(b) \\
P66 & 2D-a & 1.80 & 9.02 & 91.3 & 1.01 & 0.39 & 0.96 & Fig. 3 \\
P66 & 2D-b & 1.72 & 8.51 & 78.4 & 0.95 & 0.39 & 0.96 & Fig. 4 \\
P66 & 2D-c & 1.66 & 8.11 & 63.2 & 0.89 & 0.39 & 0.96 & Fig. 5 \\
P56 & 1D & -0.41 & 17.389 & - & - & 1.11 & 1.14 & Fig. 1(c) \\
P56 & 2D-a & -0.53 & 8.01 & 61.8 & 1.07 & 0.27 & 0.96 & Fig. 6 \\
C\text{60} & 0D & 0.0 & - & - & - & 1.61 & 1.67 & \\
\hline
\end{tabular}
\caption{Summarized results of our calculations}
\end{table}

\(\alpha\) is the angle for the monoclinic crystal when the tubes are bundled in two dimension. In the calculation of the 2D tubes, the periodic tube length \(L\) is fixed to that of the 1D tube.
between the swelled fullerene parts of the tubes (see Fig. 3). As the tubes come closer to each other, the system make a transition to the other two metastable configurations, where the tubes can interact between the swelled part and the dented linkage part (see Figs. 4 and 5). The nearest atomic distance between the different tubes is around 2.2 Å or less.

The structure shown in Fig. 5 is most stabilized among the 2D bundled P66 tubes with a binding energy between the tubes of 0.21 eV/C₆₀, but still it is metastable as compared with the isolated fullerene. However, its electronic structure is metallic. Surprisingly, as shown in Fig. 7, the energies of the valence band maximum (VBM) and the CBM nearly degenerate at the $S$ point ($= \frac{1}{2} G_1 + \frac{1}{2} G_2$). In the recent theoretical calculation by Ueda et al. [4], the 3D structures of the fullerene polymer behave as a metal. Our results indicate that the 2D structure with the monoclinic unit cell also can exhibits metallic property. Although we cannot determine whether the bands are crossed around the $S$ point or not owing to the computational accuracy of this calculation, at least the band gap less than 5 meV seems enough to show metallic conduction.

Also for the 2D bundled P56 tubes, one stable configuration has been found out, where the swelled part and dented part come closest and interact to each other. This structure shown in Fig. 6 is stabler than the isolated fullerene with an indirect band gap of 0.27 eV, and the energy gap becomes very narrow compared with that of the 1D P56 tube.

4. Summary

Among the three peanut-shaped tubes we have considered, the P56 and P66 tubes have narrower band gaps of
1 eV or more. On the other hand, they are less stable due to the existence of eight-membered rings. However, they can be stabilized in energy through the 2D coupling between the swelled fullerene part and the dented linkage part. As results, the 2D P56 tube is stable with a band-gap of 0.27 eV, and the 2D P66 tube is still metastable but becomes metallic. And it is very likely that the metallic P66 tube can be stabilized or the P56 tube can be metallic if they are bundled in 3D. Thus, the P66 tube bundled in 2D or 3D is possible substance for the metallic conduction observed in the EB irradiated fullerene film. For the qualitative analysis of the electron conduction properties, the effective masses of the electrons and holes should be investigated. Other types of peanut-shaped tubes, one of which has the lower symmetry and is predicted to have a very small energy gap (~0.1 eV) [10], should be discussed elsewhere.

In this study, the empirical tight-binding calculations have been employed for the optimization of the atomic configuration. On the other hand, the tight-binding calculation cannot evaluate the Van der Waals (VdW) interaction accurately. Both the electronic structures and the atomic optimization should be calculated from the first-principles, by using the density functional theory or other approaches which can correctly reproduce the VdW interaction.

Acknowledgements

The authors thank Prof. J. Onoe of Tokyo Institute of Technology for useful discussions. The present work is partly supported by Grants-in-Aid for the 21st Century COE “Center for Atomistic Fabrication Technology”, and for Scientific Research in Priority Areas “Development of New Quantum Simulators and Quantum Design” (Grant no. 17064012) from the Ministry of Education, Culture, Sports, Science and Technology. The computations were carried out by the supercomputer facilities at the Institute for Solid State Physics at the University of Tokyo and the Information Synergy Center at Tohoku University. The authors thank the Research Center for Computational Science, Okazaki for the use of the computer facilities.

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