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Energetics and electronic structures of one-dimensional fullerene chains encapsulated in zigzag nanotubes

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We report total-energy electronic-structure calculations that provide energetics and electronic structures of fullerenes encapsulated in zigzag carbon nanotubes (so-called peapods). It is found that the space between the nanotube and the encapsulated fullerenes is a decisive factor to determine the energetics for the encapsulation process of the fullerenes in the nanotubes and the stability of resultant structures. The reaction energies for the encapsulation processes exhibit common characteristics depending on the space inside the tube, irrespective of their metallic and semiconducting properties. It is also found that the electronic structures of peapods depend on the space and that they reflect electron states of the encapsulated fullerenes. A relative energy position of the lowest unoccupied states of the encapsulated fullerenes modulates the energy gap of the semiconducting nanotubes. Further, the interwall spacing results in a significant shift of the electron states that have originated from the fullerenes. Our results indicate that the energy gap of the semiconducting peapods exhibits interesting variation depending on both the space and the fullerenes and suggest the possibility of band-gap engineering of the all carbon materials.

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I. INTRODUCTION

Carbon nanotubes[1] are fascinating materials that exhibit interesting interplay between atomic structures and electronic properties: For instance, the nanotube becomes insulating in some cases and metallic in another depending on a tiny difference in its atomic arrangement,[2–4] this is a consequence of an anisotropy of energy bands of a graphene sheet and of quantum-mechanical boundary conditions for electronic wave functions in tubular structures. Another aspect peculiar to the tubular structure is the space inside. This feature opens a possibility of accommodating foreign species in the space inside the tube. In fact, it has been shown at an earlier stage that lead atoms indeed fill nanotubes.[5] Now it is found that fullerenes, e.g., C_{60}, C_{70}, C_{78}, C_{80}, and C_{84},[6–11] and metallofullerenes, e.g., Gd@C_{82} and Sc_2@C_{84} (Refs. 11,12) are encapsulated in the nanotubes. These are now commonly called carbon peapods. The carbon peapod is certainly unique in its morphology; the space inside the tube can be regarded as a nanometer-scale container. Yet the space not only works as a container, but is also capable of controlling electron states of those exotic materials, which we discuss in this paper.

In materials containing space inside, there are unusual electron states whose wave functions distribute not near atomic sites but in the space. In graphite, it is found that the electron states distributed between graphene layers (interlayer states) are located above the Fermi level and play important roles in excitation spectrum.[13–15] Also in the nanotubes, electron states distributed in the space inside and outside are found to exist and are located at a few eV above Fermi level.[16,17] Those states in the nanotubes are called nearly free electron (NFE) states. Hence in the peapods, atomic orbitals of foreign species stuffed in the tubes are expected to interact with the NFE states. In our previous works,[18,19] we have indeed demonstrated that the NFE states and the space affect the energetics and the electronic structures of the peapods consisting of the C_{60} and armchair (n,n) nanotubes: It has been also shown that electronic structures near the Fermi level of the peapods exhibit interesting variations depending on the tube radius. In particular, the C_{60}@(10,10) was found to be a metal with multicarriers, each of which is distributed either on the nanotube or on the C_{60} due to the significant hybridization between π orbital of the C_{60} and the NFE states. Furthermore, we have also found that the (10,10) nanotube gives the largest energy gain upon the encapsulation reaction of the C_{60}'s among the other armchair nanotubes, and that optimized values of the interwall spacing between the C_{60} and the nanotubes is 3.3 Å.

Recent spectroscopic and transport experiments have shown that the electronic structures of the peapods are modulated from those of the nanotubes.[20–22] In particular, the electron states around the energy gap are found to depend strongly on the species of the encapsulated fullerenes.[21] In spite of those experimental efforts, however, theoretical calculations are restricted to a limited class of peapods. It is of interest to clarify effects of tube radii, metallic or semiconducting characteristics of constituent nanotubes, and difference in fullerene species in energetics and electronic structures of various peapods. In this paper, we therefore study C_{60}, C_{70}, and C_{78} one-dimensional chains encapsulated in zigzag $(n,0)$ nanotubes $(15 \leqslant n \leqslant 21)$ and reveal salient features of energetical and electronic properties of these exotic carbon peapods. We find that the lowest unoccupied states of fullerenes shift downward depending on the radii of the nanotubes and take the lowest value at the optimum radius of the nanotube. This finding offers an interpretation of the band-gap modulation experimentally observed. We also find that the reaction energy on the encapsulation of the C_{60} depends not on the metallic or the semiconducting characters of

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the nanotubes but on the interwall spacing between the C_{60} and the nanotube. The electronic structures of the large-fullerene peapods also depend on the space inside the nanotube and reflect the electron states of the encapsulated fullerenes.

II. METHODS

Calculations have been performed using the local-density approximation (LDA) in the density-functional theory.[23,24] For the exchange-correlation energy among electrons, we use a functional form[25] fitted to the Monte Carlo results for the homogeneous electron gas.[26] Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme[27] combined with the separable treatment[28] are adopted to describe the electron-ion interaction. In constructing the pseudopotentials, core radii adopted for C $2s$ and $2p$ states are both 1.5 bohrs. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 50 Ry which is known to give enough convergence in discussing the relative stability of various carbon phases.[17,18,29] We impose commensurability conditions between the one-dimensional periodicity of the nanotube and that of the chain of fullerenes. Consequently, a lattice parameter c along the tube direction is 12.76 Å for all the zigzag peapods studied here.[30] Integration over one-dimensional Brillouin zone is carried out using the two k points. We carry out the calculation on $C_{60}@(n,0)$ for $15 \leqslant n \leqslant 21$ and $C_{70}@(n,0)$ for $n=17$, and 19, and $C_{78}@(19,0)$. The conjugate-gradient minimization scheme is utilized both for the electronic-structure calculation and for the geometry optimization.[31] The remaining forces in the obtained total-energy minimized geometries are typically less than 5 mRy/Å. By this criterion, the geometry is optimized within 0.004 Å, leading to an error of 0.1 meV per atom in the total energy.

III. ENERGETICS

The space inside the nanotube possesses potentiality of containing foreign atoms and molecules. However, the energetics of the encapsulation reaction have been elucidated only for the C_{60} in the metallic armchair nanotubes at present. Thus, we here perform the geometry optimization on one-dimensional fullerene chains encapsulated in semiconducting zigzag nanotubes to clarify the energetics of the encapsulation for the C_{60}, the C_{70}, and the C_{78} fullerenes. Figure 1 shows total-energy minimized geometries of $C_{60}@(15,0)$, $C_{60}@(17,0)$, and $C_{60}@(19,0)$. First, we clarify a correlation between the space and a reaction energy ΔE. The reaction energy is defined by the following:

$$(n,0)\text{tube} + C_{60} \rightarrow C_{60}@(n,0) - \Delta E.$$

In the calculation, we assume that the C_{60}'s are located at the center of the nanotube although the favorable position of the C_{60} in thicker nanotubes have been found to be dislodged from the center.[19] As shown in Fig. 2, we find that the (17,0) nanotube is the most favorable nanotube for the C_{60}'s and gives the largest $|\Delta E|$ of about 1.39 eV. In this case, the interwall spacing is 3.11 Å which is close to the interlayer distance of the graphite. It is found that the difference of each atomic position of the $C_{60}@(17,0)$ between the initial and the optimized geometries is less than 0.02 Å.

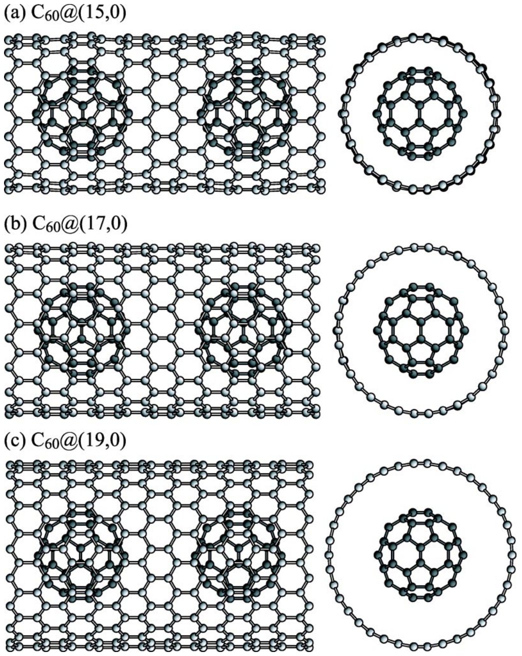

FIG. 1. Geometric structures of total-energy minimized $C_{60}@(15,0)$, $C_{60}@(17,0)$, and $C_{60}@(19,0)$.

On the other hand, for the thin $(n,0)$ nanotubes, $n \leqslant 16$, energy ΔE rapidly increase with decreasing the radius of the nanotubes. For these nanotubes, the space between the C_{60}'s and the nanotubes is smaller than the interlayer spacing of the graphite, and we find that the significant structural deformation both for the C_{60} and the nanotube takes place [Fig. 1(a)]. For instance, the calculated interwall spacing of the $C_{60}@(15,0)$ is found to be 2.76 Å. This elastic energy cost results in an endothermic reaction. For the thick nanotubes, since the C_{60}'s are located at the center of the nanotube, the

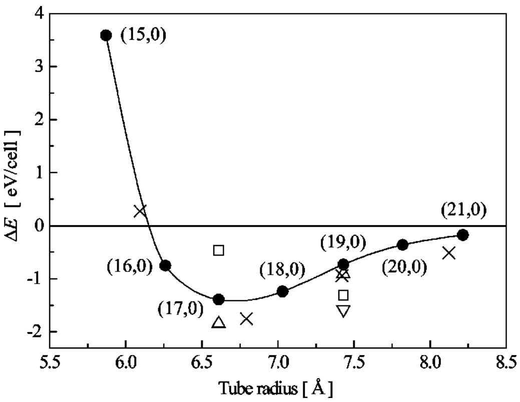

FIG. 2. Reaction energies ΔE (see text) in the encapsulation reaction of the fullerene for $(n,0)$ zigzag nanotubes. The line is a guide for eyes. Solid circles, triangles, squares, and an inverted triangle denote the ΔE for C_{60}, C_{70} (lying), C_{70} (standing), and C_{78}, respectively. The calculated energies ΔE for $C_{60}@(n,n)$ $(9 \leqslant n \leqslant 12)$ obtained in Refs. 18,19 are also shown by crosses.

space monotonically increases and the energy ΔE gradually approaches zero with increasing the tube radius (Fig. 2). When the C_{60}'s are dislodged from the center of the nanotube, however, $|\Delta E|$ approaches not zero but finite values of about 0.4 eV.[19]

Comparing the energy ΔE of the zigzag nanotube and that of the armchair nanotube, we find that the ΔE of the zigzag nanotube clearly exhibits the quantitatively same characteristics as that of the armchair nanotube (Fig. 2). The results indicate that the space in the nanotube, rather than the metallic or semiconducting characteristics or atomic arrangements of constituent nanotubes, is a decisive factor in the energetics of the peapods. Based on these findings, we may deduce energetic stability of various carbon peapods solely from the viewpoint of the space. The calculated energy gain $|\Delta E| = 1.39$ eV for C_{60}@(17,0) corresponds to 5.3 meV per atom. This value is smaller than the binding energy of graphite layers, 23 meV per atom. This difference obviously comes from the difference in number of atom pairs between the layers or between the tube and C_{60}. The layer-layer interaction in graphite and the wall-wall interaction in peapods are considered to have the character of van der Waals interaction. Sufficiently accurate description of such interaction is unavailable at present: Our calculation with generalized gradient approximation fails to reproduce the layer-layer binding of graphite, whereas the LDA is successful in providing reasonable binding energy. Hence the calculated reaction energies ΔE in this paper are of qualitative nature to some extent. Yet the universal profile shown in Fig. 2 indicates that ΔE is determined mainly by the tube radius, irrespective of the atomic and electronic structures of the constituent tubes or the species of the encapsulated fullerenes (see below).

We further study energetics of large-fullerene peapods. Here we focus on the C_{70} and C_{78} fullerenes encapsulated in the zigzag nanotubes. Optimized geometries of these peapods are shown in Fig. 3. The structures studied here are found to be energetically stable. For the C_{70} peapods, it is expected that the energetics depends on the orientation of the C_{70} due to an ellipsoidal shape of the C_{70} molecule of which a long axis (C_5 axis) is longer than a short axis (C_2 axis) by about 0.7 Å: In one case, the C_{70} molecules are aligned in the nanotube with the C_5 axis being parallel to the tube axis (lying arrangement), whereas in another those are aligned with the C_5 axis being perpendicular to the tube axis (standing arrangement). We indeed find that the lying arrangement is more energetically favorable than the standing arrangement for the (17,0) nanotube whereas the standing is more favorable than the lying for the (19,0) nanotube. For the (17,0) nanotube, the energy ΔE of the lying is lower than that of the standing by about 1.37 eV. In the standing arrangement the distance between the C_{70} and the nanotube is 2.78 Å which is close to that in the C_{60}@(16,0). The small values of $|\Delta E|$ is due to the small interwall spacing. On the other hand, since the interwall spacing of the lying arrangement is the same as that of the C_{60}@(17,0), the energy ΔE of the lying is close to that of the C_{60}@(17,0). The result indicates that the C_{70}'s encapsulated in the thin nanotubes prefer the lying arrangement. For the (19,0) nanotube, the standing arrangement is found to be lower in energy than the lying arrangement. Thus, it is expected that the C_{70}'s in the thick nanotube prefer the standing arrangement.

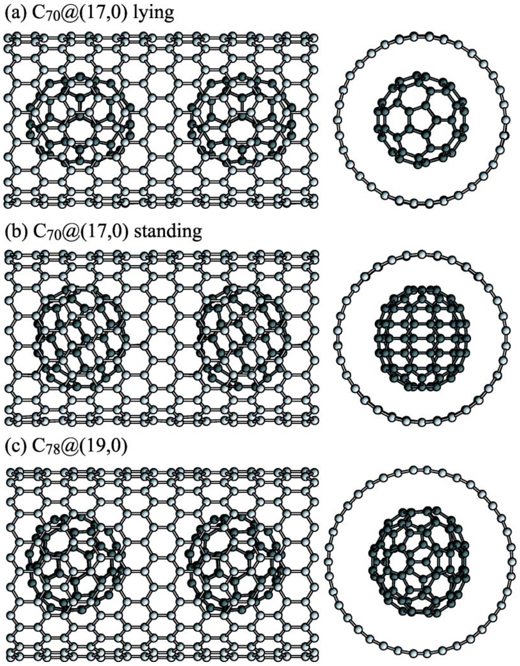

FIG. 3. Geometric structures of total-energy minimized (a) lying, and (b) standing C_{70}@(17,0) (see text), and (c) C_{78}@(19,0).

Figure 3(c) shows the fully optimized geometry of a C_{78} peapod. Hence, we consider the major isomer of the C_{78} fullerene, i.e., a C_{2v}' isomer. The $C_{78}(C_{2v}')$ possesses a relatively isotropic shape so that the energetics is not expected to exhibit large orientational dependence. We find that the energy ΔE of the C_{78}@(19,0) is almost the same as that of the C_{60}@(10,10) (Fig 2). In the former, the interwall spacing is about 3.30 Å, which is close to that in the C_{60}@(10,10). These findings also corroborate that the space between the fullerenes and nanotubes, rather than the atomic and electronic structures of the constituent nanotubes or the species of the encapsulated fullerenes, play a principal role in the energetics of the peapods.

IV. ELECTRONIC STRUCTURES

A. C_{60} peapods

The space also controls electron states near the Fermi level. Figure 4 shows calculated energy bands of the C_{60} peapods. In an isolated C_{60}, there are fivefold degenerate highest occupied h_u states and threefold degenerate lowest unoccupied t_{1u} states with the energy gap of about 2 eV.[32] Thus, it is expected that the electron states of the peapods near the gap mainly originate from the t_{1u} and h_u states of C_{60} and the π and π^* states of the nanotubes. Their electronic structures may be a simple sum of those of the C_{60} chain and the nanotubes since there is no substantial rebonding in the peapods.

Yet Fig. 4 clearly shows a different feature. The t_{1u}-like states[33] shift sensitively to the radius of the tube: The t_{1u}-like states are located above the energy gap of the empty tube in

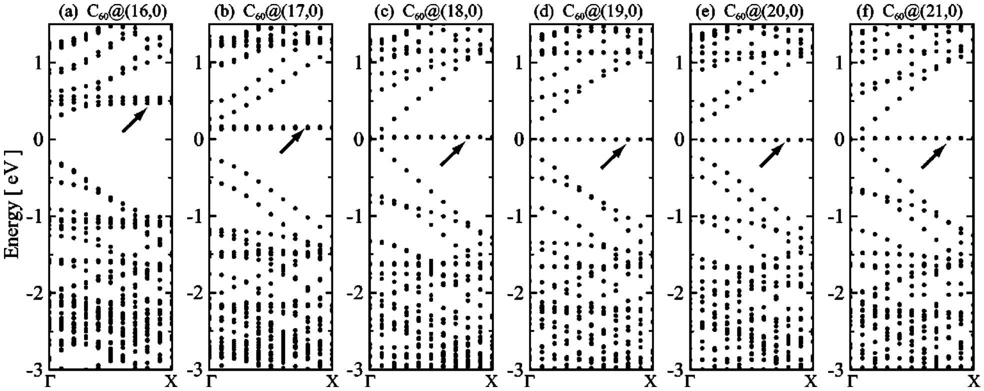

FIG. 4. Energy-band structures of zigzag peapods C_{60}@(16,0) (a), C_{60}@(17,0) (b), C_{60}@(18,0) (c), C_{60}@(19,0) (d), C_{60}@(20,0) (e), and C_{60}@(21,0) (f). Arrows indicate the t_{1u}-like electron states. Energies are measured from the midgap energy of each empty nanotube.

the C_{60}@(16,0); the states shift downwards with increasing the radius and take the lowest value in the C_{60}@(19,0) and C_{60}@(20,0); then it slightly shifts upwards for the C_{60}@(21,0). Thus, in the C_{60}@(19,0) and C_{60}@(20,0), the t_{1u}-like states are located at the midgap energy of each empty nanotube so that the energy gap of the peapods decreases by half from the empty nanotubes. The energy of the t_{1u}-like states as a function of the tube radius is summarized in Fig. 5. The t_{1u}-like states are found to shift by half eV with the 1 Å change of the tube radius. The peapods studied here are energetically stable and are expected to be synthesized in certain experimental conditions except the C_{60}@(15,0). Indeed, it has been found that the recent transport experiments on the C_{60} peapods in the field-effect transistor (FET) clearly exhibit the band-gap modulation which depends on radius and chirality of nanotubes.[21] Hence the present finding opens a possibility of controlling electronic properties of the peapods by changing the tube radius, or vice versa to identify the radius of the tube of the peapod by measuring spectroscopic properties.

The downward shift of the t_{1u}-like states is also found in the peapods consisting of the metallic tubes. The (15,0), (18,0), and (21,0) nanotubes are actually metallic, and Fig. 5 clearly shows a similar energy shift depending on the tube radius. Furthermore, we have also found a similar radius dependence of the t_{1u}-like states in the armchair peapods.[18,19] These are indicative of importance of the space in the peapods rather than the electronic structures of the nanotubes.

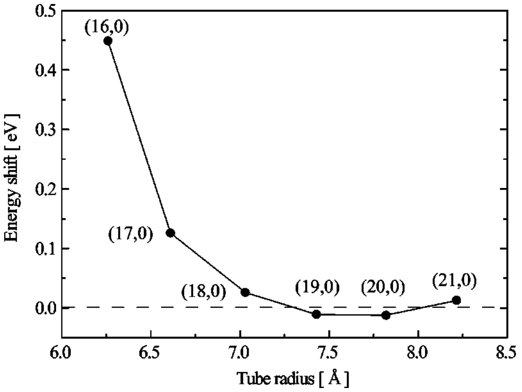

FIG. 5. The Kohn-Sham energy level of the t_{1u}-like states as a function of the tube radius in zigzag peapods C_{60}@(n,0). The reference of the energy for each peapod is taken at the Fermi level which corresponds to the midgap energy of the each empty nanotube.

The shift of the t_{1u}-like states is understandable in two different regimes. For the thin nanotube, the interwall spacing is insufficient to allow the t_{1u} states of the C_{60} to distribute in the space so that the states shift upwards and are located above the energy gap of the nanotubes. On the other hand, the downward shift around the (19,0) and (20,0) nanotubes from the (21,0) nanotube is originated from the hybridization between the π states of the C_{60} and the NFE states of the nanotubes. The energy levels of the NFE states are generally located at a couple of eV above the Fermi level in empty nanotubes.[17] These states are still above the Fermi level in all the peapods considered here. However, the hybridization between the NFE states and the π states of the C_{60} is substantially induced upon encapsulation of the fullerenes in the tube. As a result of this, most of the electron states that have originated from the π states of the C_{60} shift downward upon encapsulation. There is an optimum radius of the tube in which the space enhances the hybridization most effectively: The optimum tube radius is about 7.5 Å in which the interwall distance between the tube and the C_{60} is slightly larger than the interlayer distance of the graphite. The space is essential to control the electron states near the Fermi level of the peapods.

B. C_{70} peapods

The results presented above clearly show that there is an optimum radius of the nanotube where the unoccupied states of the encapsulated C_{60} exhibit the downward energy shift most effectively. In the C_{60} peapods, the t_{1u}-like states emerge at the midgap energy of the nanotube under the optimum interwall spacing. This situation raises a question whether the electron-state tuning is possible by encapsulating large fullerenes which possess different electron states from the C_{60} molecule. Here we study the electronic structures of the C_{70} peapods, i.e., C_{70}@(17,0) and C_{70}@(19,0), and the

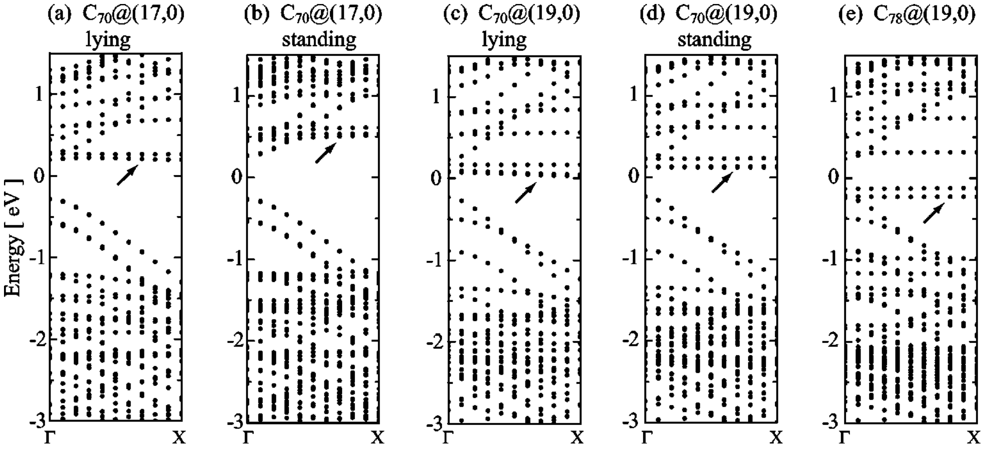

FIG. 6. Energy-band structures of zigzag peapods: (a) lying and (b) standing C_{70}@(17,0), (c) lying and (d) standing C_{70}@(19,0) (see text), and (e) C_{78}@(19,0). Arrows indicate the LU states. Energies are measured from the midgap energy of each empty nanotube.

$C_{78}(C'_{2v})$ peapod, i.e., C_{78}@(19,0). As demonstrated in the previous section, these peapods are found to be energetically stable.

Figures 6(a–d) show electronic energy bands of the C_{70}@(17,0) and the C_{70}@(19,0). Since the C_{70} molecule has the ellipsoidal shape, we consider two different orientations of the molecule (the standing and the lying arrangements) in each nanotube. In an isolated C_{70} molecule, there are the triply bunched highest occupied (HO) states and the triply bunched lowest unoccupied (LU) states.[34] These states become valence and conduction bands, respectively, with the energy gap of 1.7 eV in Fig. 6. The energy dispersion, on the other hand, is quite small. This is due to a large separation of 12.76 Å between fullerenes imposed from computational requirements. When the wall-wall distance between adjacent fullerenes is close to the layer-layer distance in graphite, the band dispersion becomes about 0.6 eV.[19] For the C_{70}@(17,0) with the lying arrangement, it is found that the LU states are located above the midgap point of the nanotube by 0.2 eV [Fig. 6(a)]. The energy of the LU states is higher than that of the t_{1u}-like states of the C_{60}@(17,0) by about 0.1 eV. In the isolated C_{70} molecule, our LDA calculations show that the LU states are higher in energy by 0.25 eV than the t_{1u} states of the C_{60} molecule. The higher LU states of the C_{70} result in the difference in the electronic structures of the peapods. The electronic structures of the peapods reflect the electron states of the encapsulated fullerenes.

In addition, the electronic structure of the C_{70}@(17,0) with standing arrangement is different from that with the lying arrangement: The LU states are located above the bottom of the conduction π^* bands of the nanotube by 0.2 eV [Fig. 6(b)]. This orientational dependence is due to the interwall spacing between the C_{70} and the nanotube. In the standing arrangement, the interwall spacing is 2.78 Å which is close to that in the C_{60}@(16,0). Therefore, the LU states shift upward by 0.4 eV compared with the lying arrangement, and are located above the energy gap of the nanotube. The results indicate that the electron states of the peapods are tunable by not only choosing the encapsulated fullerenes but also controlling the orientation of the fullerenes.

For the C_{70}@(19,0), the LU states are located in the gap of the nanotube in both standing and lying arrangements [Figs. 6(c) and 6(d)]. Furthermore, the LU states for the standing and the lying arrangements shift downward compared with those for the C_{70}@(17,0) as in the case of the C_{60} peapods. In the standing arrangement, the shift is mainly due to the wider space inside the (19,0) nanotube in which the π states of the C_{70} are allowed to be distributed inside. On the other hand, the small shift for the lying arrangement is originated from the hybridization between the π states of the C_{70} and the NFE states of the nanotube.

C. C_{78} peapods

We have demonstrated that the electronic structures of the peapods reflect the electron states of the encapsulated fullerenes as well as the fullerene-nanotube spacing. We therefore explore a possibility of the metallization of semiconducting nanotubes by encapsulating the large fullerenes possessing the deeper LU state. Earlier calculations[35,36] have shown that a C'_{2v} isomer of the C_{78} has the relatively deep lowest unoccupied state. We thus calculate a peapod consisting of C_{78} (C'_{2v} isomer). Figure 6(e) shows energy bands of the C_{78}@(19,0). The most astonishing feature is found in the energy bands near the Fermi level: The originally unoccupied states of the C_{78} [depicted by the arrow in Fig. 6(e)] shift downwards and are located near the top of the valence bands of the corresponding semiconducting (19,0) nanotube. Consequently, there are three states almost degenerate near the valence-band top at the Γ point. The squared Kohn-Sham orbital of the valence-band top at the Γ point is shown in Fig. 7. We find that the wave function has an amplitude not only on the tube but also on the C_{78}, indicative of the hybridization between the π states of the tube and the LU states of the C_{78}. The remaining two states near the valence-band top also distribute both on the tube and the C_{78} to some extent. At the X point, on the other hand, the flat bands near the valence-band top preserve the character of the C_{78} states [Fig. 7(b)]. We find that the band gap between the valence-band top at the Γ point and the conduction-band bottom at the X point

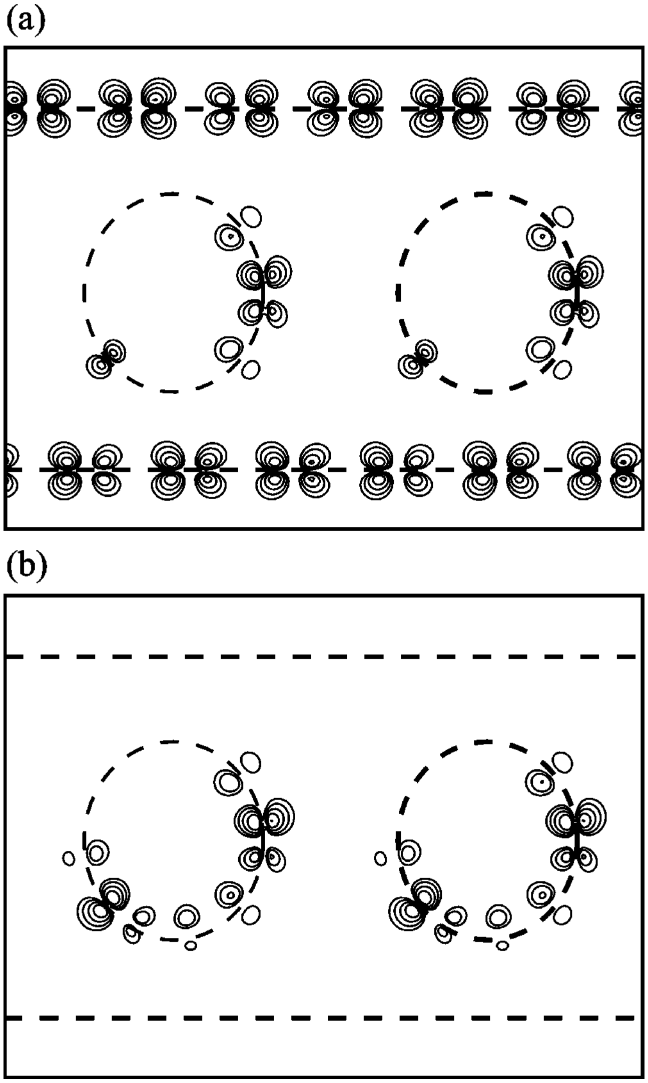

FIG. 7. The squared Kohn-Sham orbitals of C_{78}@(19,0) for (a) the valence-band top at Γ point and for (b) the valence-band top at X point. Each contour represents twice (or half) the density of the adjacent contour lines. The lowest value represented by the contour is 7.9×10^{-5} e/(a.u.)^3.

possessing the LU state character of the C_{78} is closed. Namely, the peapod is a zero-gap semiconductor in the present calculation. When the separation between the C_{78}'s becomes a realistic value which is much smaller than that in the present geometry, the dispersion of the C_{78}-origin energy bands would be half eV. In this case C_{78}@(19,0) becomes a semimetal in which electrons are at the X and holes are at the Γ points. It should be remarked that the LDA underestimates the fundamental gap of the semiconducting materials,[37] and the calculated values presented here are of qualitative nature. The result demonstrates that the electronic structures of the peapods are indeed tunable by not only controlling the space within the tube but also choosing encapsulated fullerenes. Furthermore, the result also implies the possibility of the metallization of the semiconducting nanotubes by filling the fullerenes whose LU states are deeper than that of the C_{78}.

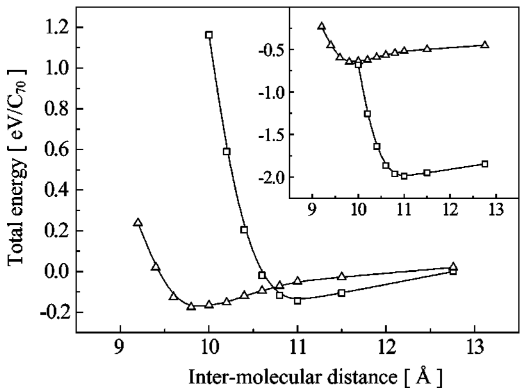

FIG. 8. The total energies of the C_{70} chains. Open squares and open triangles indicate the total energies of the standing and the lying C_{70} chains (see text), respectively. Inset: The total energies calculated by the sum of the ΔE of the C_{70}@(17,0) and the total energy of the isolated C_{70} chain. The lines are a guide for eyes. The energies are measured from that of the isolated C_{70} molecule.

Since our calculations show that the C_{78} peapod is the zero-gap semiconductor, it is beneficial to estimate effective mass (m^*) of the electrons at the bottom of the conduction band. Yet, flat dispersion bands that have originated from C_{78} is an artifact due to an imposed commensurability condition which causes the large intermolecular spacing. Therefore, we here calculate the effective mass of C_{78} chains in which the intermolecular spacing is 9.83 Å. The calculated values of the m^* is 2.0 m_e (m_e is the bare electron mass) which is close to that of the fcc C_{60} (1.5 m_e).[32]

V. ELECTRON-STATE CONTROL BY MOLECULAR FILLING

In the present work, we have demonstrated that the electron-state control is possible in the peapods by tuning the radius of the nanotube and by selecting the encapsulated fullerenes. Furthermore, in the case of the fullerenes with the large anisotropy, we find that the orientation of the fullerenes modulates the electron states of the peapods. Among them, the orientation control is a promising way to control the electron states of the peapods because the former two are only practicable under the synthesis processes. We discuss a possibility of the orientation control of the C_{70} in the (17,0) nanotube. Figure 8 shows the total energies of isolated C_{70} chains with the standing and the lying arrangements as a function of the intermolecular spacing. Optimum intermolecular spacing for the lying and the standing arrangements are found to be 11.0 Å and 9.8 Å, respectively. Experimentally, the intermolecular distances for the lying and the standing C_{70} chains in the nanotubes are found to be 11.0 Å and 10.1 Å, respectively.[11] The calculated intermolecular spacing for the isolated C_{70} chains shows good agreement with those observed for the C_{70} chains in the nanotubes experimentally. Thus it is expected that the total energies of the C_{70} peapods as a function of the intermolecular distance exhibit similar features to those obtained for the isolated C_{70} chains. To simulate the energetics of the C_{70} peapods, we add the energy ΔE to the total energies of the isolated C_{70} chains (inset of Fig. 8). It is clear from the inset of Fig. 8 that the lying arrangement undergoes structural transformation to the standing arrangement under the uniaxial stress along the tube axis. Using the relation $P = -\partial E/\partial V = -\partial E/S\partial z$ where S is the cross section of the tube and the common tangent of the two total-energy curvatures in the inset of Fig. 8, the critical pressure is found to be 1.4 GPa. Therefore, it is plausible that the orientation of the C_{70} in the (17,0) nanotube is controllable by changing the filling of the molecules inside the nanotube. Owing to these characteristics, it is expected that the border between different configurations of fullerenes may be applicable for a diode in the nanometer-scale electronic circuit.

VI. SUMMARY

The reaction energies for fullerenes encapsulated in various nanotubes have indicated that the space between the walls of the nanotube and the fullerene is the decisive factor to determine the energetics of the resultant peapod, irrespective of metallic or semiconducting characters of the nanotubes, electronic states of the fullerenes, and atomic arrangements of each constituent unit. For the C_{60}, it has been found that the (17,0) nanotube is the most favorable zigzag nanotube which results in the optimum interwall spacing of about 3.11 Å. On the other hand, we have found that the anisotropic shape of the encapsulated fullerenes induces the orientation dependence on the energetics of peapods: It has been demonstrated that the lying arrangement of the C_{70} is more energetically stable that the standing in the (17,0) nanotube whereas the standing is more stable than the lying in the (19,0) nanotube due to the ellipsoidal shape of the molecule.

It has been also found that the space in the nanotube modulates the electron states of the peapods: In the C_{60} peapods, the lowest unoccupied states of C_{60} shift downward significantly by increasing the tube radius, and the energy gap of the peapods sensitively depends on the interwall spacing. In addition to the space, the electron structure of the encapsulated fullerenes is another important factor to determine the electronic structure of the peapods. Our calculations have elucidated that the electron states near the Fermi level of the peapods reflect those of the encapsulated fullerenes. It has indeed been found that the C_{78} peapod is a zero-gap semiconductor due to the relatively deep lowest unoccupied states of the isolated C_{78} molecule. Furthermore, in the case of the fullerenes with the large anisotropy, we have also demonstrated that the orientation of the fullerenes is also capable of modulating the electron states of the peapods near the energy gap. Hence our results open a possibility of the band-gap tuning of the peapods by controlling the space inside the nanotube and orientation of the molecules and by selecting the species of the encapsulated materials.

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