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Electronic properties of peapods: effects of fullerene rotation and different types of tube

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Abstract

Effects of encapsulated fullerene rotation on peapod electronic properties are studied by using Slater–Koster tight-binding calculations. We found that the encapsulated fullerenes can rotate freely in the space of a (10, 10) tube at room temperature, and the rotation of fullerenes will affect $C_{60}@$ (10, 10) peapod electronic properties significantly; generally, orientational disorder will remove the sharp features of the average density of states (DOS). However, the rotation of fullerenes cannot induce a metal–insulator transition. Electronic properties of peapods formed by fullerenes and different types of single-walled carbon nanotube (SWNT) are studied too. Percentage calculations suggest that, unlike the multicarrier metallic $C_{60}@$ (10, 10) peapod, the $C_{60}@$ (17, 0) peapod is a semiconductor, and the effects of the encapsulated fullerenes on tube valence bands and conduction bands are asymmetrical.

1. Introduction

Since the discovery of carbon nanotubes (CNT) [1], these materials have been attracting great interest partly because of their rich electronic properties [2–10], which may be further modified via chemical doping [11, 12]. Recently, a new type of self-assembled hybrid structure called the ‘nano-peapod’, consisting of fullerene arrayed inside a SWNT, have been reported [13]. Potential applications of nano-peapods range from data storage [14] to possibly high temperature superconductors [15].

Even though peapod electronic properties have been experimental [16, 17] and theoretical [18] studied previously, some issues remain unresolved. These include the effects of encapsulated fullerene rotation, and the effects of different types of tube. Therefore, further study on peapod electronic properties is deemed necessary.

In this paper we report our calculations on these issues. The paper is organized as follows. In section 2, we introduce the Hamiltonian, and the calculation method. Then, the calculated results and discussion are given in section 3. The conclusions are shown in section 4.

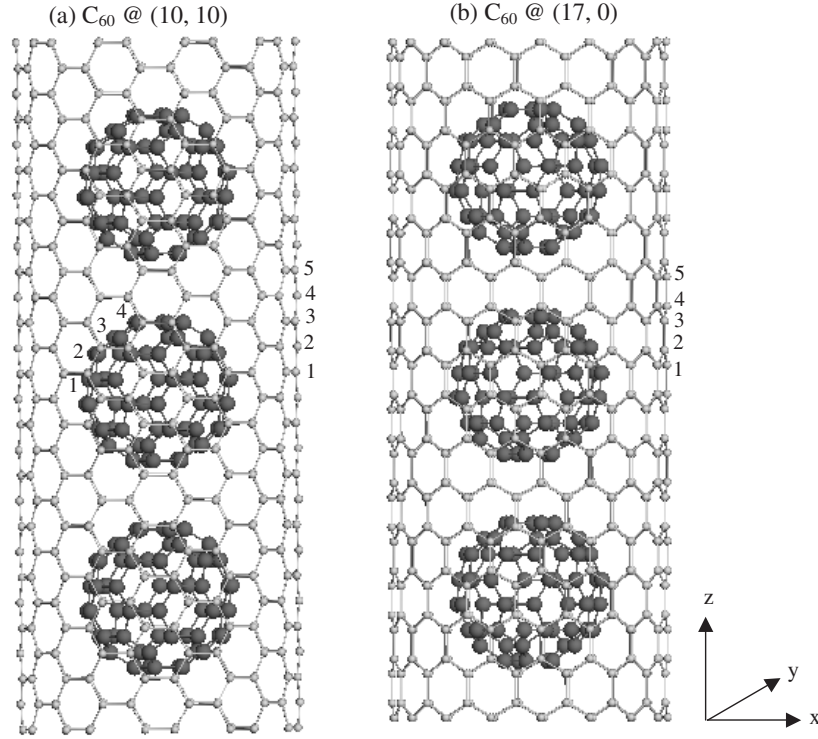


Figure 1. Geometries of fullerenes encapsulated in (a) the (10, 10) tube, (b) the (17, 0) tube. The distances between the centres of the fullerenes are 0.984 and 1.278 nm for the $C_{60}@ (10, 10)$ peapod and $C_{60}@ (17, 0)$ peapod, respectively.

2. Hamiltonian and method

Experiments [13, 15] show that, in the carbon nanotube peapods, the distance between the fullerenes is about 1.0 nm. Here, we impose a commensurability condition relating the one-dimensional periodicity of the atomic arrangements in the nanotube and that of the chain of fullerenes. Consequently, for the $C_{60}@ (10, 10)$ peapod, the lattice parameter c becomes 0.984 nm along the tube direction which corresponds to quadruple the periodicity of the (10, 10) armchair nanotube; and for the $C_{60}@ (17, 0)$ peapod the lattice parameter c is taken as 1.278 nm along the tube direction. At the beginning, the fivefold axis of the encapsulated fullerenes is parallel to the axis of the tube (as shown in figure 1). Then, rotating every fullerene around the X , Y or Z axis, we study the effects of the orientational rotation on peapod electronic properties. Since the weak inter-part interactions cause only a very small geometric deformation of the tube and fullerenes [18], here we neglect the deformation of the tube and the fullerenes in the peapods.

Since we will pay attention to the effects of encapsulated fullerene disorder, etc, and due to the computer limitation, we employ tight-binding calculations. Below, we can see that results gained by using tight-binding calculations are in agreement with that obtained by using total-energy electronic structure calculations except for the nearly free electron states [18]. The Hamiltonian of the system is written as follows:

$$H = \sum_{is} \epsilon_s^0 c_{is}^\dagger c_{is} + \sum_{jp} \epsilon_p^0 c_{jp}^\dagger c_{jp} + \sum_{ijmn} (t_{ij}^{mn} c_{im}^\dagger c_{jn} + \text{H.c.}), \quad (1)$$

where ϵ_s^0 and ϵ_p^0 are the on-site energies of the 2s and 2p orbitals, respectively. $c_{is}(c_{is}^\dagger)$ and $c_{jp}(c_{jp}^\dagger)$ denote the annihilation (creation) operators of an electron on C 2s orbitals at site i and C 2p orbitals at site j , respectively. m and n are the orbital indices. t_{ij}^{mn} are the hopping integrals which are expressed in terms of Slater–Koster parameters: $V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$, and $V_{pp\pi}$ [19].

The parameter values in equation (1) are taken to be close to those used for graphite in [20], which was also successfully used to study the properties of the SWNT with small radius [6] and the SWNT with polygonized cross sections [8], and to describe superconductivity in bulk C₆₀ [21]. Among the four orbitals per atom, the s level is located at $\epsilon_s^0 = -7.3$ eV below the triply degenerate p level taken as the zero of energy ($\epsilon_p^0 = 0.0$). The Slater–Koster hopping parameters for the nearest-neighbour pairs are taken as $V_{ss\sigma} = -4.43$ eV, $V_{sp\sigma} = 4.98$ eV, $V_{pp\sigma} = 6.38$ eV, and $V_{pp\pi} = -2.66$ eV. The second-neighbour interactions are taken into account by using $V_{ss\sigma} = -0.18Y$ eV, $V_{sp\sigma} = 0.21Y$ eV, $V_{pp\sigma} = 0.27Y$ eV, and $V_{pp\pi} = -0.11Y$ eV, where $Y = (0.3335/r_{ij})^2$ is a scaling factor and depends on the interatomic distance r_{ij} (expressed in nanometres).

The calculations for energy band structures of the isolated SWNT and the peapods are carried out in a supercell, and we employed 1000 k points along the tube axis. Then, the DOS are calculated.

In order to investigate the local electronic properties of the system, here we employ the recursion method [22] to calculate the local DOS by using a continued-fraction development of the Green function diagonal elements in the complex energy plane. In our calculations, the multiband terminator is chosen to close the continued fraction [23]. Due to good itinerant properties of the electrons in the SWNT, here 300 levels of continued fraction were computed. The imaginary part of the energy is taken to be small enough (0.001 68 eV); thus the calculated DOS are not sensitive to the value used and show clearly the peaks in the DOS curves, which can be compared directly with the experimentally observed DOS.

3. Calculated results and discussion

First, we test the reasonableness of the tight-binding calculations on the peapods. The band structures of the isolated (10, 10) tube and the C₆₀@(10, 10) peapod are shown in figures 2(a) and (b), respectively. Comparing figure 2 with previous total-energy electronic structure calculation results [18], we can see that the tight-binding calculations can reproduce the LDA σ and π states very well. From figure 2, we see that the features of these band structures are almost identical except for the positions near -1.4 , 0.0 , and 0.6 eV (those positions correspond to the fullerene energy levels H_u, T_{1u}, and T_{1g}, respectively). The calculated band structures near the Fermi level are consistent with a rigid shift of the Fermi level induced by fullerene doping, which indicates electron injection into the fullerene T_{1u} orbitals.

As a standard, we study in detail the peapod electronic properties. The total DOS of the peapod can be gained from its energy band structures, and the calculated results are shown in figure 3(a). We can see that the position of the Fermi level corresponds to the fullerene T_{1u} orbital, and due to interactions among the fullerenes and the tube, T_{1u} and T_{1g} orbitals are widened. There are five peaks for the T_{1u} orbital, which is not equal to the degenerate degree of the T_{1u} orbital. It is also interesting to note that, like the case of the ropes formed by armchair nanotubes [7, 24], there are a pseudogap and a real gap near -0.4 and 0.3 eV, respectively. So the electronic structure of the peapod is not a simple sum of those of fullerenes and the nanotube.

Furthermore, we calculated the local DOS of the fullerenes and (10, 10) tube in this peapod by using recursion method. The results are shown in figures 3(b)–(j). From figures 3(b)–(e), we can see that local DOS of the fullerene’s different atoms are significantly different.

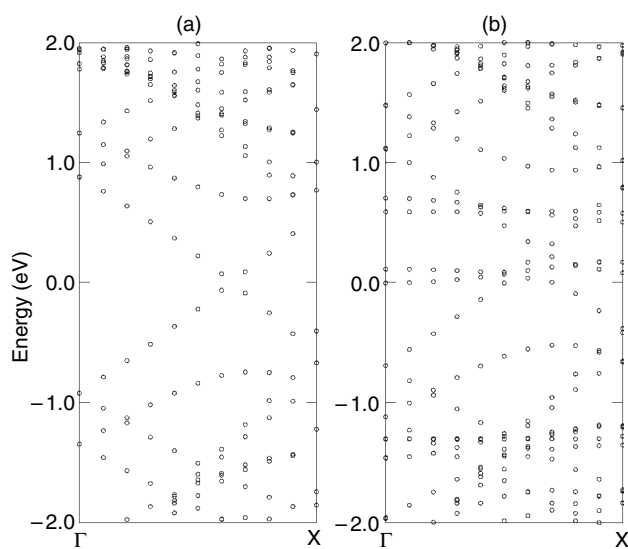


Figure 2. The band structures of (a) an isolated (10, 10) tube and (b) a $C_{60}@ (10, 10)$ peapod. The Fermi level is set as 0.0 eV.

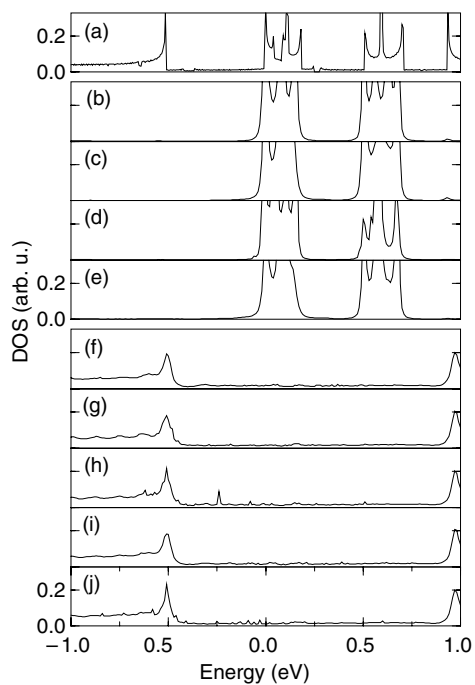


Figure 3. (a) The total DOS of the $C_{60}@ (10, 10)$ peapod. (b)–(e) Local DOS of the layers in the fullerene, corresponding to those (1, 2, 3, 4) of the fullerene shown in figure 1(a), respectively. (f)–(j) Local DOS of the layers in the (10, 10) tube of the peapod, corresponding to the layers 1, 2, 3, 4, 5 of the tube shown in figure 1(a), respectively. The Fermi level is set as 0.0 eV.

However, the change of the (10, 10) tube electronic properties is negligible, as can be seen from figures 3(f)–(j). Since both the tube and the fullerenes have significant DOS values at the

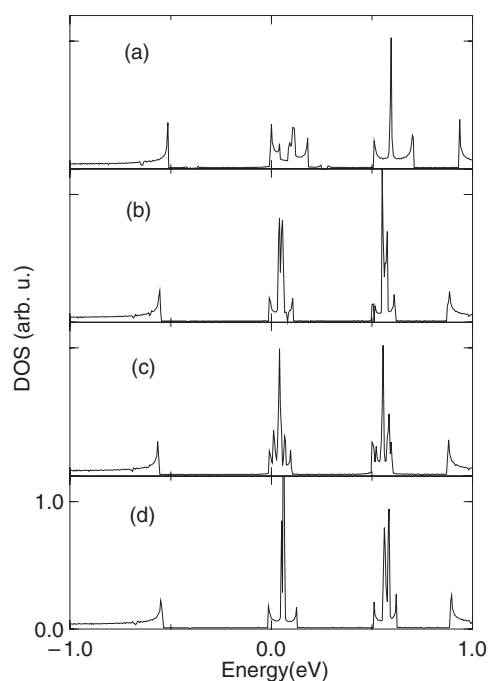


Figure 4. DOS of the peapods for different orientational order; (a) the geometry of the peapod is shown as figure 1(a), then the fullerenes rotate around the X axis by angles (b) $\pi/3.0$, (c) $2\pi/3.0$, and (d) π . The Fermi level is set as 0.0 eV.

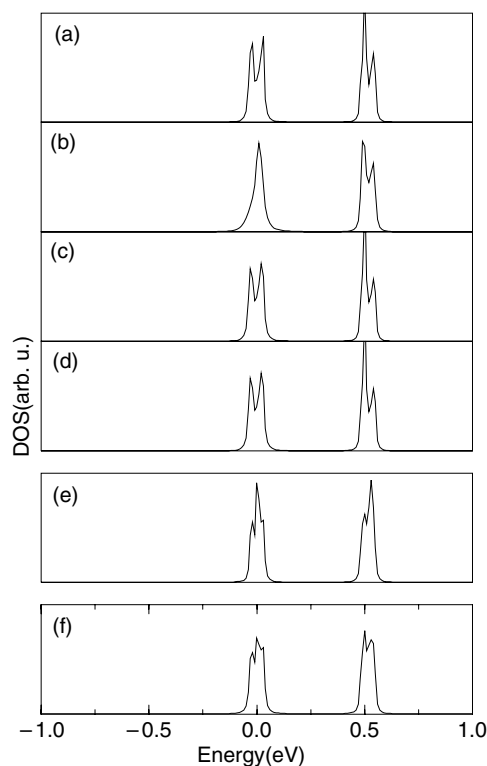


Figure 5. (a)–(d) The local DOS of the layers in the fullerene, corresponding to layers 1, 2, 3, 4 shown in figure 1(a), respectively. Here, the calculated fullerene does not rotate. (e) The total DOS of one fullerene. Here, the fullerene is randomly rotated around the X , Y or Z axis. (f) The total DOS of some fullerenes.

Fermi level, the $C_{60}@ (10, 10)$ peapod is a metal with multicarriers, each of which distributes either on the tube or on the fullerene chain. However, due to the higher DOS of fullerenes at the Fermi level, the electron transport is expected to dominate in the fullerene chain rather than in the tube wall. And the high value of the DOS at the Fermi level indicates the possibility of superconductivity [11].

Now, we investigate effects of different orientational orders by rotating all encapsulated fullerenes around the X , Y or Z axis by the same angle. Our calculations show that the effects of all encapsulated fullerenes rotated around the Z axis are not significant; however, when all fullerenes rotate around the X (or Y) axis, the electronic structures of the peapod may be affected significantly. Some typical DOS are shown in figure 4. We can see that the encapsulated fullerene rotation around the X axis changes the number of peaks, the value of DOS and the width of the fullerene T_{1u} and T_{1g} orbital bands significantly. However, in all cases, there is high value of the DOS at the Fermi level, and the change of total electronic energy induced by rotations is less than 0.1 meV/atom. Furthermore, using equation (1) in [25], we have calculated the change of the one-electron energy and the Coulomb repulsion arising from possible charge transfers between inequivalent sites induced by the rotation of the encapsulated fullerenes, and found that the former term is nearly one order of magnitude larger than the latter one, which is in agreement with the case of the ropes formed by single-walled carbon

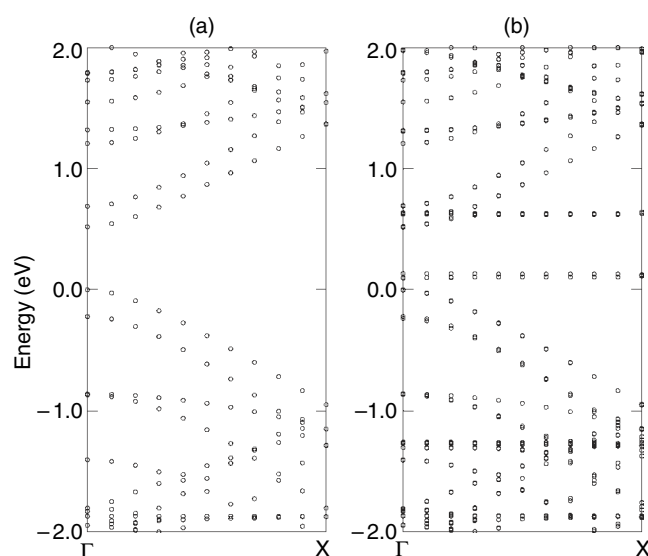


Figure 6. The band structures of (a) an isolated (17, 0) tube and (b) a $C_{60}@ (17, 0)$ peapod. The Fermi level is set as 0.0 eV.

nanotubes [26]. These indicate that the encapsulated fullerenes in this peapod can rotate freely at room temperature, and the fullerene rotation cannot induce the phase transition from metal to insulator.

Really, fullerenes in the peapod are orientationally disordered at room temperature. Below, we simulate this case through randomly rotating fullerenes, then calculate the local DOS of some fullerenes and the total DOS of the fullerene chain by using the recursion method. Two types of fullerene are considered: one is the case where the calculation fullerenes do not rotate, and the other is the case where the calculation fullerenes rotate randomly. The results gained are shown in figure 5. Comparing figures 5(a)–(d) with figures 3(b)–(e), we can see that, even though the fullerene does not rotate, the other fullerenes' orientational disorder reduces the width of this fullerene's T_{1u} and T_{1g} orbital bands, and changes the outline of DOS curves. Comparing figures 5(a)–(d) with figure 5(e), we find that DOS of different fullerenes may differ significantly due to the orientational disorder. And like in the case of C_{60} solid [27], the orientational disorder removes sharp features of the total DOS, which can be seen from figure 5(f). However, the orientational disorder barely affects the (10, 10) tube local DOS.

For comparison, the electronic properties of $C_{60}@ (17, 0)$ peapod have also been investigated. The band structures of the isolated (17, 0) tube and the $C_{60}@ (17, 0)$ peapod are shown in figures 6(a) and (b), respectively. The changes of the band structures induced by the fullerene doping in the (17, 0) tube are similar to that of the $C_{60}@ (10, 10)$ peapod. But here there is no charge transfer between the tube and the fullerenes. Apparently, this peapod is a semiconductor, and the width of the gap is reduced from 0.5 to 0.1 eV due to fullerene doping.

The local DOS of the $C_{60}@ (17, 0)$ peapod are shown in figure 7. From figures 7(a)–(d), we find that, here, the changes of the fullerene electronic structures are not as significant as that of the $C_{60}@ (10, 10)$ peapod. On the other hand, comparing figure 7(e) with (f)–(j), we can see that doped fullerenes produce two peaks near 0.1 and 0.6 eV positions. Apparently, the effects on the valence band and conduction band are asymmetrical, and along the tube axis,

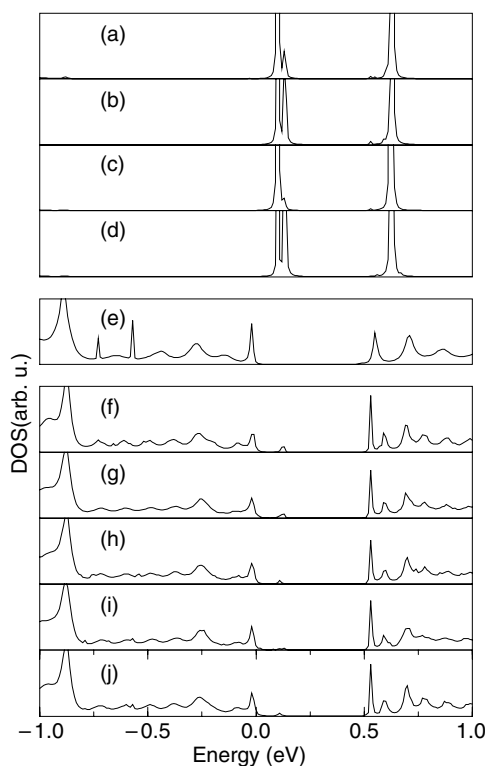


Figure 7. (a)–(d) Local DOS of the layers in the fullerene, corresponding to the layers 1, 2, 3, 4 shown in figure 1(a) for the fullerene, respectively. (e) The total DOS of the isolated (17, 0) tube. (f)–(j) Local DOS of the layers in the (17, 0) tube of the peapod, corresponding to the layers 1, 2, 3, 4, 5, shown in figure 1(b) for the tube, respectively. The Fermi level is set as 0.0 eV.

the local DOS of the (17, 0) tube changes slightly, which is in agreement with the experimental results, qualitatively [16].

The effects of the encapsulated fullerene rotation are studied too. Our calculations show that, here, these effects are not as significant as that in the $C_{60}@ (10, 10)$ peapod. We have also investigated the origin of the significant difference in fullerene rotation effects between these two peapods by altering the spatial distance between the encapsulated fullerenes. Our calculations show that these differences are mainly determined by the different spatial distances between the constituent units. This indicates a convenient way to modulate the peapod electronic properties by controlling the density of encapsulated fullerenes.

4. Conclusion

To summarize, using Slater–Koster tight-binding calculations, we found that the encapsulated fullerene rotations in the space of a (10, 10) tube induce a small energy change; thus fullerenes in this peapod can rotate freely at room temperature. Peapod electronic properties are not a simple sum of those of the tube and the fullerenes. And different orientational order can induce significant differences of electronic properties; generally, orientational disorder will remove the sharp features of the average DOS. However, rotation of fullerenes cannot induce a metal–insulator transition. Electronic properties of the peapods formed by fullerenes and different types of SWNT are studied too. Percentage calculations suggest that $C_{60}@ (10, 10)$

peapod is still a metal; at the Fermi level, there is a large value of the DOS, which indicates that this material may become a superconductor, and the effects of the encapsulated fullerenes on the tube local electronic structures are negligible. However, $C_{60}@ (17, 0)$ peapod is a semiconductor, and the encapsulated fullerenes asymmetrically alter the tube valence bands and conduction bands significantly. Our work also suggests a convenient way to modulate peapod electronic properties by altering the density of the encapsulated fullerenes.

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