

Charge Transfer and Gap States in Semiconducting Nanopeapods: a Theoretical Study

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The electronic structures of nanopeapods that consist of a semiconducting nanotube and various fullerenes, such as C_{60} , C_{82} , $La@C_{60}$, and $La@C_{82}$ are investigated using a first-principles method. For all the systems studied, molecular states originating from fullerenes are found within the energy gap of the semiconducting nanotube, often resulting in effective hole doping of nanotubes as the Fermi level shifts. In the case where C_{60} and $La@C_{60}$ are encapsulated, a rigid band model considering the work function of each constituent explains the band structure of the full system. The charge redistribution in nanopeapods with C_{82} and $La@C_{82}$, on the other hand, leads to a rigid shift of fullerene bands.

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I. INTRODUCTION

Because of their unique structural and electronic properties, carbon nanotubes, especially the semiconducting ones, have been regarded as promising components of the nano-size electronic device [1,2]. Depending on the chirality and the radius, the energy gap of a semiconducting nanotube varies up to 0.8 eV. Recently, nanotubes incorporating a periodic array of fullerenes, such as C_{60} and C_{82} , have been receiving considerable attention [3]. This class of nanomaterials has been dubbed as “nanopeapods”, reflecting structural similarities to real peapods. The mass production of the nanopeapod is now achieved through chemical treatments, such as oxidative etching which creates perforations on the side wall of nanotubes, facilitating the suck-in motion of fullerenes [4,5].

Since the nature of the interaction between a nanotube and fullerenes are of the van der Waals type, it is rather surprising that experiments showed substantial changes in the electronic properties of nanotubes upon encapsulation of fullerenes. For example, the scanning-tunneling-microscope (STM) image captured the density of states of the conduction band oscillating along the nanotube with a period commensurate with the underlying C_{60} arrays [6,7]. When the Gd atom is encapsulated inside the C_{82} , the band gap is found to decrease significantly at the location of C_{82} [8]. Accordingly, the metallofullerene nanopeapod showed an ambipolar character when used as a field-effect transistor [9]. On the

other hand, the conductivity of nanopeapods was found to increase compared to that of pristine nanotubes [10, 11]. A temperature-induced transition from the p - to n -type character was also observed [12].

In spite of the growing experimental data, especially on semiconducting nanopeapods, theoretical studies on these materials are very rare [13–15]. For a metallic nanotube with the encapsulation of C_{60} , Okada *et al.* proposed multicarrier properties by observing fullerene bands crossing the Fermi level together with π and π^* bands of the nanotube [13]. They argued that the t_{1u} bands shift down because these states possess a nearly-free-electron-like (NFE) character which originates from the empty space between the nanotube and C_{60} . In another work, we showed that the STM image of a nanopeapod was strongly correlated with the molecular states of the fullerenes inside [15].

In this paper, we carry out first-principles calculations to study the electronic structure of the semiconducting nanopeapod. We focus on the charge transfer between fullerenes and a nanotube, as well as the positions of the energy levels related to the fullerenes. We consider various types of fullerenes and metallofullerenes as a “pea”. It is found that the encapsulated fullerene frequently leads to the effective doping of the semiconducting nanotube with a p -type character. We also show that band structures can be understood based on the separate bands of the constituent system, *i.e.*, the nanotube and the fullerene.

II. MODEL SYSTEM AND COMPUTATIONAL METHOD

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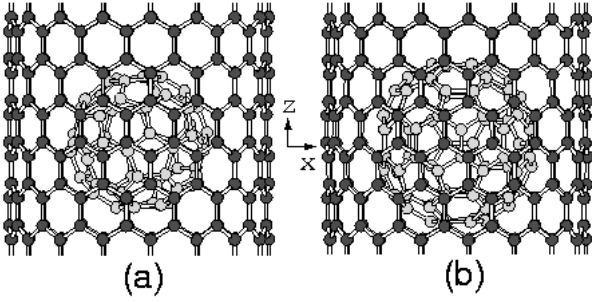


Fig. 1. Unit cell of two representative models: (a) $C_{60}@ (17,0)$ and (b) $C_{82}@ (17,0)$. Dark and light circles indicate the nanotube and the fullerenes, respectively.

We choose a (17,0) carbon nanotube with a diameter of 13.2 Å and incorporate C_{60} and C_{82} with or without a La atom. Due to the computational difficulties in dealing with f -electrons in Gd with which experiments were carried out [8,9], we replace Gd with isovalent La which would behave similarly to Gd in the current situation. The local density approximation within the pseudopotential formalism [16] is employed and a functional form developed by Perdew and Zunger [17] is used for the exchange-correlation energy of electrons. Ultrasoft pseudopotentials [18] are used to lower the energy cutoff down to 25 Ry. This accelerates computational speeds significantly in systems including a large vacuum space. All pseudopotentials are generated by solving relativistic Schrödinger equations for neutral atoms. For La, we treat 5s and 5p semicore states as valence electrons because the interaction between them and the low-lying states of the fullerene is substantial [19].

Fullerenes are repeated along the direction of the nanotube with a center-to-center distance of 12.7 Å, to be commensurate with the periodicity of the (17,0) nanotube. As a result, the minimum atom-atom separation between neighboring fullerenes is 5.0 - 5.5 Å, implying that the electronic states from different fullerenes interact very little. In Fig. 1, unit cells of two representative models are shown. The lateral (xy) dimension of a tetragonal supercell is 20 Å × 20 Å with a tube separation of 6.8 Å. The resulting vacuum space is big enough to avoid the interaction between neighboring nanopeapods. Four \mathbf{k} -points are sampled along the one-dimensional Brillouin zone in the z direction. The atomic positions are relaxed until the Hellmann-Feynman forces are reduced to within 0.05 eV/Å.

III. RESULTS AND DISCUSSION

1. Relaxed Geometry

We find that La is in the most stable position in C_{60} when it is displaced 2.5 Å below the fullerene surface or

1.14 Å from the center of C_{60} . The total energy is lowered by 2.18 eV as La moves from the center of the fullerene to the most stable position. The azimuthal variation of the La position does not affect the total energy.

Among various isomers of C_{82} , we choose the one with C_{2v} symmetry since it is known to be most stable when three electrons are transferred from encapsulated lanthanides [20] to C_{82} . The orientation of C_{82} is chosen so that a hexagon right above the La atom faces the nanotube wall. The distance between the La atom and neighboring C atoms is 2.57 Å in the isolated C_{82} , in good agreement with the experimental value of 2.55 Å [21].

2. Encapsulation Energy

In Table 1, the reaction energies of the process (metallo)fullerene + nanotube → nanopeapod are presented. The encapsulation energy for $C_{60}@ (17,0)$ is -1.61 eV per unit cell, and this is larger than -0.51 eV for $C_{60}@ (10,10)$ [13]. Part of the difference can be attributed to a smaller inter-fullerene spacing used in Ref. 13. On the other hand, the reaction energy of $C_{82}@ (17,0)$ is 0.23 eV/(unit cell); *i.e.*, it is an endothermic process. This is due to the larger radius of C_{82} which forces the distance between the fullerene and the nanotube to be less than the equilibrium value (~ 3.3 Å). We also note that the La atom affects the reaction energy only by 0.1 eV.

3. Band Structure

In Fig. 2, we display the computed band structures of the model systems: (17,0), $C_{60}@ (17,0)$, $La@C_{60}@ (17,0)$, $C_{82}@ (17,0)$, and $La@C_{82}@ (17,0)$. The flat bands present for all nanopeapods are associated with molecular states of fullerenes. Their vanishing dispersions result from the small overlap between fullerene states, as mentioned above. We first note that various encapsulations do not change much of the original band gap of the (17,0) nanotube. Only increases of $\lesssim 0.1$ eV are found for $C_{82}@ (17,0)$ and $La@C_{82}@ (17,0)$, which are largely attributed to local deformations of the nanotube induced by C_{82} [22,23].

Table 1. Encapsulation energy (E_{enc}) for each model system. Energies are in eV.

Model	E_{enc} (eV/unit cell)
$C_{60}@ (17,0)$	-1.61
$La@C_{60}@ (17,0)$	-1.56
$C_{82}@ (17,0)$	+0.23
$La@C_{82}@ (17,0)$	+0.16

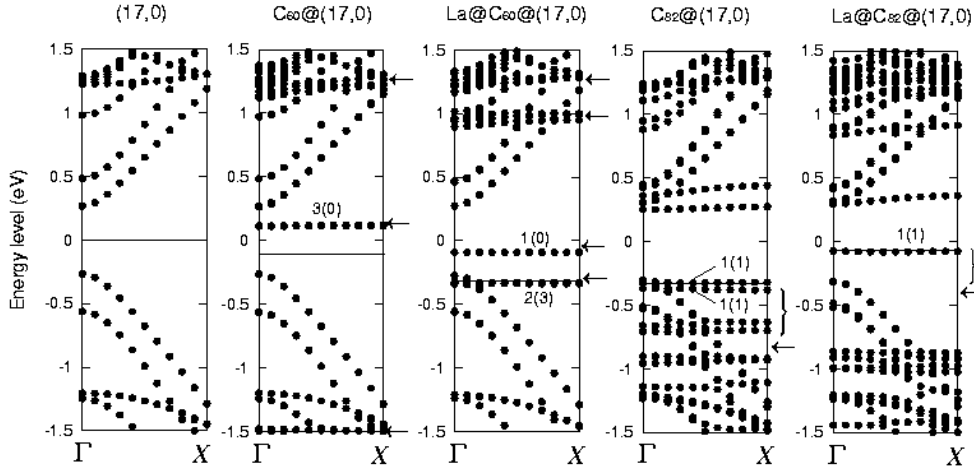


Fig. 2. Band structures of the model systems. The zero of the energy level is set to the middle of the nanotube gap while the Fermi level is indicated by a horizontal solid line. The two numbers assigned for molecular states around the Fermi level represent the degeneracy and the approximate occupation numbers. For example, ‘2(3)’ means that the state is doubly degenerate with three electrons occupying it. The arrows indicate the energy levels of the predicted molecular states (see text). For clarity, the predicted molecular states in $C_{82}@ (17,0)$ and $La@C_{82}@ (17,0)$ are marked only for those near the Fermi level. The curly brackets at the right side of band diagrams indicate the discrepancy between the predicted and the actual levels.

The gap state in $C_{60}@ (17,0)$ corresponds to the t_{1u} states of C_{60} . Upon encapsulation of the La atom, the threefold degeneracy of the t_{1u} states is lifted into 2+1 since the La atom relaxed into an off-center position breaks the inherent symmetry of an isolated C_{60} . Three electrons are transferred from the La atom to the doubly degenerate states of C_{60} . This band is close to the edge of the valence band, leaving a small hole pocket in the valence band of the nanotube. On the other hand, the encapsulation of the La atom into C_{82} significantly changes the fullerene states and it is difficult to make one-to-one mapping between flat bands in $C_{82}@ (17,0)$ and $La@C_{82}@ (17,0)$. While hole-type doping is found for $C_{82}@ (17,0)$, a partially occupied gap state in $La@C_{82}@ (17,0)$ is in the middle of the conduction and the valence bands of the nanotube. This is consistent with the experiment in Ref. 9 where an ambipolar character was found for nanopapods incorporating $Gd@C_{82}$.

4. Fermi-level Alignment

In the above, the band structures of nanopapods were found to strongly reflect the molecular states of the fullerene. This poses an intriguing question as to whether one can predict the band structure of the nanopapod simply by combining each band of the constituent. To get an answer to this, we carry out separate calculations for the (17,0) nanotube and for the fullerenes and overlay the fullerene band on top of the nanotube band. When superposing band structures, it is essential to match the vacuum level (ϵ_{vac}) of each system. The vacuum level is taken to be the value of the self-consistent Kohn-Sham (KS) potential averaged over a plane in between two

Table 2. Convergence of the work function ($\epsilon_{vac} - \epsilon_F$) with respect to the lateral dimension of the supercell (L). The unit of the work function is eV.

$L(\text{\AA})$	V_{full}	$V_{full} - V_{XC}$
20	3.60	4.54
30	3.84	4.54
40	3.93	4.55

neighboring nanotubes. The determination of a vacuum level in the presence of a nanotube is known to be difficult due to the slow decay of the electronic density [24]. We find that this problem can be alleviated if the exchange-correlation potential is omitted in averaging the potential. This is reasonable, at least within the local density approximation, since the exchange-correlation potential in the far-out region should go to zero eventually as the electron densities decay.

In Table 2, the work functions of a (17,0) nanotube is presented with respect to the lateral dimension of the supercell. We define the work function by $\epsilon_{vac} - \epsilon_F$ where the Fermi level ϵ_F is set to the middle of the band gap and the vacuum level ϵ_{vac} is measured by averaging the KS potential (see above). It can be seen that the work function computed with the full potential converges very slowly as a function of the cell dimension while that evaluated by excluding the exchange-correlation part is already saturated at 20 \AA . The computed work function of the nanotube (4.55 eV) is close to the experimental work function of graphite (4.5 eV).

Now that the vacuum level can be precisely estimated, one can construct the band structure of the whole system by matching their vacuum levels. We first apply

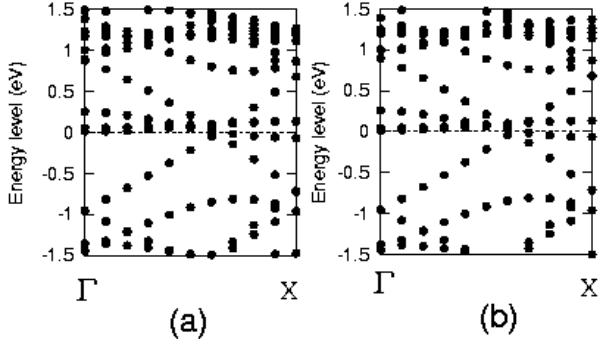


Fig. 3. Electronic structure of $C_{60}@ (10,10)$: (a) the band structure of the whole system and (b) the band structure constructed by overlaying two separate bands.

this scheme to $C_{60}@ (10,10)$ because its band structure was analyzed in detail in Ref. 13. Figure 3(a) is the band structure of $C_{60}@ (10,10)$ calculated with the same computational setup as in this study. It agrees very well with the result presented in Ref. 13. In Fig. 3(b), we overlay the band structure of the C_{60} array on that of the (10,10) nanotube. To recapitulate, the difference in work functions between two systems is considered in adjusting relative positions. It can be seen that Fig. 3(b) is a perfect match with Fig. 3(a). This implies that band mixing and charge redistribution between C_{60} and the nanotube are negligible. The multicarrier properties of $C_{60}@ (10,10)$ can thus be explained without resorting to the NFE character because it is absent in an isolated C_{60} . This conclusion is at variance with that in Ref. 13.

Now we apply the same procedure to semiconducting nanopeapods. The estimated locations of fullerene bands are indicated by the arrows on the right side of the band diagrams in Fig. 2. These arrows are pointing at the flat bands of $C_{60}@ (17,0)$ and $La@C_{60}@ (17,0)$ closely. This implies that charge transfer between the semiconducting nanotube and the fullerene is quite small, to be consistent with experiments [11,25]. The apparent up-shift by 0.3 – 0.5 eV for $C_{82}@ (17,0)$ and $La@C_{82}@ (17,0)$, on the other hand, will be explained below.

5. Charge Transfer

In the above, it was found that the band structures of $C_{82}@ (17,0)$ and $La@C_{82}@ (17,0)$ were not fully explained based on the separate bands alone and that the additional up-shift should be accounted for. To check the significance of atomic relaxations due to the small tube-fullerene separations, we calculate on the as-deformed (hollow) nanotube and $La@C_{82}$. The expected location of the flat band is almost unchanged, indicating that the atomic relaxation does not account for rigid shifts of molecular states. Instead, we find that the charge transfer from the nanotube to C_{82} or $La@C_{82}$ affects the band structure by resetting the work function of the fullerene.

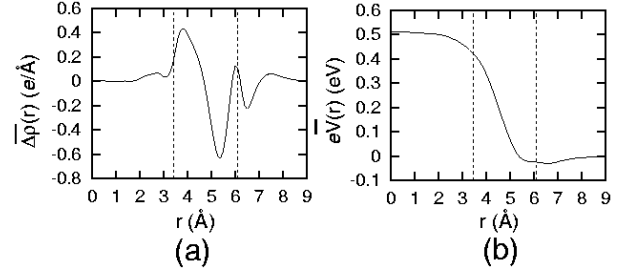


Fig. 4. Charge redistribution and resulting Coulomb potential averaged in the cylindrical coordinates with the z -axis along the carbon nanotube (CNT): (a) charge redistribution defined by $\overline{\Delta\rho}(r) = r \int \Delta\rho(r, z, \phi) dz d\phi$ where $\Delta\rho = \rho_{C_{82}@CNT} - \rho_{CNT} - \rho_{C_{82}}$ and (b) average of the electrostatic potential ($V_H(r)$) induced by $\Delta\rho$ defined by $\overline{V}(r) = \int V_H(r) dz d\phi / 2\pi L_z$ where L_z is the length of a supercell along the tube direction. The vertical dashed lines indicate the outermost positions of C_{82} and the (17,0) nanotube.

This is revealed in a detailed analysis of the charge distribution.

In Fig. 4, the cylindrical average of the changes in the electronic densities, $\Delta\rho (= \rho_{C_{82}@CNT} - \rho_{CNT} - \rho_{C_{82}})$, is presented. The electronic densities of separate systems are calculated by fixing the atomic coordinates to the positions of the relaxed nanopeapods. A substantial amount of charge redistribution is found between the nanotube and the fullerene. (See Fig. 4(a).) As a result, the electrostatic potential induced by $\Delta\rho$ is higher at the fullerene site (see Fig. 4(b)), and this in turn shifts the band structure of C_{82} rigidly by ~ 0.4 eV. This accounts for the actual up-shift of 0.3 eV found in Fig. 2. The same argument applies to $La@C_{82}@ (17,0)$. We also find that the up-shifts of the fullerene bands in $C_{60}@ (9,9)$ (compared to those in $C_{60}@ (10,10)$) shown in Ref. 13 originate from a similar charge redistribution. On the other hand, the analysis of $C_{60}@ (17,0)$ shows a small accumulation of charge in the interlayer space and the potential difference between the nanotube and C_{60} is less than 0.1 eV, to be consistent with the analysis given in the previous section.

IV. DISCUSSION

In Fig. 2, only p -type doping is observed. It is an interesting question whether n -type doping can also be achieved by simply changing the encapsulated material. This is unlikely to occur with the carbon-based fullerene unless a small-radius fullerene is used. We try an azafullerene ($C_{48}N_{12}$) [26] since the disruption of the π -bonding network by nitrogen atoms may lower the electron affinity of the fullerene. We find that the computed HOMO of $C_{48}N_{12}$ lies at -4.31 eV with respect to the vacuum level. If the band-combining scheme proposed above is followed, the HOMO of $C_{48}N_{12}$ will lie only

0.03 eV below the conduction band minimum of the nanotube. This suggests that the aza-fullerene can dope the nanotube with an *n*-type character at room temperature conditions.

In summary, we have carried out first-principles studies on semiconducting nanopeapods. We find that the nanotube is hole doped when La@C₆₀ and C₈₂ are inserted inside the (17,0) nanotube while the La@C₈₂@(17,0) is of an ambipolar character. The relative positions of the molecular states of C₆₀ and La@C₆₀ can be predicted if the vacuum level of the separate systems is matched. In the cases of C₈₂ and La@C₈₂, charge redistribution in the space between the nanotube and the fullerenes shifts the energy levels of the molecular states. We believe that these findings will be very useful in developing nanopeapods-based electronic devices.

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