Energetics and Electronic Structures of Encapsulated C_{60} in a Carbon Nanotube

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We report total-energy electronic structure calculations that provide energetics of encapsulation of C_{60} in the carbon nanotube and electronic structures of the resulting carbon peapods. We find that the encapsulating process is exothermic for the $(10, 10)$ nanotube, whereas the processes are endothermic for the $(8, 8)$ and $(9, 9)$ nanotubes, indicative that the minimum radius of the nanotube for the encapsulation is 6.4 Å. We also find that the C_{60}@$(10, 10)$ is a metal with multicarriers each of which distributes either along the nanotube or on the C_{60} chain. This unusual feature is due to the nearly free electron state that is inherent to hierarchical solids with sufficient space inside.

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Discoveries of fullerenes [1] and carbon nanotubes [2] have triggered a great expansion of both theoretical and experimental research on the materials. Local atomic structures of these new materials are not new but similar to that of graphite: The sp^2 hybridization renders a carbon atom threefold coordinated with its neighbors. Novelty lies in the global atomic network of the materials, however: The fullerene has a closed network with zero dimension, whereas the nanotube has a one-dimensional tubule network. This network topology decisively affects electronic properties of the materials [3–6], in a range from insulators to metals, and to superconductors under certain conditions [7], in their solid forms [8,9]. In the solid forms, fullerenes or nanotubes are constituent units which are weakly bound in some cases (the fcc C_{60}, the nanotube bundle [10], etc.) and strongly bonded in another (C_{60} polymers [11,12]). Therefore fullerenes and nanotubes may be regarded as natural super atoms which could be self-organized to become a unique class of solids with structural hierarchy. One of the prominent features of the hierarchical solids is the space between or within the constituent units. The space generates peculiar electron states called nearly free electron (NFE) states [13,14] whose amplitudes are not near atomic sites but in the spacious region of the hierarchical solids.

Recently, fullerenes *and* tubes were assembled: Transmission electron microscopy clearly shows that fullerenes (C_{60}, C_{70}, and C_{80}) are aligned in a chain and encapsulated in carbon nanotubes [15–20]. This eccentric structure, occasionally called a carbon peapod, is an ultimate version of the hierarchical solids consisting of fullerenes and nanotubes and exhibits unprecedented properties that we will discuss in this Letter.

We here report total-energy electronic-structure calculations performed for one-dimensional chains of C_{60} which are encapsulated in nanotubes. We take (n, n) nanotubes ($n = 8$, 9, and 10) as representatives and clarify salient characteristics of carbon peapods. We find that electronic structure of the peapod is not a simple sum of those of fullerenes and nanotubes. In the $(10, 10)$ peapod, a NFE state located between the tube and the fullerenes is found to work as an acceptor state, controlling relative locations of electronic levels and the Fermi energy ε_F. As a result, the $(10, 10)$ peapod is a metal with multicarriers each of which is distributed either on the nanotube or on the chain of the fullerenes. We also find that the incorporation of C_{60} into the $(10, 10)$ tube is exothermic: The energy gain in forming the peapod from C_{60} plus the empty $(10, 10)$ tube is 0.51 eV per C_{60}. On the other hand, the incorporation of C_{60} in the $(8, 8)$ and $(9, 9)$ nanotubes is found to be endothermic due to large structural deformation of both fullerenes and nanotubes upon incorporation. This indicates that the smallest radius of the nanotube which is capable of encapsulating C_{60} is about 6.4 Å (see below).

All calculations have been performed using the local-density approximation (LDA) in the density-functional theory [21,22]. For the exchange-correlation energy among electrons, we use a functional form [23] fitted to the Monte Carlo results for the homogeneous electron gas [24]. Norm-conserving pseudopotentials generated by using the Troullier-Martins scheme are adopted to describe the electron-ion interaction [25,26]. In constructing the pseudopotentials, core radii adopted for C $2s$ and $2p$ states are both 1.5 bohr. 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 of total energy to discuss the relative stability of various carbon phases [25]. We adopt a supercell model in which a peapod is placed with its nanotube wall being separated by 6.5 Å from another wall of an adjacent peapod. The conjugate-gradient minimization scheme is utilized both for the electronic-structure calculation and for the geometry optimization [27]. In the geometry optimization, we impose a commensurability condition between the one-dimensional periodicity of the atomic arrangements in the nanotube and that of the chain of C_{60}s. Consequently, the lattice parameter c become 9.824 Å along the tube direction which corresponds to the quadruple of the

periodicity of the armchair nanotube. Integration over one-dimensional Brillouin zone is carried out using the two k points.

Figure 1 shows total-energy minimized atomic geometries of C_{60} encapsulated in the $(8,8)$, $(9,9)$, and $(10,10)$ nanotubes. In the $(10,10)$ peapod, $C_{60}@(10,10)$, C_{60} inside and the nanotube outside almost keep their original shapes before encapsulation. The calculated distance between the wall of the $(10,10)$ nanotube and the nearest atom of C_{60} is 3.31 Å which is close to the interlayer distance of graphite (3.34 Å) or the inter-C_{60} distance in the fcc C_{60}. On the other hand, the space provided by the $(9,9)$ and the $(8,8)$ nanotube is insufficient for C_{60}: Both the tube and the fullerenes are substantially distorted in the $(9,9)$ peapod, $C_{60}@(9,9)$, and in the $(8,8)$ peapod, $C_{60}@(8,8)$. The fullerenes inside are elongated along the tube direction and the tube silhouette itself becomes undulating. The difference in diameter between the thinnest and thickest parts in the $(8,8)$ peapod is 0.6 Å which is visible in Fig. 1(c). The calculated distances between the wall of the nanotubes and the nearest atoms of C_{60} are 2.75 and 2.45 Å in $C_{60}@(9,9)$ and $C_{60}@(8,8)$, respectively.

These characteristics in the geometry are reflected in total energies of the peapods. The energy difference in the reaction,

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

is shown in Fig. 2. The reaction is exothermic for $n = 10$ and endothermic for $n = 9$ and 8: ΔE are -0.51 eV, 0.27 eV, and 15.19 eV for $n = 10$, 9, and 8, respectively. It is thus concluded that the $(10,10)$ nanotube is capable of accommodating C_{60} inside and the encapsulation is energetically favorable. Further, once C_{60} is trapped inside, the escaping process is unlikely even if ends of the tube are open or there are holes on sidewalls since the escaping barrier is at least more than 0.51 eV. On the other hand, it costs substantial energy for the $(8,8)$ and $(9,9)$ nanotubes to accommodate C_{60}. The energy cost may be reduced when we release the commensurability condition on the periodicity. Yet we provisionally conclude that the encapsulation process is unlikely for the $(8,8)$ nanotube. We here consider only armchair nanotubes. There are indeed chiral nanotubes with a variety of radii. From the present calculations it is clear that the tube-C_{60} interaction in the stable peapod is not due to chemical bonds. Hence from Fig. 2, we argue that the minimum radius of the nanotube for the encapsulation of C_{60} is about 6.4 Å.

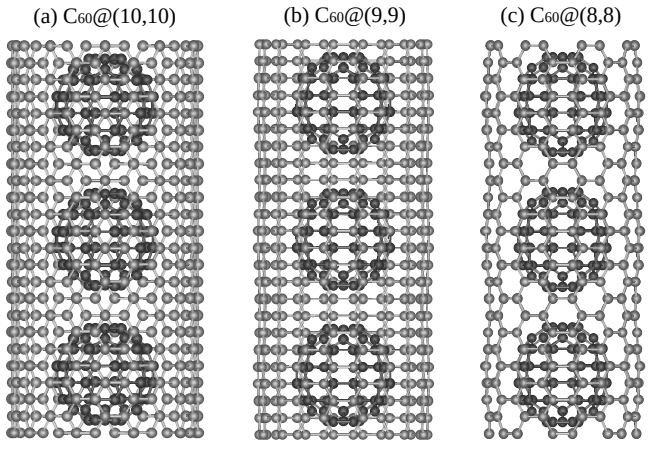

FIG. 1. Total-energy optimized geometries of C_{60} encapsulated in (a) the $(10,10)$, (b) the $(9,9)$, and (c) the $(8,8)$ nanotubes. Distances between C_{60}s are 3.14, 3.15, and 2.45 Å, for $(10,10)$, $(9,9)$, and $(8,8)$ peapods, respectively.

Electronic energy bands for the $(10,10)$, the $(9,9)$, and the $(8,8)$ peapods are shown in Figs. 3(a), 3(b), and 3(c), respectively. In an isolated C_{60}, there are the fivefold degenerate highest occupied h_u state and the threefold degenerate lowest unoccupied t_{1u} state. In the fcc C_{60}, both h_u and t_{1u} show the dispersion of $\sim$0.6 eV [3] and become valence and conduction bands, respectively. The energy gap remains finite and is about 1 eV [3]. As for the (n,n) nanotube, there are two energy bands near Fermi energy, and the two bands cross with ε_F at $k \simeq 2\pi/3$ of Brillouin zone [5]. Therefore it may be expected in $C_{60}@(n,n)$ that the two bands originated from the nanotube cross ε_F and are located in the gap of C_{60}, and that the peapod is metallic [28].

Yet Fig. 3(a) clearly shows a new feature that is missing in the discussion above. Four bands cross the Fermi level in the $(10,10)$ peapod, $C_{60}@(10,10)$: Two of them have large linear dispersion, keeping the character of the π orbitals on the nanotube, whereas the other two have less dispersion similar to the π state on the C_{60} chain. It is found that the latter two bands keep the character of the t_{1u} state of C_{60}. The $(10,10)$ peapod is thus a metal with

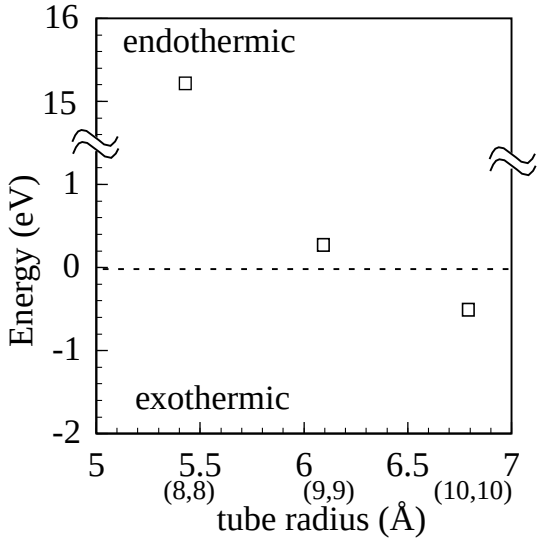

FIG. 2. Reaction energies ΔE (see text) per C_{60} in the encapsulation reaction for the $(8,8)$, $(9,9)$, and $(10,10)$ nanotubes. The energy approaches zero with increasing radius when we place C_{60} at the center of the tube. A simple linear interpolation shows that the reaction energy cross zero at the tube radius of 6.4 Å.

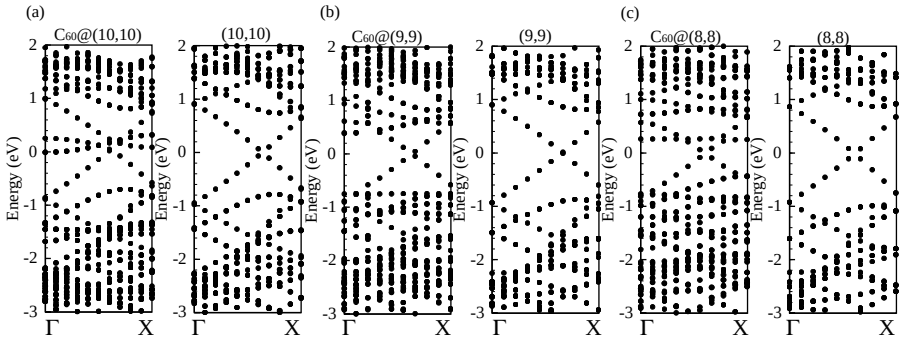

FIG. 3. Energy band structures of encapsulated $C_{60}@(n,n)$ and of isolated (n,n) nanotube. (a) $n = 10$, (b) $n = 9$, and (c) $n = 8$. Energies are measured from the Fermi level energy ε_F.

multicarriers, each of which distributes mainly either on the tube or on the C_{60} chain. On the other hand, energy bands of the $(8,8)$ and $(9,9)$ peapods do not exhibit such a feature [Figs. 3(b) and 3(c)]. Only two bands which have π character of the nanotube cross the Fermi level. In the $(8,8)$ peapod, structural distortion is so substantial that the resulting energy bands are not the sum of electron states of the constituent units. However, the energy bands of the $(8,8)$ and $(9,9)$ peapods are understandable in terms of the electron states of the constituents before the encapsulation plus the effects of the atomic distortion. The $(8,8)$ and $(9,9)$ peapods are metals and, in sharp contrast to the $(10,10)$ peapod, the charge density at ε_F distributes only along the walls of the nanotubes.

The difference in energy bands between the $(10,10)$ peapod and the $(8,8)$ and $(9,9)$ peapods is attributed to the space inherent to the hierarchical solids, as we explain below. Figure 4(a) shows electron charge density of the $(10,10)$ peapod, $C_{60}@(10,10)$. We observe the low charge density between the C_{60} and the nanotube, which indicates that the constituent units are bound weakly as in the fcc C_{60} or in the nanotube bundle. The peapod, $C_{60}@(n,n)$, has certainly the hybrid bonding networks with mixed dimensionality. When we carefully examine the charge density, an important role of the NFE state is elucidated. In Fig. 4(a), the difference between the charge density of $C_{60}@(10,10)$ and the sum of the charge densities of the nanotube and of the C_{60} chain is also shown. It is clear that electrons are transferred mainly from π orbitals of the nanotube to the space between the tube and C_{60}: The distribution of the electron rich region $(\Delta\rho^-)$ is similar to that of the NFE state. The energy level of the NFE state is generally located at a couple of eV above ε_F in nanotubes [14]. This state is still above ε_F even in $C_{60}@(10,10)$. The hybridization between the NFE state and the π and σ orbitals of C_{60} is, however, substantially induced upon encapsulation of the fullerenes in the tube. The hybridization occurs not with particular states of an isolated C_{60} but with most π and σ orbitals. Analysis of wave functions of the Kohn-Sham orbitals in a range of $-4 \sim 3$ eV in $C_{60}@(10,10)$ confirms this situation. As a result of this, most of the electron states originated in p orbitals of C_{60} shift downward upon encapsulation. These downward shifts of C_{60} states render the peapod, $C_{60}@(10,10)$, a metallic system with different characters of multicarriers, as is shown in Fig. 3(a). The electronic structure of the $C_{60}@(10,10)$ obtained by using the generalized tight-binding model does not show these downward shifts [26]. Although the model used reproduces the LDA σ and π states very well, it cannot describe the NFE state.

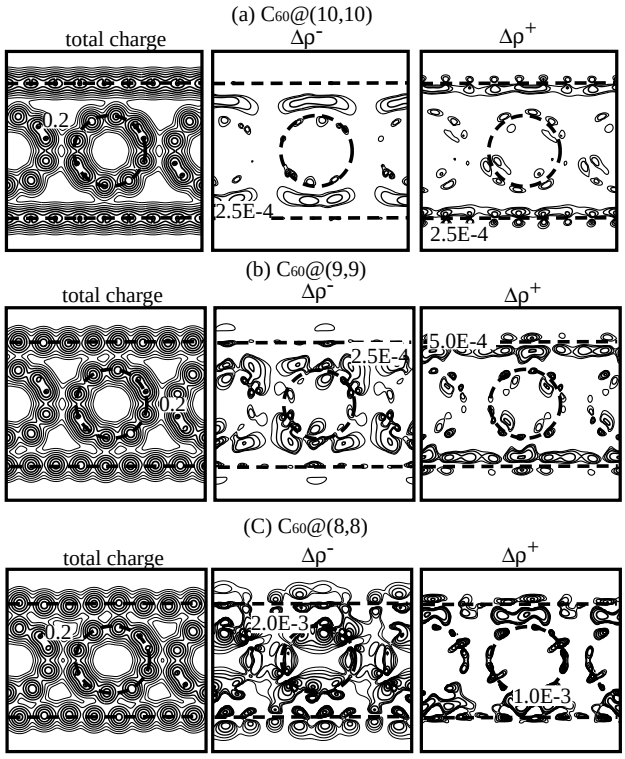

FIG. 4. Contour plots of the total valence charge density of $C_{60}@(n,n)$. (a) $n = 10$, (b) $n = 9$, and (c) $n = 8$. The contour plot of more negatively charged (electron rich) area, $\Delta\rho^-$, and that of the more positively charged, $\Delta\rho^+$, than a simple sum of two self-consistent charge densities of the tubes and C_{60} are also shown. Each contour represents twice (or half) the density of the adjacent contour lines. The values shown in figures are in units of $e/(\text{a.u.})^3$.

The charge densities of the thinner peapods are quite different from that of $C_{60}@(10,10)$ [Figs. 4(b) and 4(c)]. We certainly observe charge redistribution upon encapsulation: Electrons are transferred from π orbitals of the nanotube to the spacious region inside the tube and around the fullerenes. Yet no single specific state such as the NFE state is responsible for this charge transfer. This is because the space between the constituents in the $(9,9)$ and $(8,8)$ peapods is not sufficient to generate the NFE state located at a couple of eV near ε_F: Probably the NFE state is above the vacuum level. In this case, relative location of electron states originating from the nanotube and from the C_{60} is essentially unchanged by the encapsulation. The resulting energy bands are thus given in Figs. 3(b) and 3(c). When the NFE state appears in a suitable energy range as in $C_{60}@(10,10)$, it selectively hybridizes with p orbitals of C_{60} and hereby produces the interesting variation of energy bands at ε_F. The space inherent to the hierarchical solids thus controls the electron states of $C_{60}@(n,n)$.

One-dimensional conductors are generally expected to show the metal-insulator transition associated with lattice distortion (Peierls transition [29]). An earlier theoretical calculation [30] shows that the nanotube itself is robust against the Peierls instability. It is thus expected that the metallic nature of $C_{60}@(8,8)$ and $C_{60}@(9,9)$ is preserved. In $C_{60}@(10,10)$, however, some carriers are distributed along the chain of C_{60}, leading to displacements of C_{60} molecules. The calculated energy bands of $C_{60}@(10,10)$ near ε_F in Fig. 3(a) show that the filling is incommensurate: Thus incommensurate charge density waves are generally expected. Since the space is decisive to control energy bands, however, we expect that the filling is sensitive to the radius of the encapsulating nanotube. Hence displacements of fullerenes in peapods may exhibit variation depending on the tube radii and, in other cases, on sizes of fullerenes. Some experimental images by the transmission electron microscope [15–18] indeed show dimerization of C_{60} molecules in the peapods. This might be due to the Peierls-type transition. Even in this case, $C_{60}@(10,10)$ is still a metal but the state along the wall of the nanotube is responsible for the metallic nature.

In summary, we have found the peapod $C_{60}@(10,10)$ is stable and the reaction of the encapsulation of C_{60} in $(10,10)$ nanotube is exothermic with the energy gain of 0.51 eV. We have also evaluated that the minimum radius of the nanotube which is capable of encapsulating C_{60} is 6.4 Å. We have also found that the peapod $C_{60}@(10,10)$ is a metal with multicarriers each of which distributes either along the nanotube or on the fullerenes. This unusual electronic structure is due to the space which generates the nearly free-electron states inherent to the hierarchical solids.

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