

## Semiconducting form of the first-row elements: $C_{60}$ chain encapsulated in BN nanotubes

Susumu Okada,<sup>1</sup> Susumu Saito,<sup>2</sup> and Atsushi Oshiyama<sup>1</sup>

<sup>1</sup>*Institute of Physics, University of Tsukuba, Tennodai, Tsukuba 305-8571, Japan*

*and Center for Computational Physics, University of Tsukuba, Tennodai, Tsukuba 305-8577, Japan*

<sup>2</sup>*Department of Physics, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152-8551, Japan*

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We report first-principles total-energy electronic-structure calculations that provide energetics of encapsulation of  $C_{60}$  in nanotubes consisting of boron and nitrogen atoms and electronic structures of resulting “BNC peapods.” We find that the encapsulating process is exothermic for (10,10) and (9,9) nanotubes. The energy gain upon the encapsulation is larger than that for carbon peapods, so that the BN nanotube is a promising candidate to accommodate the fullerenes inside. The material is predicted to be a new form of ternary semiconductor with interesting structural hierarchy.

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During this decade, important new forms of carbon, i.e. fullerenes<sup>1,2</sup> and carbon nanotubes,<sup>3</sup> have been synthesized. These discoveries have triggered many theoretical and experimental studies on these materials. Novelty of carbon nanostructure materials lies in the global atomic network and structural hierarchy: The fullerene has a closed network with zero dimension, whereas the nanotube has a one-dimensional tubule network. This network topology governs electronic properties of the materials<sup>4-7</sup> being semiconductors, metals, and superconductor<sup>8</sup> under certain conditions.<sup>9,10</sup> In the solid forms,<sup>2,11</sup> the fullerenes and nanotubes are constituent units weakly bound each other. Thus they are regarded as superatoms which are assembled into infinite numbers of unique classes of solids with structural hierarchy. Recently interesting form of solid carbon has been synthesized, in which the fullerenes are aligned in a chain and encapsulated in carbon nanotubes.<sup>12-16</sup> The unusual structure occasionally called “carbon peapods” is another version of hierarchical solids which consist of both fullerenes and carbon nanotubes as constituent units. Their electronic structures near the Fermi level are controlled by the inter-unit space and the distribution of the nearly free electron state (NFE)<sup>17</sup> whose amplitude is not near atomic sites but in the spacious region of the hierarchical solids.<sup>18</sup>

On the other hand, similar tubular forms of honeycomb networks consisting of boron and nitrogen atoms have been already synthesized: Multi-walled BN nanotubes<sup>19</sup> and single-walled BN-nanotubes<sup>20,21</sup> have been reported. In sharp contrast to the carbon nanotubes, the single-walled BN nanotubes are insulating with large energy gap<sup>22,23</sup> in accordance with the fact that the honeycomb sheet of BN is insulating with large energy gap.<sup>24,25</sup> Moreover, experimental images by the transmission electron microscope show self-assemblages of multi-walled BN nanotubes into bundles.<sup>26</sup> The BN nanotubes are also regarded as constituent units of hierarchical solids as in the case of carbon nanotubes. Therefore, it is possible to design compounds with a unique structural hierarchy consisting of different superatomic species. The  $C_{60}$  chain encapsulated in the BN nanotube is such an example that is expected to exhibit interesting variation of the electronic structure due to the inter-unit interaction in the hierarchical solid.

We here report total-energy calculations performed for one-dimensional chains of  $C_{60}$  which are encapsulated in BN nanotubes. We take (n,n) BN nanotubes ( $n=9$  and 10) and clarify salient characteristics of the BNC peapods. We find that the incorporation of  $C_{60}$  into both BN tubes is exothermic: The energy gains on formation of the (10,10) and (9,9) peapods are 1.3 eV and 0.1 eV per  $C_{60}$ . Furthermore, the activation barriers on sliding and rotating motions of the  $C_{60}$  within the BN tube are about 40 and 20 meV, respectively. The electronic structure of the BNC peapods is found to be semiconductor in which the lowest conduction band is  $t_{1u}$  band of the  $C_{60}$  chain and the top of valence band possesses  $h_u$  character of the  $C_{60}$ , while the highest-occupied states of BN tube are also found to reside in the same energy region as the  $C_{60} h_u$  states.

All calculations have been performed using the local-density approximation (LDA) in the density-functional theory.<sup>27,28</sup> For the exchange-correlation energy among electrons, we use a functional form<sup>29</sup> fitted to the Monte Carlo results for the homogeneous electron gas.<sup>30</sup> Norm-conserving pseudopotentials generated by using the Troullier–Martins scheme are adopted to describe the electron-ion interaction.<sup>31,32</sup> The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 50 Ry which gives enough convergence of relative total energies of carbon-related materials<sup>31</sup> and  $h$ -BN.<sup>33</sup> We adopt a supercell model in which a peapod is placed with its nanotube wall separated from other walls of an adjacent peapods by 6.5 Å. The conjugate-gradient minimization scheme is utilized both for the electronic-structure calculation and for the geometry optimization.<sup>34</sup> 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  $c$  is 9.97 Å along the tube direction which corresponds to the quadruple of the periodicity of the armchair nanotube. The lattice parameter  $c$  is fixed during the structural optimization. Furthermore, for the initial geometries, we assume that the walls of the BN tube and  $C_{60}$  are partially arranged in AB-stacking structure. Integration over one-dimensional Brillouin zone is carried out using the two  $k$  points.

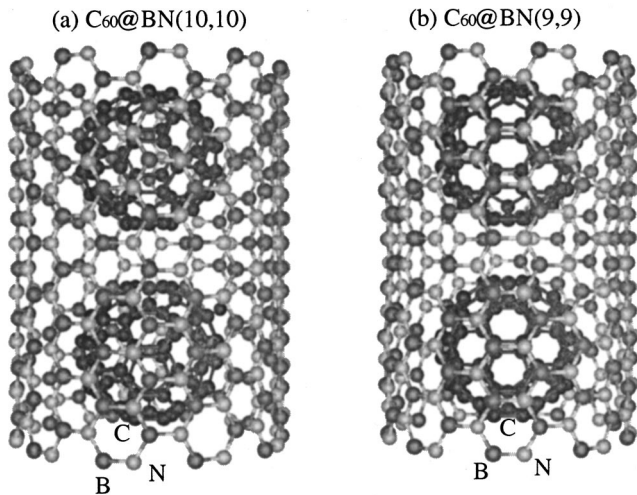


FIG. 1. Optimized geometries of the  $C_{60}$  chain encapsulated in (a) the (10,10) and (b) the (9,9) BN nanotubes. Distances between  $C_{60}$ s are 3.44 Å and 3.00 Å for (10,10) and (9,9) peapods, respectively. Solid, pale shaded, and dark shaded circles denote C, N, and B atoms, respectively.

Figure 1 shows optimized atomic geometries of  $C_{60}$ s encapsulated in the (9,9) and (10,10) BN nanotubes. Since the bond length of the  $h$ -BN (1.44 Å) is slightly longer than that of the graphite (1.42 Å), an inner space provided by these BN tubes may be sufficient to accommodate the  $C_{60}$ . Actually, the structural deformations of both tubes and  $C_{60}$  due to the encapsulation are found to be smaller than those in the carbon peapods. On the other hand, the isolated BN nanotube itself exhibits buckling on their circumference:<sup>35</sup> Each B atom forms small facet with its adjacent three N atoms due to the difference of the atomic species. Therefore, the walls of optimized BN nanotubes are found to be slightly undulating, even though the  $C_{60}$ s are not incorporated.

The characteristics in the geometry are reflected in total energy of the BNC peapods. The energy difference ( $\Delta E$ ) on the reaction, which is given by  $BN(n,n) + C_{60} \rightarrow C_{60}@BN(n,n) - \Delta E$ , is listed in the Table I together with the energy differences on the same reaction for C peapods. The reaction is exothermic for both  $n=9$  and  $n=10$ :  $\Delta E$  are  $-0.12$  eV and  $-1.27$  eV for  $n=9$  and 10, respectively. Thus the both BN nanotubes, (9,9) and (10,10), are capable of accommodating the  $C_{60}$ s inside and the encapsulation is

TABLE I. Reaction energies  $\Delta E$  (see text) per  $C_{60}$  in the encapsulation reaction for the (9,9) and (10,10) BN nanotubes (BN-NT) and for the (8,8), (9,9), and (10,10) carbon nanotubes (C-NT).

	$C_{60}@$ (10,10)	$C_{60}@$ (9,9)	$C_{60}@$ (8,8)
BN-NT	-1.267	-0.118	-
C-NT	-0.508	0.273	15.19

energetically favorable. As shown in Table I, the energy gains upon the encapsulation of  $C_{60}$ s into BN nanotubes are larger than those into carbon nanotubes by about 0.7 eV/ $C_{60}$  for (10,10) tube and 0.4 eV/ $C_{60}$  for (9,9) tube. Therefore, it can be concluded that the BNC peapods are more energetically favorable than the C peapods. Further, once the  $C_{60}$ s are trapped inside the (10,10) BN tube, escaping process is unlikely to take place even if the tubes possess open end or the defects on their side wall, because the escaping barrier is more than at least 1.2 eV per  $C_{60}$ . On the other hand, the energy barriers for the diffusion of  $C_{60}$  calculated for (10,10) peapods is less than about 0.042 eV/ $C_{60}$  which is considerably smaller than that of the escaping barriers [Fig. 2(a)]. Also the energy barrier for the rotation of  $C_{60}$  inside the (10,10) BN tube is about 0.020 eV per  $C_{60}$  which is the same order with the diffusion barrier inside the tube [Fig. 2(b)]. Therefore, the  $C_{60}$ s encapsulated in the (10,10) or larger BN tube may be almost freely sliding and rotating inside the tube at room temperature.

Electronic energy bands of  $C_{60}$  encapsulated in (9,9) and (10,10) BN nanotubes are shown in Figs. 3(a) and (b), 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 solid, both  $t_{1u}$  and  $h_u$  states possess the dispersion of about a half eV and become valence and conduction bands, respectively. Its energy gap is about 1 eV. In the BN nanotubes, since the  $h$ -BN sheet is insulator with direct energy gap of about 5 eV at the  $K$  point,<sup>24,36</sup> the  $(n,n)$  BN tubes are also insulator with large energy gap: The top of the valence band is at the middle of one-dimensional Brillouin zone whereas the bottom of conduction band is at the  $\Gamma$  point possessing the NFE character whose distribution is concentric with the nanotube. In the BNC peapods, the  $t_{1u}$ ,  $t_{1g}$ , and  $h_g$ , which are the lowest, second lowest, and third lowest conduction bands of solid  $C_{60}$ , are found to emerge at the energy gap of the BN tubes

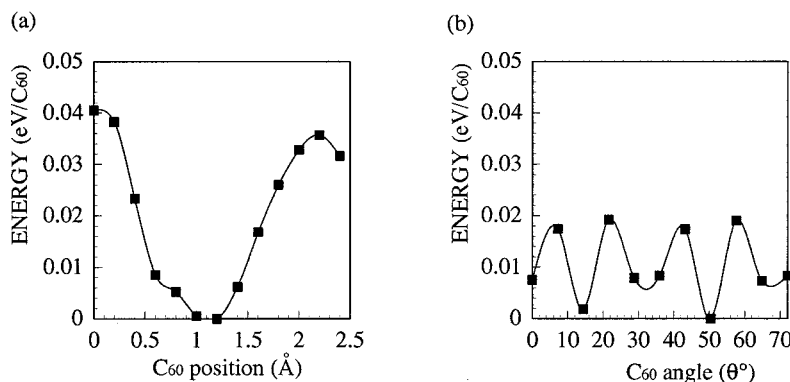


FIG. 2. (a) Total energy of the (10,10) BNC peapod as a function of the position of the  $C_{60}$  molecule inside the tube. Center of mass of the  $C_{60}$  is always on the tube axis. (b) Total energy of the (10,10) BNC peapod as a function of the rotational angle of the  $C_{60}$ .

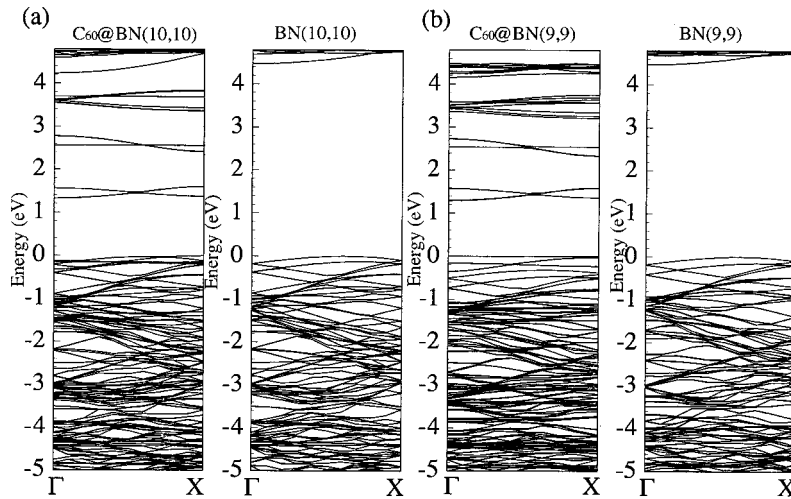


FIG. 3. Energy band structure of encapsulated  $C_{60}@BN(n,n)$  and isolated  $(n,n)$  BN nanotube for (a)  $n=10$  and (b)  $n=9$ . Energies are measured from the top of the valence band.

(Fig. 3). Furthermore, the top of the valence band also has  $\pi$  character of the  $C_{60}$ , so that the energy gap is opened between the  $h_u$  and  $t_{1u}$  states of  $C_{60}$ . Thus, as far as thermal processes involving the electron states around the gap are concerned, the BNC peapods are practically regarded as the one-dimensional semiconductor consisting of the  $C_{60}$  chain. In particular, the lower conduction band is totally originated from the electron states of the  $C_{60}$  chain.

The characteristics of the electronic structure of the peapods imply that the one-dimensional  $\pi$  electron system on the  $C_{60}$  chain is expected to take place by injecting the electrons into the  $t_{1u}$  and  $t_{1g}$  states. In this case, the material may exhibit superconductivity with a strong anisotropy. Otherwise, the metal-insulator transition may take place associated to the lattice distortion (Peierls transition<sup>37</sup>). The injected electrons are distributed on the one-dimensional  $C_{60}$  chain and induce the displacement of  $C_{60}$  molecules. Furthermore, the encapsulated  $C_{60}$  may show a rich variety of their displacement, such as dimerization or trimerization, depending on the number of electrons injected into the systems.

In the case of C peapods,  $C_{60}@BN(10,10)$ , the electron states possessing  $\pi$  character of the  $C_{60}$  were found to shift downward significantly, and the  $t_{1u}$  states cross the Fermi energy.<sup>17</sup> In the  $C_{60}@BN(n,n)$ , similar downward shift of the electron states of  $C_{60}$  might also take place due to the hybridization between the  $\pi$  states of  $C_{60}$  and the NFE states of BN tube which are located at about 5 eV above the top of valence band. However, since the BN tube is an insulator with the large energy gap, the  $t_{1u}$  state does not cross the Fermi level even if the  $\pi$  states of  $C_{60}$  shift downward significantly.

The hybridization is elucidated by examining the charge density of the peapods. Figures 4(a) and (b) show the charge density of the  $BN(10,10)$  peapod,  $C_{60}@BN(10,10)$ , and that of the  $BN(9,9)$  peapod,  $C_{60}@BN(9,9)$ , respectively. We find low charge density between the BN nanotubes and  $C_{60}$ , which indicates that the constituent units are weakly bound as in the case of the solid  $C_{60}$ , the carbon peapods, and the bundle of nanotubes. Therefore, the BNC peapods certainly have the hybrid networks of different superatomic species with mixed dimensionality. When we carefully check the

charge density, we can clarify an important role of the NFE states. In Fig. 4(a), the difference between the charge density of the  $C_{60}@BN(10,10)$  and the sum of the self-consistent charge densities of the empty  $BN(10,10)$  nanotube and the isolated  $C_{60}$  chain,  $\Delta\rho = \rho_{\text{peapod}} - (\rho_{BN(n,n)} + \rho_{C_{60}})$ , is also shown. It is clear that the electrons are transferred mainly from the  $\pi$  orbitals of both the BN nanotube and  $C_{60}$  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 states as in the case of (10,10) carbon peapods. Similar charge redistribution is also found in the  $C_{60}@BN(9,9)$  [Fig. 4(b)]. In this case, the space between the BN tube and  $C_{60}$  is insufficient to render the complete distribution of NFE states. It is noteworthy that the NFE states are still located at about 5 eV or more above the valence band top and that the distribution

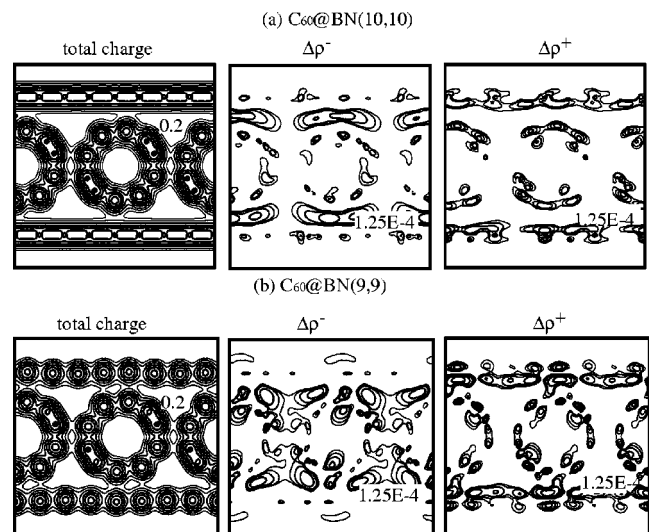


FIG. 4. Contour plots of the total valence charge density of  $C_{60}@BN(n,n)$ . (a)  $n=10$  and (b)  $n=9$ . The contour plot of more negatively charged (electron rich) area,  $\Delta\rho^-$ , and that of more positively charged,  $\Delta\rho^+$ , than a simple sum of two self-consistent charge densities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



is not the NFE states itself. However, the hybridization between the NFE state and the  $\pi$  and  $\sigma$  orbitals of  $C_{60}$  substantially induces the large energy gain upon the encapsulation of fullerenes in the BN nanotubes.

In the carbon peapods, it has been observed that the fullerenes encapsulated in the carbon nanotubes are rearranged and coalesce into longer capsules following exposure to electron beam.<sup>12,14,15</sup> Eventually, the capsules form another continuous nanotube inside of the outer nanotubes and the peapods become double-walled carbon nanotubes.<sup>12,14,15</sup> Thus, the similar reaction is expected to take place for the  $C_{60}$  chain within the BN nanotube. In the case, synthetic substances are double-walled nanotubes consisting of the outer BN nanotube and the inner carbon nanotube, and they might be a nanoscale coaxial cable or a conducting wire coated by the insulating film of the BN honeycomb sheet.

In summary, we have found that the BNC peapods are stable and that the reactions of the encapsulation of  $C_{60}$  in

(10,10) and (9,9) tubes are exothermic with energy gains of 1.27 eV and 0.12 eV per  $C_{60}$ . These energy gains are larger than those of the carbon peapods. We have also found that the BNC peapods are semiconducting with moderate energy gap. Since the lower conduction bands possess the  $\pi^*$  characters of  $C_{60}$ , i.e.,  $t_{1u}$ ,  $t_{1g}$ , and  $h_{1g}$ , electronic properties of the electron-doped peapods may exhibit strong one-dimensional character. Finally, hybridization between NFE states and  $\pi$  orbitals of  $C_{60}$  is also found as in the case of the carbon peapods.

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<sup>36</sup>The bottom of the conduction band of the h-BN sheet is at  $K$  point with unoccupied  $\pi$  character, while the NFE state which is distributed about 2–3 Å above and below the sheet is also found to emerge in the same energy region at the  $\Gamma$  point. In the GW calculation, the h-BN sheet has indirect gap between  $K$  and  $\Gamma$  points.<sup>25</sup> The bottom of conduction band possess the nearly free electron state character.  
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