Energetics and electronic structures of potassium-intercalated C_{60} peapods

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Total-energy electronic-structure calculations were performed to explore energetics and electronic structures of a one-dimensional array of C_{60} and potassium atoms encapsulated in metallic nanotubes. We find that the electron states of the potassium intercalated peapods depend on the number of potassium atoms intercalated. Intercalation induces substantial hybridization between π electron states of C_{60} and the nanotube. The local density of states around the Fermi level shows that the potassium intercalated C_{60}-peapod is a novel metal whose carriers are distributed on both the C_{60} and the nanotube.

Since the discovery of one-dimensional arrays of fullerenes encapsulated in nanotubes,[1] known as fullerene peapods, there have been a lot of experimental[2–6] and theoretical[7–9] works on this new form of a crystalline carbon. The structures of the peapods are characterized by an interesting combination of one- and zero-dimensional constituent units, i.e., carbon nanotubes and fullerenes. It has been shown that the multiplicity of the combination of the constituent units induces an interesting variety of electronic properties: The energy gap of peapods was found to depend not only on the encapsulated fullerene species but also on the space between the nanotube and the fullerenes.[8,9] Moreover, metallic nanotubes containing a C_{60} chain were found to be semimetals with multicarriers each of which is distributed either along the nanotube or on the C_{60} chain.[7] These facts suggest that intercalation of foreign atoms or molecules into peapods results in different electronic properties from those of the conventional fullerene compounds.[10–14] Several studies reported that the chemical doping of $FeCl_3$ or potassium atoms results in the injection of holes or electrons into peapods, respectively.[15–17] In the case of potassium intercalation, the atoms are accommodated not only in an intratube spacing but also in an intertube spacing of bundles of nanotubes. Indeed, recent high-resolution transmission electron microscopy (HR-TEM) experiments clearly demonstrated that the potassium atoms are located at the spacious regions surrounded by two C_{60}s and a wall of the nanotube.[18] Thus, alkali-intercalated C_{60}-peapod can be regarded as a novel fullerene-based conductor with a different dimensionality with respect to the conventional C_{60} fullerides, such as K_3C_{60}[10–14] and Na_2CsC_{60},[19,20] and is expected to be a stable alkali-intercalated fulleride due to their encapsulated structure.

The purpose of this work is to reveal the energetics of the encapsulation of potassium atoms into peapods and electronic structures of resulting K_xC_{60}-peapods ($x=1, 2, 3, 4, 6$, and 8). In this work, we take a peapod consisting of the C_{60} and the metallic (10,10) nanotube to study a possibility of a C_{60} conductor with different characteristics to the conventional C_{60} fullerides. Our first-principles total-energy calculations show that encapsulations are exothermic processes due to an ionic interaction between potassium atoms and the peapod in all the potassium compositions examined. The electronic structure does not exhibit a rigid band nature but

strongly depends on the number of potassium atoms intercalated: The energy level of t_{1u} states shifts upward and their width increases by increasing the number of potassium atoms. The calculated density of states at the Fermi level depends also on the potassium amount. The distribution of the wave functions indicates that substantial hybridization between the π states of C_{60} and the nanotube takes place. These results clearly indicate that the potassium-intercalated peapods are novel one-dimensional conductors in which the electrons are distributed both on C_{60} and nanotubes.

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 result 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] The valence wave functions are expanded by the plane-wave basis set with a cut-off energy of 50 Ry which is known to give enough convergence of total energy to discuss the relative stability of the various carbon phases.[7,25] 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 encapsulated C_{60}s and K atoms. Consequently, the lattice parameter c becomes 9.824 Å along the tube direction which corresponds to the quadruple of the periodicity of the armchair nanotube. Integration over the one-dimensional Brillouin zone is carried out using four k points.

Figure 1 shows the geometric structures of K_xC_{60}-peapods ($x=1, 2, 3, 4, 6$, and 8). The potassium atoms are located at about 2.5 Å above the wall of the nanotube, which is close to the spacing between the potassium and graphite layers in the graphite intercalation compound (K-GIC).[28] We first focus on the energetics of potassium intercalated C_{60}-peapods for different amounts of potassium atoms. The stability of K_xC_{60}-peapods is evaluated by calculating the energy difference of the following reaction:
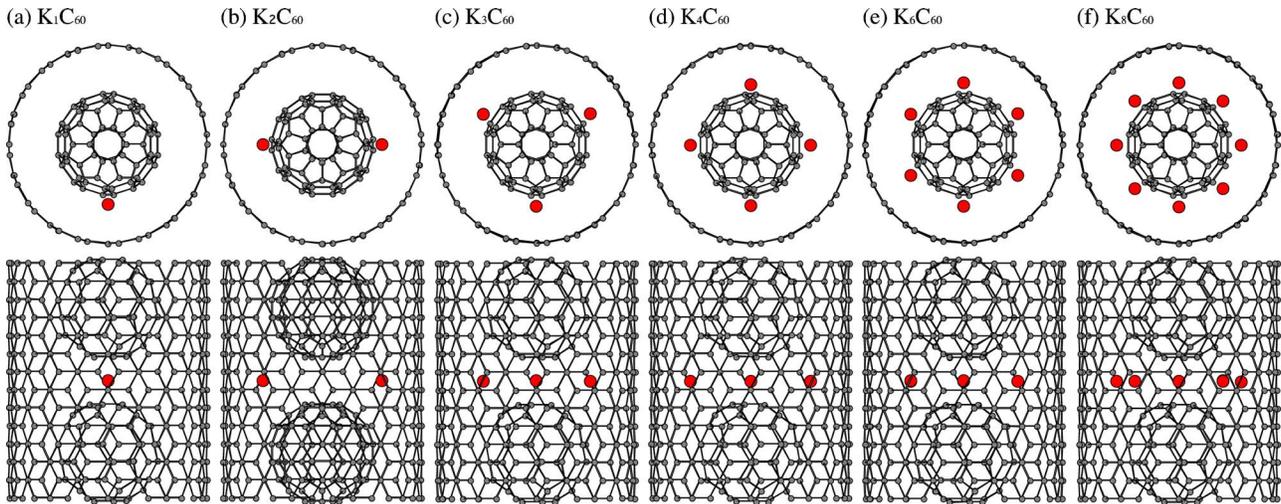
FIG. 1. (Color online) Top and side views of geometric structures of potassium intercalated C_{60}-peapods, (a) K_1C_{60}, (b) K_2C_{60}, (c) K_3C_{60}, (d) K_4C_{60}, (e) K_6C_{60}, and (f) K_8C_{60}. Gray (red) circles denote carbon and potassium atoms, respectively.

$$C_{60} @ (10,10)\text{tube} + x\text{K} \rightarrow K_xC_{60} @ (10,10)\text{tube} - \Delta E.$$
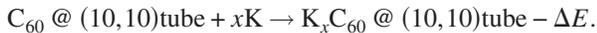
The total energy of the potassium atom is obtained as the total energy per atom in the bulk potassium crystal. The encapsulation process turns out to be exothermic for all the potassium compositions considered, as shown in Fig. 2. Thus, as in the case of the other potassium-intercalated carbon materials, e.g., K_3C_{60}, K_x-nanotubes, and K-GIC, potassium atoms are stabilized by encapsulation in the space inside the nanotube. Although the formation energy monotonically decreases with increasing the number of potassium atoms studied here, the formation energy per potassium atom has a minimum for the composition $x=3$. This result suggests that $x=3$ is a relatively preferable composition for peapods consisting of C_{60} and the (10,10) nanotube. For x greater than three, the Coulomb repulsive interaction between the potassium ions might lead to an increase in the energy cost for the encapsulation.

Figure 3 shows the electronic structures of the K_xC_{60}-peapods in terms of electronic energy band and density of states. The intercalation results in the charge transfer from the 4s electron of potassium atoms to the peapods, so
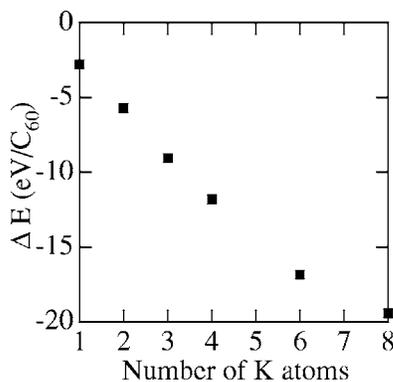
FIG. 2. Reaction energies ΔE (see text) in the intercalation reaction of the potassium atoms for the C_{60} chain encapsulated in (10, 10) nanotube.

that not only the t_{1u} states of C_{60} but also the π^* bands of the nanotubes cross the Fermi energy. We find that the electron states around the Fermi energy are remarkably modulated from that of the pristine peapods:[7] The t_{1u} and h_u states shift upward in energy by increasing the number of potassium atoms intercalated. We found that the magnitude of the shift of the bottom of the t_{1u} states to that of pristine phase is 0.32, 0.34, 0.44, 0.42, 0.55, and 0.47 eV for $x=1$, 2, 3, 4, 6, and 8, respectively. Thus, in sharp contrast to the pristine C_{60}-peapods, the t_{1u} states of the K_xC_{60}-peapods do not emerge near the crossing point of the two linear dispersion bands of the metallic nanotubes. The result interprets the recent photoemission spectroscopic experiment reported by Rauf *et al.*[29] In addition to the shift, the band width of the t_{1u} states is also found to increase with increasing the potassium intercalation. The calculated width of the t_{1u} band is 0.24, 0.25, 0.29, 0.36, 0.41, and 0.40 eV for $x=1$, 2, 3, 4, 6, and 8, respectively.

The modulation of the electron states of the peapods indicates that the substantial interaction takes place not only between C_{60}s but also between C_{60} and the nanotube. Indeed, in our previous calculations for pristine peapods,[7–9] it was shown that the t_{1u} band of C_{60} chains encapsulated in the nanotubes of which diameter is smaller than 13 Å shifts upward in energy compared with those encapsulated in the (10,10) or thicker nanotubes: For thin nanotubes, the inter-wall spacing between the C_{60} and the nanotube is insufficient to allow the t_{1u} states of C_{60} to be distributed in the space so that substantial interaction between the π states of the constituent units induces a large hybridization resulting in the upward shift of the t_{1u} state. In the K_xC_{60}-peapods, as shown in Fig. 3, the upward shift of t_{1u} states indicates that intercalation of potassium atoms extends the distribution of the π electron states of both the nanotubes and the C_{60}. The extended distribution of π electron states effectively decreases the inter-wall spacing between the constituent units so that a large hybridization takes place between π states in the units. The hybridization results in the upward shift and width increase of the t_{1u} band. This fact is corroborated by the analysis of the distribution of squared wave functions shown in
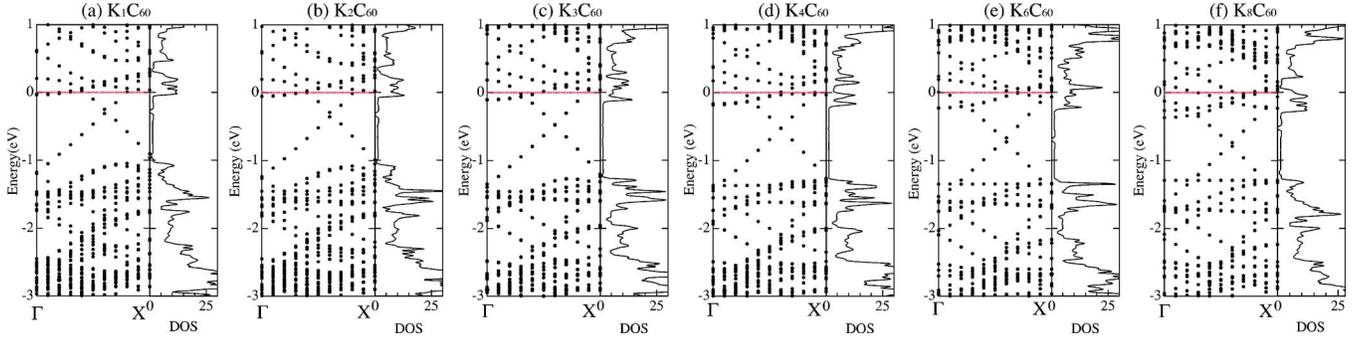
FIG. 3. (Color online) Electronic structures of potassium intercalated C_{60}-peapods, (a) K_1C_{60}, (b) K_2C_{60}, (c) K_3C_{60}, (d) K_4C_{60}, (e) K_6C_{60}, and (f) K_8C_{60}. Right and left panels of each figure are the electronic energy band and density of states (DOS), respectively. Energies are measured from the Fermi level energy E_F. Dotted vertical lines denote the Fermi level energy.

Fig. 4: It is found that the two of three t_{1u} states of K_3C_{60}-peapods, which are located at just below the Fermi energy at the Γ point, keep their π electron character of C_{60} [Figs. 4(a) and 4(b)]. In sharp contrast to these two states, the wave function of the highest branch of the t_{1u} band clearly exhibits a hybridized character between π states of C_{60} and the nanotube [Fig. 4(c)].

Calculated density of states (DOS) for potassium intercalated peapods are shown in the right panel of each electronic structure in Fig. 3. For the integration over the one-dimensional Brillouin zone (BZ), we use 20 k points in the first BZ. Since C_{60}s inside the nanotube are weakly bound to each other, the π electron states form narrow dispersion bands which result in substantial peaks in the DOS. Thus, the intercalation of potassium atoms results in a large DOS at the Fermi level [$N(E_F)$] similar to the case of the face-centered cubic phase of alkali metal intercalated C_{60}. The estimated values of $N(E_F)$ of the K_xC_{60}-peapods are 11.16, 9.06, 5.85, 4.07, 8.05, and 5.49 states per C_{60} for $x=1$, 2, 3, 4, 6, and 8, respectively, which are comparable to the alkali-metal-intercalated superconducting fullerides.[14] By reflecting a double-peak structure of the t_{1u} band, the $N(E_F)$ strongly depends on the number of potassium atoms intercalated. In K_xC_{60}-peapods with metallic nanotubes studied here, it should be noted that the number of potassium atoms is not identical to the number of electrons injected into C_{60}, because the two π^* bands of the metallic nanotubes with linear dispersion can accommodate electrons provided by potassium atoms. The number of electrons injected into C_{60} is estimated to be $0.9e$, $1.3e$, $1.8e$, $3.9e$, $4.7e$, and $5.5e$ for x $=1$, 2, 3, 4, 6, and 8, respectively. Hence the systems are candidates for a superconducting material possessing different dimensionality and alkali-atom composition from the conventional superconducting fullerides A_3C_{60}.
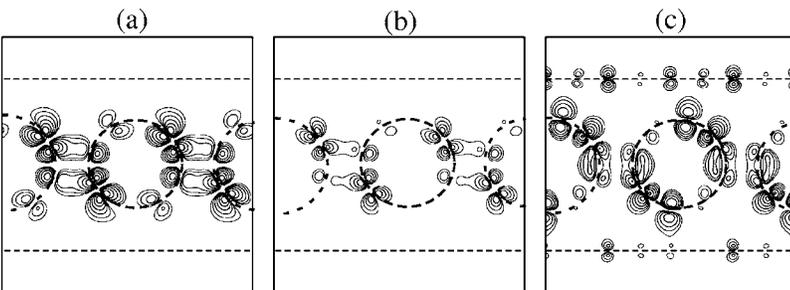
In Fig. 5, the local density of states near the Fermi level $\rho_{E_F}(\mathbf{r})$ of the K_xC_{60}-peapods are shown. It is defined by

$$\rho_{E_F}(\mathbf{r}) = -\frac{1}{\pi} \operatorname{Im} \sum_{n,\mathbf{k}} \int_{E_F-\Delta}^{E_F+\Delta} dE \frac{|\phi_{n\mathbf{k}}(\mathbf{r})|^2}{E - \epsilon_{n\mathbf{k}} + i\delta},$$

where $\Delta = 0.1$ eV which is the typical phonon energy in fullerides, and 4 k points in the one-dimensional BZ are taken for the k summation. The distribution clearly exhibits their π electron character in which electrons are located both on the nanotube and on the C_{60}. Hence, it is corroborated that a C_{60} chain encapsulated in a metallic nanotube with potassium atoms is a novel metal with multicarriers each of which possesses a different effective mass resulting in an interesting variety of conducting properties: Besides the carriers with light effective mass on the nanotubes, heavy carriers on C_{60} chains form additional conducting channels resulting in the modulation of the ballistic conducting properties of the pristine metallic nanotubes. Indeed, the recent experimental work indicated that the conducting properties of the peapods can be modulated by potassium doping.[29]

In summary, our calculations, based on the density functional theory, have clarified that intercalation of potassium atoms into the C_{60} chain encapsulated in the metallic nanotube results in a novel class of metallic fullerides with different dimensionality from those reported in previous works. We found that the encapsulation of potassium atoms is exothermic due to the substantial ionic interaction between potassium atoms and the peapod. It was clarified that the electronic structure of potassium intercalated peapods strongly depends on the number of potassium atoms exhibiting different characteristics to that of the face-centered-cubic phase of K_3C_{60}. A large hybridized character of t_{1u} states of K_xC_{60}-peapods exhibits that the intercalation of potassium

FIG. 4. Contour plots of the squared wave function at the Γ point of the t_{1u}-like states of K_3C_{60}-peapod. (a) The lowest, (b) the second lowest, and (c) the highest branches of the t_{1u}-like states. Each contour represents the twice (or half) of the density of the adjacent contour lines. The lowest values represented by the contour is 1.562×10^{-4} $e/(\text{a.u.})^3$. The dotted circle and lines denote the atomic positions of C_{60} and nanotube, respectively.
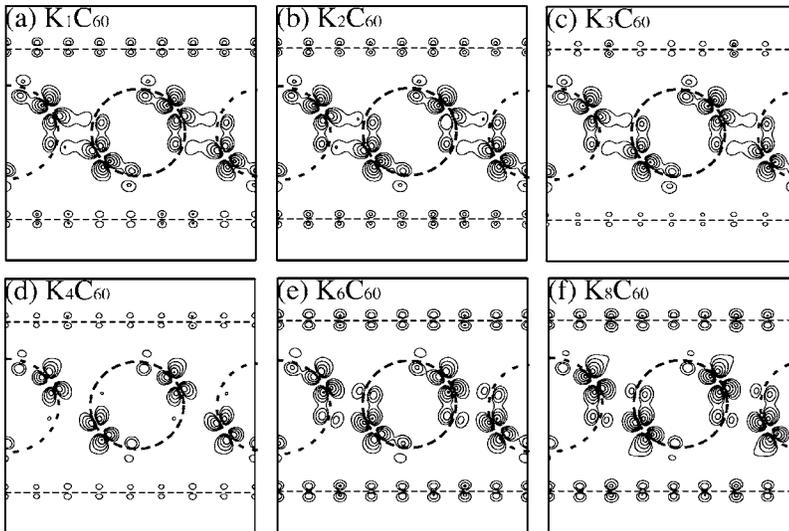
FIG. 5. Contour plots of the local density of states near the Fermi level ($\rho_{E_F}(\mathbf{r})$) of the K_xC_{60}-peapods, (a) K_1C_{60}, (b) K_2C_{60}, (c) K_3C_{60}, (d) K_4C_{60}, (e) K_6C_{60}, and (f) K_8C_{60}. Each contour represents the twice (or half) of the density of the adjacent contour lines. The lowest values represented by the contour is $6.25 \times 10^{-4} e/(\text{a.u.})^3$. The dotted circle and lines denote the atomic positions of C_{60} and nanotube, respectively.

atoms increases the interaction between π states of the C_{60} and nanotube. The local density of states around the Fermi level shows that the K_xC_{60}-peapods are metallic fullerides possessing different conducting properties from pristine nanotubes.

ACKNOWLEDGMENTS

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