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Metal-semiconductor and semiconductor-semiconductor transitions in carbon nanotubes induced by intercalating alkali atoms

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We show that the intercalating of alkali atoms with adequate concentration can transform a metallic single-walled carbon nanotube (SWCNT) into a semiconductor tube or a semiconductor SWCNT into a semiconductor tube with different band gaps due to a unique feature of the band structures in some SWCNTs as quasi-one-dimensional materials. As examples, we predict the intercalated structure Li_2C_{60} in the (5,0) tube to be a semiconductor while the pure (5,0) tube is a metal and the structure Li_2C_{112} in the (4,2) tube to be a semiconductor with a direct gap while the pure (4,2) tube has an indirect gap. Results of other alkali atoms intercalating in various carbon nanotubes show that this transition mechanism is quite general.

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Carbon nanotubes[1] have novel electronic properties attributed to their quasi-one-dimensional structures. The tubes can be either metals or semiconductors depending on their diameters and chiral vectors.[2–4] For the applications in nanodevices, nanotubes containing heterojunctions and metal-semiconductor junctions connected by two different types of carbon nanotubes were investigated.[5–8] Under pressure, carbon nanotubes could undergo metal-semiconductor transitions.[9–11] Meanwhile, atoms intercalating into carbon nanotubes can modify the electronic properties, which has attracted much attention.[12–23] As a kind of typical electron-donor dopant, alkali atoms can be intercalated into carbon nanotubes, which have been investigated experimentally[13–18] and theoretically.[19–23] For K-, Br-, and Cs-intercalated single-walled carbon nanotubes (SWCNTs),[13–17] the intercalating can enhance the conductance. Theoretical studies[19–21] show that the alkali atom intercalating shifts up the Fermi energy, which transforms a semiconductor tube into a metal tube when the bands are half-filled. However, is it possible for an atom intercalating to transform a metal tube into a semiconductor tube or a semiconductor tube into a semiconductor tube with different band gaps? If we can control the metal-semiconductor and semiconductor-semiconductor transitions with the concentrations of intercalating atoms, heterojunctions can be manufactured within a single tube by simply intercalating, while the same helicity remains in the tube.

In this paper, we show that intercalating of alkali atoms could transform a metal tube into a semiconductor tube or a semiconductor tube into a semiconductor tube with different band gaps due to a unique feature of band structures in some SWCNTs as quasi-one-dimensional materials. Let us first consider the band structures of pure carbon nanotubes. For the pure (5,0) carbon nanotube, there is a singly degenerate band near the Fermi energy in the band structure. In the segment (A to B) of this band as shown in Fig. 1(a), there is only one energy eigenvalue corresponding to a wave vector $\mathbf{k}$. This feature of band structure is due to the curvature effects of nanotubes with small diameters. This property of band structure exists not only in the (5,0) tube, but also in many nanotubes of other sizes and helicities, such as in the (4,2), (7,0) tubes shown in Figs. 1(b) and 1(c). The unit cell of the nanotubes can be changed by atoms intercalating. For example, if the unit cell of the nanotube is enlarged three times, then due to the band folding, this single energy band is folded to the boundary of the Brillouin zone. The energy degeneracy is generally eliminated by the structure perturbation due to the intercalating and a gap in the band structures will appear. When the electrons from dopant atoms fully fill in all the energy bands below the gap, the nanotube becomes a semiconductor. This metal-semiconductor transition needs two preconditions: One is the folding of a singly degenerate band in the band structures. The other is the filling of electrons in the energy bands below the gap. We show that through adequate intercalating of alkali atoms, the above two preconditions can be satisfied and the intercalating of alkali atoms will induce the metal-semiconductor and semiconductor-semiconductor transitions in some carbon nanotubes.

We have performed the calculations of total energies and band structures of alkali-intercalated SWCNTs using VASP (Vienna Ab initio Simulation Package).[24,25] The approach is based on an iterative solution of the Kohn-Sham equations of density-functional theory in a plane-wave basis set with Vanderbilt ultrasoft pseudopotentials.[26] We use the exchange correlation with the generalized gradient approximation given by Perdew and Wang.[27] We set the plane-wave cutoff energy to be 400 eV. The Monkhorst-Pack scheme is used to sample the Brillouin zone. The optimizations of the lattice constants and the atom coordinates are made by minimization of the total energy. The tolerance of energy convergence is 10^{-4} eV. All the structures are fully relaxed with a mesh of $1\times1\times9$ and the mesh of $\mathbf{k}$ space is increased to $1\times1\times16$ for Li_2C_{112}, K_2C_{112}, and $1\times1\times20$ for other structures to obtain accurate energies and band structures with atoms fixed after relaxations.

There are different positions for intercalating atoms: inside the tube,[19] outside the tube,[22] and at the intersection channels of bundles.[20,23] We consider the intercalating inside the tubes, where the intercalating atoms are favored to locate along the axis of tube. The mechanism could also be applied

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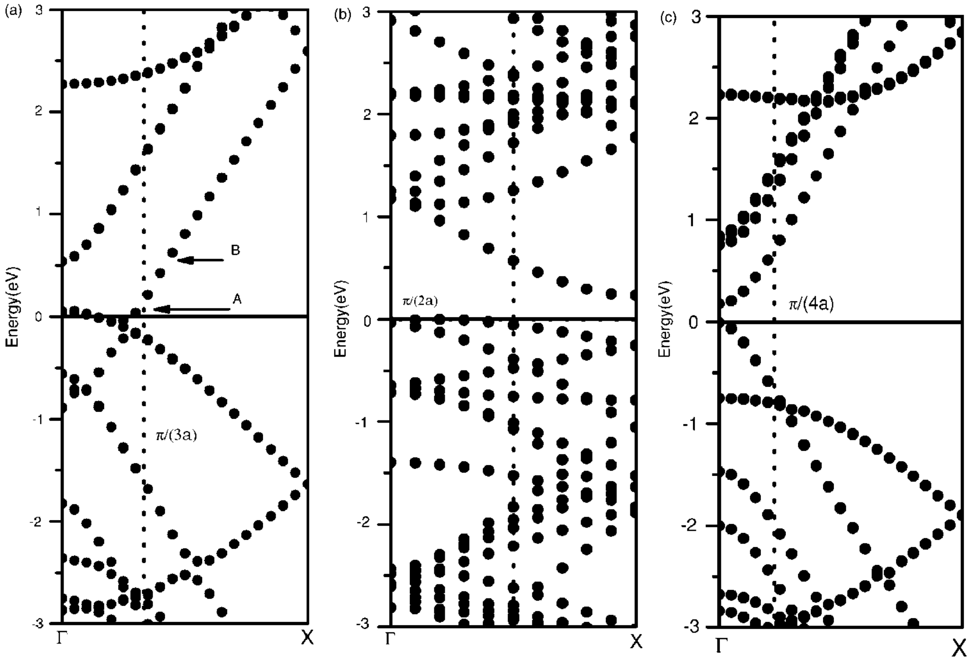

FIG. 1. Band structures of pure tubes: (a) the (5,0) tube, (b) the (4,2) tube, (c) the (7,0) tube. The Fermi energy E_F has been set at zero.

to the case of intercalating on the outside surface of the tubes. We first consider the (5,0) tube intercalated with Li atoms, which is one of the simplest cases for the donor intercalating. Stable intercalated structures with different concentrations of Li atoms are shown in Fig. 2. There is a chiral vector $\mathbf{C}_h$ for each carbon nanotube. The projection of the start point of this vector on the axis is marked as **O**. The alkali atom positions are given through the coordinates of the Z axis from the origin point **O**. For an isolated Li atom, the favorite adsorbed site is on the center of the hexagonal carbon units. The cell of Li_2C_{60} contains six favorite sites for Li atoms denoted as A to F as shown in Fig. 2 and thus there are three kinds of possible structures, which are marked with I, II, and III. Li atoms are located at A and D for structure I, A and C for structure II, and A and B for structure III. The structure parameters are shown in Table I. As is shown in Fig. 1(a), the pure (5,0) tube is a metal, in agreement with other theoretical results.[28] For the structure Li_2C_{60} (I), Li intercalating causes the band structure [shown in Fig. 1(a)] to be folded at $k = \pi/(3a)$, where a is the lattice constant, and the Fermi energy to be shifted up to the ending point of the band at the boundary of the Brillouin zone, as is shown in Fig. 3(a). This intercalated tube is a semimetal. The structure Li_2C_{60} (II) has less symmetry as compared to Li_2C_{60} (I). For Li_2C_{60} (II), there are two different distances between neighboring Li atoms in the carbon nanotube: one is 4.36 Å and the other is 8.36 Å, as is shown in Table I. This intercalating structure is calculated to be a semiconductor with a gap of 30 meV at the X point of the band structure, as is shown in Fig. 3(b). For the structure Li_2C_{60} (III), where the two distances between the neighboring Li atoms are 3.10 Å and 9.62 Å, respectively, there is a gap of 123 meV at the X point of the band structure, as is shown in Fig. 3(c). Now we explain how the metal-semiconductor transitions occur in the Li_2C_{60} structures. As is shown in Fig. 1(a), there is a "singly degenerate band" in the pure (5,0) tube near the Fermi energy. In the segment (A to B) of this band, where the energy ranges from 0.05 eV to 0.56 eV with wave vector $\mathbf{k}$ changing from $k = 0.28\pi/a$ to $k = 0.43\pi/a$, there is only one energy eigenvalue corresponding to a wave vector $\mathbf{k}$. Thus the band

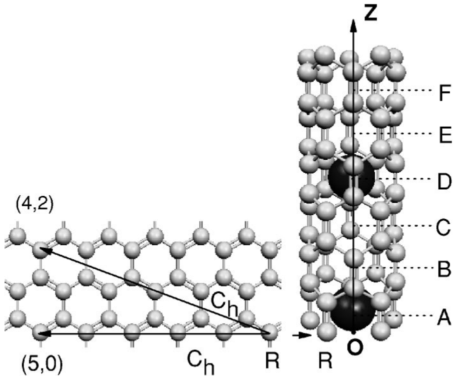

FIG. 2. Carbon nanotubes and the coordinates for intercalating positions. Atomic positions are given through the coordinates of the Z axis and the origin point is marked as **O**. The structure Li_2C_{60} is given as an example.

TABLE I. Structural parameters and formation energies for the intercalated tubes. The radii are for the intercalated tubes. The positions of intercalating atoms are along the axis of the tube and are measured from the **O** point shown in Fig. 2.

Nanotube	Radius (Å)	Structures	Atom positions (Å)	Formation energies (eV)	Cell length (Å)
(5,0)	2.06	Li_2C_{60} (I)	0.71,7.06	2.90	12.72
(5,0)	2.06	Li_2C_{60} (II)	0.47,4.83	2.88	12.72
(5,0)	2.06	LiC_{60} (III)	0.62,3.72	2.79	12.72
(4,2)	2.15	Li_2C_{112}	−0.08,3.58	2.46	22.54
(7,0)	2.81	K_2C_{112}	0.67,5.02	1.85	17.05

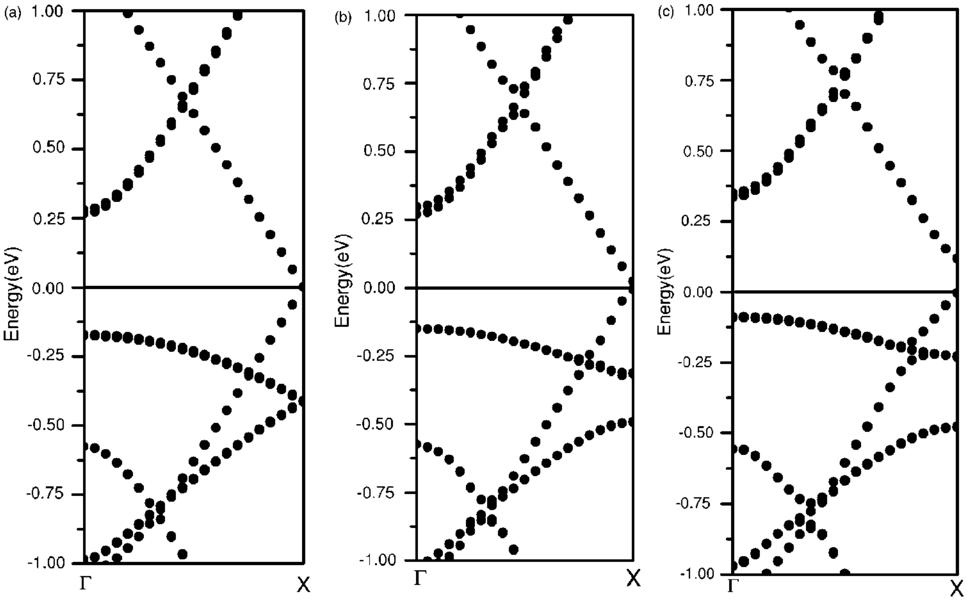

FIG. 3. Band structures of the (5,0) tube intercalated with Li atoms: (a) Li_2C_{60} (I), (b) Li_2C_{60} (II), (c) Li_2C_{60} (III). The Fermi energy E_F has been set at zero.

structure folded at $k=\pi/(3a)$ would make the singly degenerate band end at the boundary of the Brillouin zone when the unit cell is enlarged three times. Since 2N (N is the number of lattice sites) electrons fill one energy band fully, intercalating two Li atoms in each unit cell would shift up the Fermi energy to the boundary of the Brillouin zone. It is noted that the folding position of **k** should be between $k=0.28\pi/a$ and $k=0.43\pi/a$. For example, the structure LiC_{40} whose band structure is folded at $k=\pi/(2a)$ is still metallic because $k=\pi/(2a)$ is not in the wave-vector range of a singly degenerate band.

Now we consider the stability of the above Li-intercalated tubes. We have calculated the formation energies E_h to determine whether the intercalating is exothermic. The formation energy E_h per alkali atom is defined as follows: $E_h=(E_0+nE_m-E_d)/n$, where E_d and E_0 are the energies per cell with and without alkali atoms intercalated, E_m is the energy of free alkali atoms, and n is the number of alkali atoms in each cell. The structures with $E_h>0$ can be formed because it is exothermic for atoms to be intercalated into the tube. If E_h is larger than the formation energy of alkali atoms in the bulk bcc metal (1.90 eV and 1.03 eV for Li and K bulks, respectively), it is exothermic for alkali atoms to be intercalated into the tube as compared to forming the bulk alkali metal. From our calculations, the structures Li_2C_{60} (I, II, III) are stable, as E_h is from 2.79 eV to 2.90 eV. The reason that these structures are stable can be explained by comparing the case of intercalation in graphite. It is expected that the intercalated structures are stable if the diameters of the tube and the bonding length of Li and carbon atoms are matched and the distances of Li atoms are not too small as compared to the distances in the bcc bulk. For Li-intercalated graphite, the distance between Li atoms and the sheet is 1.85 Å,[29] while the radius of the (5,0) tube is 2.04 Å. Thus the (5,0) tube is suitable for Li intercalating. The calculations show that the variation of the radii of the tubes after intercalating is less than 0.03 Å, as is shown in Table I. When the Li atoms are intercalated into the tubes, there is a charge transfer from Li atoms to the tubes and there is a Coulomb repulsion between Li atoms. The equilibrium distance between Li atoms in the Li bulk is 3.04 Å. For all the intercalated structures we calculated, the smallest distance of Li atoms is 3.10 Å for Li_2C_{60} (III), as is shown in Table I. Thus these structures should be stable. As is shown in Table I, the structure Li_2C_{60} (I) is the ground state and the structures (II, III) are metastable for this concentration. The formation energy for Li_2C_{60} (II) is close to that of structure (I), which is only 0.02 eV higher. Thus structure (II) might be formed experimentally.

The above transition mechanism can be generalized to Li atoms intercalating in other tubes. As is shown in Fig. 1(b), the pure (4,2) tube is a semiconductor with an indirect gap of 264 meV and there is a "singly degenerate band" near the Fermi energy. In the segment of this band, where the energy ranges from 0.20 eV to 1.05 eV with wave vector **k** changing from $k=0.18\pi/a$ to $k=\pi/a$, there is only one energy eigenvalue corresponding to a wave vector k. For the structure Li_2C_{112}, whose structure parameters are shown in Table I, the band structure is folded at $k=\pi/(2a)$ and there is a direct gap of 313 meV at the point of X, as is shown in Fig. 4(a). The radius of the (4,2) tube is 2.14 Å, which is suitable for Li atoms intercalating because the distance between Li atoms and the sheet is 1.85 Å (Ref. 29) for Li-intercalated graphite. The formation energy E_h is equal to 2.46 eV for the structure Li_2C_{112}, and the structure Li_2C_{112} in the (4,2) tube is stable. Thus Li intercalating can also induce semiconductor-semiconductor transitions, transforming the indirect gap into the direct gap with different gaps, as is shown in the case of Li_2C_{112}.

In the following, we consider the intercalatings of other alkali atoms, such as K atoms, in the carbon nanotubes. It has been predicted that potassium intercalating in the (7,0) and (8,0) tubes is stable.[19] As is shown in Fig. 1(c), the pure (7,0) tube is a semiconductor with a direct gap of 181 meV and there is a "singly degenerate band" near the Fermi energy. In the segment of this band, where the energy ranges from 0.17 eV to 0.72 eV with wave vector **k** changing from $k=0$ to $k=0.27\pi/a$, there is only one energy eigenvalue cor-

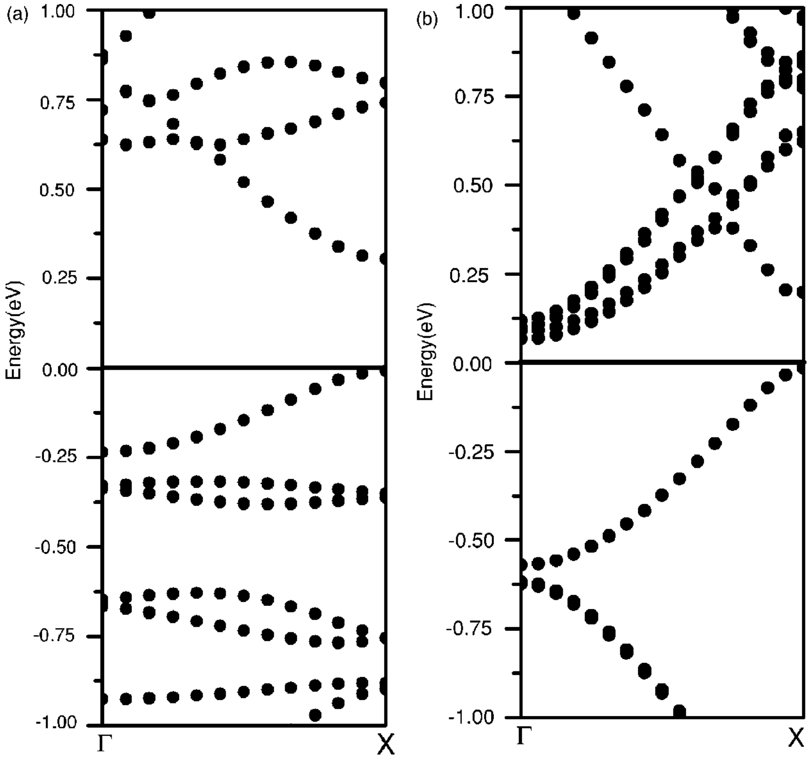

FIG. 4. Band structures of carbon nanotubes intercalated with Li and K atoms: (a) Li_2C_{112} in the (4,2) tube, (b) K_2C_{112} in the (7,0) tube. The Fermi energy E_F has been set at zero.

responding to a wave vector k. In order to have a semiconductor-semiconductor transition, the band should be folded at $k=\pi/(4a)$. For the structure K_2C_{112} shown in Table I, the band structure is folded at $k=\pi/(4a)$ and there is an indirect gap of 80 meV, as is shown in Fig. 4(b). Similarly, we can also deduce that the structures $K_2C_{28\times m}$ (m is an integer larger than 4) are semiconductors. However, for the structure KC_{28}, the band structure is not folded and the intercalated structure is a metal, which agrees with the results of Ref. 19. The structure K_2C_{112} is stable because its formation energy $E_h>0$. Thus, K atoms intercalating can also induce semiconductor-semiconductor transitions, transforming the direct gap to an indirect gap with different gaps, as shown in the case of K_2C_{112}.

In summary, we have shown that the adequate intercalating of alkali atoms into some types of carbon nanotubes could transform the metal and semiconductor tubes into semiconductor tubes. The transitions occur if the following points are satisfied: (i) there is a "singly degenerate band" near the Fermi energy; (ii) the diameters of the carbon nanotubes and the bonding length of alkali and carbon atoms are matched in order to have an exothermic intercalating; (iii) the changes of the band structures are small except for the shift of the Fermi energy after intercalating; (iv) the concentration of intercalating atoms should be adequate. The size of the unit cell and folding multiple of the band structures are determined by the structures of the intercalated tubes. The electrons from dopant atoms shift up the Fermi energy to the ending point of the singly degenerate band at the boundary of the Brillouin zone. Then the gap in the band structures appears as a result of structure perturbation due to the intercalating. As examples, the metal-semiconductor transition for the case of Li_2C_{60} in the (5,0) tube and the semiconductor-semiconductor transition for the case of Li_2C_{112} in the (4,2) tube are predicted by our calculations. Results of other alkali atoms in various carbon nanotubes show that this transition mechanism is quite general and there are possibilities to induce metal-semiconductor transitions and semiconductor-semiconductor transitions in various nanotubes by the intercalating of alkali atoms. Using this mechanism, one can transform semiconductor nanotubes with an indirect band energy gap into those with a direct energy gap, which is very important for fabricating the light-emitting devices. At the same time, this would also lead to a new method for forming the heterojunctions and be useful and important in the applications of nanodevices.

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