First-Principles Study of Li-Intercalated Carbon Nanotube Ropes

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We studied Li-intercalated carbon nanotube ropes by first-principles methods. Results show charge transfer between Li and C and small structural deformation due to intercalation. Both the interior of the nanotube and the interstitial space are susceptible for intercalation. The Li intercalation potential of a single-walled nanotube rope is comparable to that of graphite and almost independent of the Li density up to around LiC_2, as observed in recent experiments. This density is significantly higher than that of Li-intercalated graphite, making the nanorope a promising candidate for the anode material in battery applications.

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Carbon nanotubes are attracting interest as constituents of novel nanoscale materials and device applications [1–3]. Novel mechanic, electronic, magnetic [2], and chemical properties [3] in these one-dimensional materials have been discovered. Single-walled nanotubes (SWNTs) form nanorope bundles with close-packed two-dimensional triangular lattices [4]. These rope crystallites might offer an all-carbon host lattice for intercalation and energy storage. On analogy of the Li intercalated graphite [5], carbon nanorope is expected to be a candidate of anode materials for Li-ion battery applications [6]. Recent experiments found much higher Li capacity ($Li_{1.6}C_6$) in SWNTs than those of graphite (LiC_6) [7]. The Li capacity can be further improved up to $Li_{2.7}C_6$ after processing [8]. This high capacity of Li in nanorope implies a lower weight and a longer lifetime in the battery applications [9].

First-principles calculations have been successfully used to identify the cathode materials for lithium batteries [10]. K-doped small individual carbon nanotubes were studied by first-principles electronic structure calculations [11]. An empirical force field model was also employed to simulate K-doped SWNT ropes [12]. However, there is no first-principles study on the Li-intercalated SWNT ropes. There are a lot of open questions such as the following: (1) What is the maximum intercalation density? (2) Where do the intercalated ions sit? (3) Does the intercalation modify the structure of the nanotube? In this Letter, we present results obtained from first-principles SCF pseudopotential calculations. Several systems of the intercalated nanotube bundle are studied and compared with the experiments.

We use the Car-Parrinello algorithm with local density approximation to carry out first-principles pseudopotential total-energy calculation [13]. A plane-wave basis with an energy cutoff of 35 Ry and Γ point approximation are used [14]. The ion-electron interaction is modeled by the Troullier-Martin norm-conserving nonlocal pseudopotential [15] in the Kleinman-Bylander form [16]. The plane-wave pseudopotential program, CASTEP [17], is used for structural minimization on selected systems.

The tube bundle is modeled by a uniform two-dimensional hexagonal lattice. The SWNTs studied here include both (10,0), (12,0) zigzag and (8,8), (10,10) armchair tubes. The Li-intercalated graphite and bulk Li are also investigated as references. The initial configuration of Li atoms is assumed to be on high-symmetric sites which maximize the Li-Li distance (see Table II for details).

Figure 1 shows the relaxed structure and charge density of the (10,0) tube bundle with 5 Li atoms per unit cell.

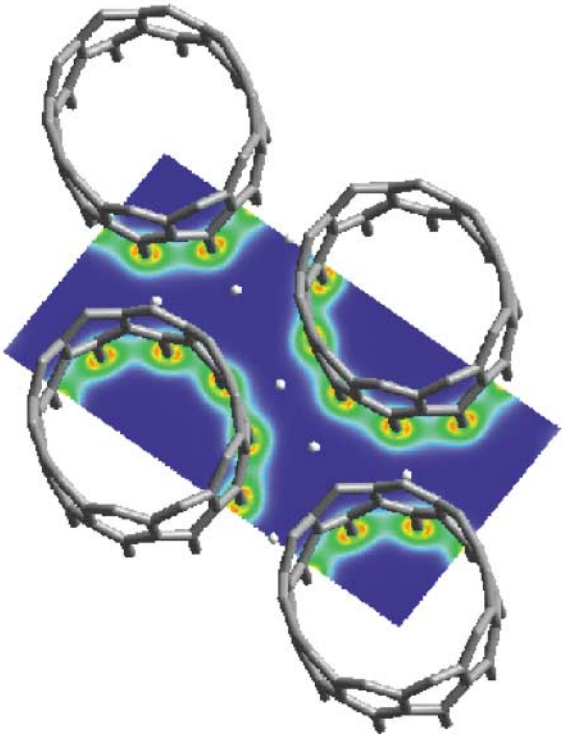

FIG. 1 (color). Geometric structure and total electron density distribution [slice at the (100) direction] of the relaxed Li-intercalated (10,0) tube bundle Li_5C_{40}. Small white balls denote Li atoms. Red, yellow, green, and blue colors on the slice indicate electron density from higher to lower. No significant electron density on lithium sites is found, indicating charge transfer between Li and nanotubes.

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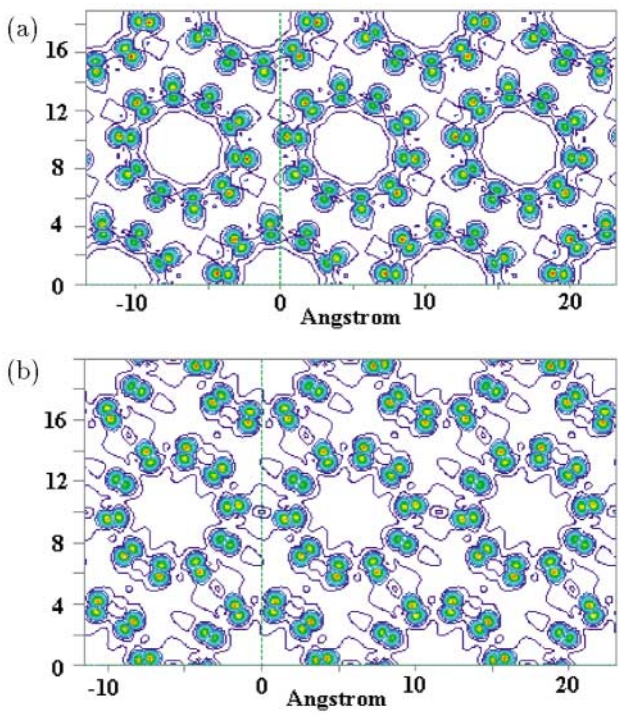

FIG. 2 (color). Contour plots of the occupied conduction orbital densities near Fermi level (a), and empty orbital densities above Fermi level (b) of the (10,0) tube bundle on the (001) plane. Red, yellow, green, and blue colors indicate electron density from higher to lower. Conduction orbitals are obviously derived from π bonds between C atoms. In (a), there is a very low conduction electron density pass through Li sites, whereas more distinct distributions of empty states are found around Li ions in (b). Both indicate charge transfer between Li and C.

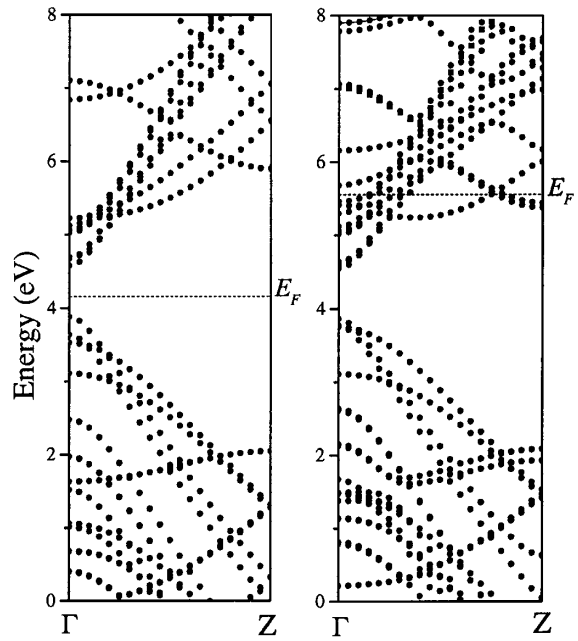

FIG. 3. Electronic band structures of pure (left) and Li intercalated (right) (10,0) tube bundles. Most of the bands are not affected by Li atoms, whereas some new conduction bands are introduced. Most conduction electrons reside on the bands associated with the carbon nanotube, indicating charge transfer from Li to nanotube.

After structural minimization, the Li atoms only slightly shift from their initial symmetric configuration. This shows that symmetry and maximum Li-Li distance are good criteria for choosing Li configuration. The intercalation modifies the shape of nanotubes (see Figs. 1 and 2). The deformation from circular tube as measured by the aspect ratio ($r_{\max}/r_{\min}$) is 10% in our calculation. This differs from the previous empirical simulation on K-doped (10,10) SWNT [12] (about 20% estimated from their published figure). The discrepancy between first-principles and empirical calculations demonstrates the importance of the quantum effect and the insufficiency of empirical potential in such systems.

There is almost no total charge density distribution in the space between SWNTs (Fig. 1). Further understanding of the charge distribution can be seen in the contour plots of occupied (a) and empty (b) orbitals near the Fermi level (Fig. 2). The conduction band orbitals are concentrated on the nanotubes, while the empty states have some distribution passing through the Li sites. In Fig. 3, we compare the band structure near Fermi energy of pure and intercalated bundles. Although the individual (10,0) tube and its bundle are all semiconductors, the intercalated tube bundle is found to be metallic. For the valence band, only a small modification upon intercalation is observed. In contrast, the hybridization between lithium and carbon has a significant influence on the conduction band and introduces some new states, similar to that found in Ref. [11]. All these analyses show that there is almost complete charge transfer and the conduction electrons mainly occupy the bands originated from carbon nanotubes.

Our calculation on other nanotubes such as the (10,10) tube bundle shows a similar charge transfer between Li and the carbon host. The observation of charge transfer agrees with the previous *ab initio* calculation on K-doped individual small carbon nanotubes [11]. A similar effect is well known in alkali-metal-doped fullerenes [18]. Experimentally, the charge transfer is supported by Raman [19] and NMR [20] measurements on alkali-metal-doped SWNT materials. These suggest that the cohesion between Li and the carbon nanotube is mainly ionic. We have tried a simple model in which complete charge transfer and uniform charge distribution on C atoms are assumed. We find that this simple model is not sufficient to describe our results, indicating the importance of screening and electron correlations.

To understand where the Li ions sit, we compare the intercalation energy of two typical Li sites—the center of the tube and the interstitial site of the hexagonal lattice. The total energy and equation of states of the tube bundle are calculated via the Car-Parrinello electronic minimization method [14]. The optimal distance between neighboring tubes is then determined. The intercalation energy is

TABLE I. The energy ΔE (one Li per unit cell) between the Li reside in the interstitial site (a) or at the center of the nanotube (c) (see Table II for coordinates). For a smaller tube, the interstitial site is preferred while the center is better for a larger tube.

Nanotube	(10,0)	(12,0)	(8,8)	(10,10)
Radius (Å)	3.91	4.70	5.42	6.78
ΔE (eV)	0.24	−0.54	−0.20	−2.20

obtained by subtracting the energy of the pure nanorope from the total energy of the intercalated system. SWNT bundles composed of (10,0), (8,8), (12,0), and (10,10) tubes are studied (Table I). In general, the energy of the Li atoms inside the tube is found to be lower than or comparable to that outside the tube, implying that both the inside and outside of the nanotube are favorable for intercalation. For a smaller tube, the center of the tube is less favorable because of the strong core repulse between Li ions and carbon walls.

We further studied the intercalation density by putting a different number of lithium atoms at both interstitial sites and the inside of the tubes. Typical Li configurations are illustrated in Table II. We find that energetically both the outside and inside of the nanotube are comparable up to high intercalation density. For instance, the energy difference of nine Li ions all inside or outside the (10,10) tube is only 0.36 eV per Li atom. We also find that the intercalation energy is not sensitive to Li arrangements at higher concentration. All these results imply that both the inside and the outside of the tubes can be simultaneously intercalated to achieve higher Li density.

In recent experiments, the intercalation density of the as-prepared SWNTs bundles sample was found to be $Li_{1.6}C_6$ [7] and improved up to $Li_{2.7}C_6$ after proper ball milling [8]. We suggest that the ball-milling process creates defects or breaks the nanotube, allowing the Li ions to intercalate inside of the tube. To understand the experimental intercalation density, we study the intercalated (10,0), (12,0), and (10,10) tube bundles with intercalation density up to $Li_{0.7}C$. The intercalation energy as a function of intercalation density is compared with that of graphite in Fig. 4. We find that the intercalation energy per carbon atom increases linearly with the intercalation density for different tube bundles up to about $Li_{0.6}C$. In contrast, the Li intercalation in graphite is already saturated at around $Li_{0.35}C$. We also find that the intercalation potentials, defined by taking the derivative of intercalation energy with respect to intercalation density for all tube bundles, are almost the same. It is comparable to that of graphite and about 0.1 eV higher than the formation energy of bulk lithium.

The nature of higher Li capacity in the nanotube can be related to the low carbon density in the nanotube bundle. For example, the average atomic volume for carbon in the (10,10) tube bundle is about 60% larger than that of graphite. The calculated saturation intercalation density

TABLE II. Examples of Li-intercalation configurations in our study for a (10,10) tube bundle with a 18.0 Å × 18.0 Å × 2.46 Å hexagonal unit cell. For a given Li concentration, symmetric configuration is chosen to maximize the Li-Li distance. $a-f$ are the site indexes and the number in the bracket is their degeneracy. a, b, and e sites are outside the tube and c, d, and f are inside. x, y, and z denote fractional coordinates based on hexagonal lattice of nanorope. N is the Li number in the unit cell which contains 40 carbon atoms. X means there is a Li atom on the site while O means none.

Site	a (2)	b (3)	c (1)	d (8)	e (6)	f (4)
x	0.333	0.5	0	0.278	0.278	0.096
y	0.667	0.5	0	0	0.556	0.131
z	0.5	0	0	0	0.50	0.5
$N = 2$	X	O	O	O	O	O
$N = 3$	X	O	X	O	O	O
$N = 5$	X	X	O	O	O	O
$N = 6$	X	X	X	O	O	O
$N = 13$	X	X	O	X	O	O
$N = 20$	O	X	X	X	X	O
$N = 24$	X	X	X	X	X	X

is also about 60% higher in the (10,10) tube bundle than graphite. Additional understanding of high Li concentration can be gained by examining the work function (WF) of the nanotube. Recent experiments suggest that the WF of SWNT bundles is 0.2 eV higher than that of graphite [21]. Thus, the electron in a nanorope has a lower energy than those in graphite.

In summary, we have performed first-principles calculations on the total energy and electronic structures of Li-intercalated SWNT nanoropes. The main conclusions

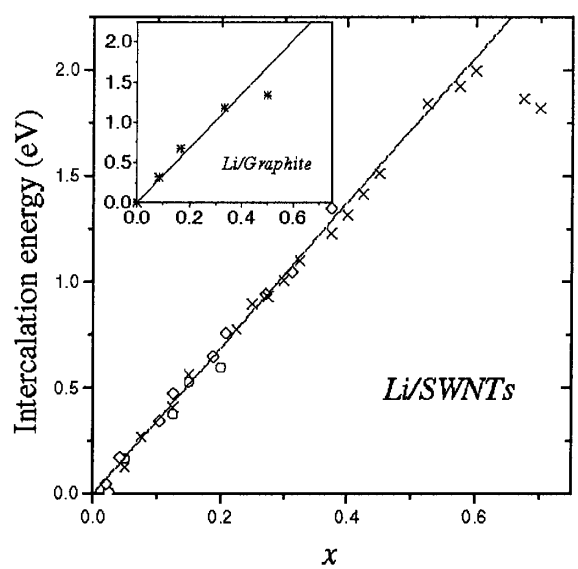

FIG. 4. Intercalation energy per carbon atom as a function of intercalation density, x, of Li_xC systems. The inset shows intercalation energy for graphite. Crosses—(10,10) tube bundle; open squares—(12,0) tube bundle; open circles—(10,0) tube bundle. Solid lines are linear fits of the data up to saturation density, $Li_{0.6}C$ for nanorope and $Li_{0.35}C$ for graphite.

are (1) almost complete charge transfer occurs between Li atoms and SWNTs, (2) the deformation of nanotube structure after intercalation is relatively small, (3) energetically the inside of the tube is as favorable as interstitial sites for intercalation, (4) the intercalation potential of Li/SWNT is comparable to the formation energy of bulk Li and independent of Li density up to about $Li_{0.5}C$, and (5) the intercalation density of a SWNT bundle is significantly higher than that of graphite. These results suggest that the nanorope is a promising candidate material for anode in battery application.

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