Electronic properties of K-doped single-wall carbon nanotube bundles

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We have investigated electronic properties of K-doped single-wall carbon nanotube bundles by the first principles calculations. The lattice expands up to 8% at K0.1C with negative binding energies, where distortion of tube walls is negligible up to K0.25C with full relaxation, contrary to the previous reports. Partial charge transfer occurs from potassium atom to the tube. The Fermi level and the amount of charge transfer increase with increasing doping concentration and saturate at large concentration, strongly indicating that the charge transfer is mainly responsible for conductivity increase of the tubes.

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Single-wall carbon nanotubes (SWNT’s) can be viewed as a single graphene sheet rolled into a cylinder with diameters in the range of 1–2 nm and lengths of several hundreds micrometer. They coalesce into a long crystalline bundle consisting of a few tubes to thousands of tubes packed in a triangular lattice, corresponding to 30–600 tubes per bundle.12 The concentric tubes are separated by van der Waals interactions with a typical interlayer spacing similar to that of graphite.

A SWNT bundle can be doped with alkali metals, but little is known about the electronic properties and the exact positions of the dopants. For an isolated SWNT, binding sites of dopants are located at the external surface of the tube through physisorption or chemisorption, and presumably in the interior of the tube if its ends are open. In a SWNT bundle, the interstitial channels between tubes provide additional intercalation sites. The intercalation of potassium into SWNT bundles has attracted much interest recently, due to their possibility of new superconducting phases,3–5 and potential application to hydrogen storage.6,7

Li- and K-doped SWNT tube bundles have been reported to enhance conductivity and hydrogen storage capacity. It has been argued whether the conductivity enhancement by doping is by an increase of charge transfer or tube–tube interactions. Lee et al. found that the charge transfer induced by doping governs the conductivity enhancement rather than the tube–tube interactions,4 while Ruzicka et al. concluded that the tube–tube interactions influence conductivity by doping more strongly than the effect of the charge transfer.5 In recent experiments, a one-to-one map among Fermi level, charge carrier concentration, and electrical conductivity was established. Fermi level shift by the redox reactions determined the electrical conductivity of the Li-doped SWNT bulk material, i.e., the Fermi level shift was proportional to conductivity increase.8 These results indicate that the tuning of the Fermi level and charge transfer induced by doping could control the conductivity. Another group also suggested that the induced charge transfer is responsible for conductivity enhancement in K-doped SWNT bundles.3,4,9 On the other hand, it has been suggested that the charge transfer with about 0.1e per C atom by chemical doping can shift the Fermi level by almost 2 eV.4 This interesting issue of conductivity enhancement, however, has not been clarified theoretically up to now. In addition, it has been reported that alkali-doped tubes increase hydrogen storage capacity,6,7 although results have not been clearly corroborated yet. The main difficulty arises from the absence of theoretical models for adsorption sites, H2 adsorption mechanism, swelling of the tube bundles, and storage capacity of hydrogen.

The issues on the structures of K-doped SWNT bundles have been challenged by theoretical calculations. The doped K-atoms are located at the interstitial sites of tube bundles,10,11 with the same tube spacings to be maintained even after the doping, whereas the tube walls are severely distorted at K0.1C.11 The Fermi level also shifts into a conduction band of pure tube bundle after Li-doping. The charge transfer occurs from Li atoms to tubes, where Li-doping is saturated at Li0.6C.12 However, no systematic relation of the Fermi level to the conductivity is provided in terms of doping concentrations.

In this report, we perform the first principles calculations systematically for a K-doped SWNT bundle in terms of doping concentrations. The bundle lattice expands up to 8% at K0.1C and no tube distortion is observed, in contrast with previous reports.11 We find a systematic relation between the amount of charge transfer and the Fermi level shift as a function of K/C ratio. We further demonstrate that the conductivity of the doped tubes is enhanced by the charge transfer from potassium atoms to the tubes, rather than by the tube–tube interactions.

We calculate the electronic structures of a K-doped SWNT bundle using density functional theory (DFT) within the local density approximation (LDA). The ionic potentials are described by a norm-conserving nonlocal pseudopotential generated by Troullier–Martins in Kleinman–Bylander form.13,14 Exchange-correlation functions parametrized by the Perdew–Zunger scheme are used.15 A plane-wave basis set with an energy cutoff of 55 Ry is used. Integration over Brillouin zone is carried out using 10 k-point sampling, which is generated by the Monkhorst–Pack scheme.16 The convergency criterion for structure optimization is that all forces be \( \leq 0.005 \) Ry/Å. The energies are converged to \( 10^{-3} \) eV.

The tube bundle is modeled by a hexagonal unit cell with \( \gamma = 60 \) deg. We choose a (5,5) armchair SWNT bundle, where 20 carbon atoms are included in the primitive cell.
The box size of the hexagonal unit cell is initially chosen to be 10.13 Å $^3$ with a tube diameter of 6.78 Å and an intertube distance of 3.35 Å between the tube walls. The proper number of potassium atoms ($K_x C_x$, $x = 0.05, 0.1, 0.15$, and $0.25$) are doped in the tube bundles. We consider that the doped potassium atoms are located at the interstitial channel sites and have a symmetric configuration so as to maximize the K–K distance.

Figures 1(a)–1(d) shows the total energies of fully relaxed geometry as a function of the intertube distance with different doping concentration. The interstitial channel sites of the doped K-atom are represented as solid circles. In our calculation, the intertube distance of a pure tube bundle is optimized to 3.2 Å. The lattice constant increases with increasing potassium content, as shown in Fig. 1(e). The lattice constant expands by 8% at $K_{0.1} C$ and saturates to 25% at $K_{0.15} C$. Their intertube distances expand to 4.0 and 5.65 Å, respectively. These values are comparable with the interlayer distance of 5.35 Å at $K_{0.125} C$ in graphite (stage I). We note that the distortions of the tube wall were negligible for all cases up to $K_{0.25} C$ with full relaxation, contrary to the previous reports that the tube walls were severely distorted by about 10%–20% for the doped (10,10) SWNT bundle. This is perhaps due to the inappropriate treatments of the lattice expansion by the doping.

Binding energies are also presented in Fig. 1(f). We define the binding energy as follows:

$$E_b = E_i(CNT + K) - E_i(CNT) - n_K E_s(K),$$

where $E_i$ is the energy of the system, $E_s$ is the energy of the isolated atom, and $n_K$ is the number of potassium atoms.

<table>
<thead>
<tr>
<th>K/C</th>
<th>Intertube distance (Å)</th>
<th>K–K (Å)</th>
<th>C–K (Å)</th>
<th>Mulliken charge (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{0.05} C$</td>
<td>3.95</td>
<td>10.73 (6.96)</td>
<td>2.96</td>
<td>0.806</td>
</tr>
<tr>
<td>$K_{0.1} C$</td>
<td>4.00</td>
<td>6.20</td>
<td>2.98</td>
<td>0.783, 0.782</td>
</tr>
<tr>
<td>$K_{0.15} C$</td>
<td>5.65 (5.35)</td>
<td>6.22 (4.92)</td>
<td>3.13</td>
<td>0.445, 0.490, 0.490</td>
</tr>
<tr>
<td>$K_{0.25} C$</td>
<td>5.83</td>
<td>3.90</td>
<td>3.25</td>
<td>0.534, 0.473, 0.474, -0.197, -0.199</td>
</tr>
</tbody>
</table>
where \( E_t(CNT+K) \) and \( E_t(CNT) \) are the total energy of tube bundle with and without potassium atoms inside, respectively. The \( E_s(K) \) is the self-energy of the potassium atom and \( n_K \) is the number of potassium atoms. The binding energies maintain negative values up to \( K \leq 0.1 \) C and become positive from \( K > 0.15 \) C, i.e., the doping of potassium atoms up to \( K_{0.1}C \) is exothermic process. Further increase of doping concentration requires an extra energy. In general, the binding energy is correlated with the K–K separation distance. The K–K separation distance becomes shorter with increasing K-doping, whereas the binding energy decreases up to \( K_{0.1}C \). We note here that the binding energy is not solely determined by the K–K separation distance. With further increasing doping content, the binding energy continues to increase, following similar trends to the electrostatic repulsive energy. At low doping content, the repulsive energy is negligible due to a large K–K separation distance. Instead, the attractive interactions between tube walls and potassium atoms govern the binding energy. Furthermore, the electrostatic repulsive energy is minimized by reducing the amount of charge transfer from potassium to the tube, as shown in Table I. Yet, \( K_{0.25}C \) adopts too many potassium atoms at the interstitial sites and leaves perhaps no room for additional hydrogen storage. This suggests that excessive doping may not be advantageous to the hydrogen storage.

We present the band structure and density of states (DOS) of the K-doped tube bundle in Fig. 2. The band structure of a pure (undoped) (5,5) SWNT bundle and the corresponding hexagonal Brillouin zone are shown in Fig. 2(a). \( \pi \) and \( \pi^* \) bands cross at the Fermi level along the tube axis. The band dispersion perpendicular to the tube axis may not be negligible, particularly near the region from 3 to \(-5\) eV, as can be seen from the G-M band in Fig. 2(a). With potassium doping, the Fermi level shifts up to the conduction band due to the charge transfer from potassium to the tube wall. With potassium doping, the Fermi level shifts up to the conduction band due to the charge transfer from potassium to the tube wall.  

We note here that a new peak near \(-12.5\) eV develops with potassium doping and its intensity increases with increasing doping concentration, as shown in Figs. 2(b)–2(d). At \( K_{0.05}C \), the band dispersion perpendicular to the tube axis seems to be reduced, although the degeneracies were increased due to the potassium doping. At high doping concentration, as shown in Fig. 2(d), band dispersion is significantly reduced. This can be understood by the lattice expansion with the doping, which will reduce the tube–tube interactions.

FIG. 2. (a) Band structure and DOS for pure tube bundle involved hexagonal Brillouin zone. (b)–(d) Band structures and the corresponding DOS for \( K_xC \) (a) pure (5,5) CNT, (b) \( x = 0.05 \), (c) \( x = 0.1 \), and (d) \( x = 0.15 \). The DOS is in units of \( 2N \) number of states/eV per primitive cell.

FIG. 3. (a) The Fermi level shift and electrical conductivity of Li-doped SWNT from Ref. 8 and (b) the corresponding Fermi level shift and the amount of charge transfer of K-doped SWNT bundle as a function of doping content. (c) The DOS at the Fermi level and (d) that of \( s \) orbital of potassium atoms in terms of doping content.
It has been suggested that in Li-doped SWNT, the Fermi level shift is strongly correlated to the electrical conductivity with Li/C ratio. Figure 3(a) shows that the Fermi level shift and electrical conductivity increase have similar trends with increasing Li/C ratio. In our calculations, we present the Fermi level shifts of potassium atoms increases rather gradually with increasing K/C ratio, as shown in Fig. 3(b). The Fermi level shift increases abruptly with increasing K/C ratio up to K/C = 0.05 and saturates to near 2 eV. Similar trends are shown in the amount of charge transfer. This result strongly suggests that the conductivity of the doped tubes is governed by the amount of charge transfer. Experimentally the normalized conductivity of K-doped and Li-doped SWNT at the atomic ratio of 0.04 is about 13 and 2, respectively, suggesting that the conductivity is enhanced more effectively by the K-doping than by the Li-doping at low doping content. The amount of charge transfer per carbon atom are 0.04 e, 0.08 e, 0.07 e, and 0.05 e for K/C (x = 0.05, 0.1, 0.15, and 0.25), and the corresponding Fermi level shifts are 1.6 eV, 1.7 eV, 2.3 eV, and 2.0 eV. These values are in good agreement with the previous estimation of the Fermi level shift of about 2 eV for a charge transfer of 0.1 e per carbon atom.

Figure 3(c) shows the DOS at the Fermi level as a function of K/C atomic ratio. The DOS increases rapidly and saturates at K_{0.05}C, revealing similar trends to the Fermi level shift and the change of charge transfer, as shown in Fig. 3(b). This suggests that higher T_c may not be expected with higher alkali metal doping in the tube. The DOS of s orbitals of potassium atoms increases rather gradually with increasing doping content, as shown in Fig. 3(d). This follows a very similar trend to the conductivity increase shown in Fig. 3(a). This change should be observable experimentally to monitor the doping concentration, in addition to the Fermi level shift and conductivity enhancement.

Figure 4 shows the contour plots of the total electron density distribution in the (001) plane for (a) pure and the doped K_0.05C with (b) x = 0.05, (c) x = 0.1, and (d) x = 0.15. Contours are shown in the range between 0.05 and 2.0 Coulomb/Å^3 with a spacing of 0.1.

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The intercalation energy, similar to the binding energy, may be defined by subtracting the energy of a pure tube bundle from the total energy of the K-intercalated tube bundle. See, for instance, Ref. 12.

Mulliken charges localized at each atom are calculated by introducing atomic orbital basis sets.

