Modification of the electronic structure in a carbon nanotube with the charge dopant encapsulation

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We present the first-principles study of effects of the charge dopants such as cesium and iodine encapsulated on the electronic structure of carbon nanotubes (CNTs). An encapsulated cesium atom donates an electron to the nanotube and produces donorlike states below the conduction bands. In contrast, an iodine trimer (I_3) accepts an electron from the nanotube and produces an acceptorlike state above the valence band maximum. We find that a Cs atom inside a metallic armchair CNT gives rise to spatial oscillations of the density of states near the Fermi level. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2929381]

The tubular form which has the hollow space inside makes researchers insert atoms or molecules such as fullerenes[1–4] and hydrocarbons[5–7] to obtain useful physical properties. The doping of a semiconductor is essential to be used for electronic devices. Recent experiments have reported that encapsulation of alkali metal (Cs) or halogen elements (I) inside the carbon nanotube (CNT) is feasible.[8–11] It has been reported that the field emission and electrical current can be improved by doping of these materials.[12,13] The scanning tunneling spectroscopy (STS) study of the Cs-encapsulated CNT shows local change of electronic structure.[14] The previous theoretical studies, however, considered only a high doping (dense packing of dopants). The effect of the charge donor or acceptor on the local electronic structure of the semiconducting or metallic CNT without the interaction between the neighboring images in the periodic supercell has not been fully understood yet.

In this letter, we investigate the influence of an encapsulated charge doping atom (Cs, I) on the electronic structure of CNTs using the first-principles density functional calculations. For the Cs-encapsulated CNT, an electron is transferred from an inserted Cs atom to the CNT and produces donorlike states below the conduction bands. For the I_3-encapsulated CNT, in contrast, the iodine trimer (I_3) accepts an electron from the CNT and produces an acceptorlike state above the valence band maximum (VBM). These findings may lead us to understand the local electronic properties of dopant-encapsulated CNTs.

We performed *ab initio* density functional calculations within the local density approximation using a pseudoatomic orbital basis set.[15,16] The norm-conserving pseudopotential[17] is employed with an energy cutoff of 120 Ry. We adopt Ceperley–Alder exchange-correlation potential.[18] Here, we choose Cs and I as an electron donor and an acceptor, respectively. The scalar relativistic effects important for heavy atoms such as Cs and I are taken into account. We treat four electrons ($2s^2 2p^2$) for C, nine electrons ($5s^2 5p^6 6s^1$) for Cs, and 17 electrons ($4d^{10} 5s^2 5p^5$) for I as valence electrons. For dopant encapsulation, the semiconducting (10, 0) and metallic (5, 5) CNTs which have similar diameters (~7 Å) are

chosen. The periodicity of CNTs along the tube axis is from 8 to 10 nm, containing 800–1000 carbon atoms. The I_3^- or I_5^- are experimentally found to form[9] inside the CNT, which was confirmed by the first-principles study. Therefore, we put an iodine atom or a trimer (I_3) inside the CNT. The energy minimum position of the encapsulated charge dopant atom is found to be at the axis of the nanotube.

To see the spatial change of the electronic structure, we constructed the simulated STS data with the projected density of states of carbon atoms which lie in different positions along the CNT axis. At first, the optimized geometry of the Cs-encapsulated (10, 0) CNT and the simulated STS map of the structure are presented in Fig. 1(a). A violet-colored sphere at the center of the CNT represents a Cs atom. We found that the electronic structure of the CNT near the Cs atom is changed and it recovers the original DOS of the (10, 0) CNT far from the Cs site. Our Mulliken population analysis shows that the Cs atom gives approximately one electron to the CNT and becomes a Cs^+ ion. The carbon π electrons which were originally extended over the whole nanotube become bound near the Cs^+ ion. The local electronic states are overall downward shifted and bound states are produced near the Cs-embedded site. In Fig. 1(a), one of the bound states is shown in the energy band gap. According to the angular momentum ($l=3$) of the bound states, this state originates from the conduction band minimum (CBM) (~0.25 eV). The other two bound states occur (~0.5 and ~0.7 eV) above the Fermi level. Besides, relatively localized states with high densities are shown above 1.5 eV. We observe the DOS depression of the CBM near the Cs atom. The DOS of the valence band also decreases because of the local downshift. These results are in good agreement with the experiment.[14]

Next, we investigate the hole doping effect of iodine. A recent experiment reports that iodine atoms inside the CNT form I_3 or I_5. The short chain structures accept an electron from the nanotube and become I_3^- or I_5^-.[9] The electronic structure and geometry of I_3-encapsulated CNT is shown in Fig. 1(b). An acceptorlike state bound near the iodine trimer appears near the VBM. The depression of the DOS of the valence band is observed near the I_3 position since the acceptorlike state originates from the VBM. As expected, this tendency is the opposite of the case where the Cs atom is encapsulated inside the tube. The transferred electrons are

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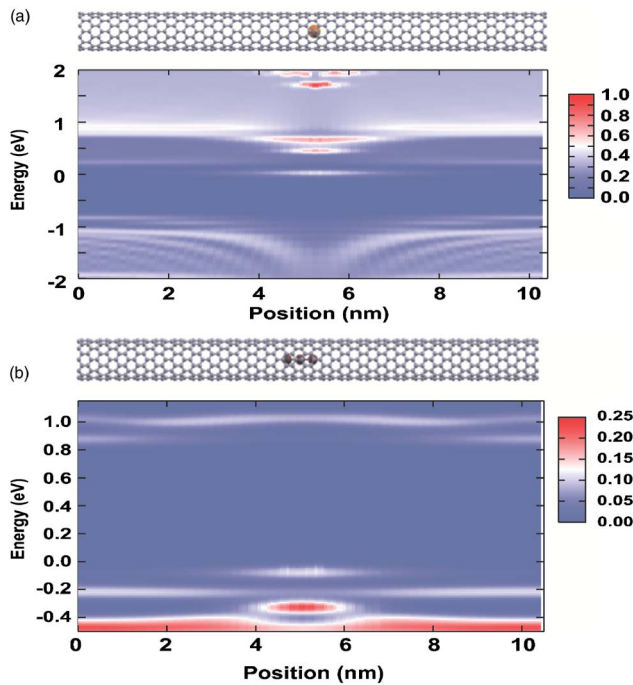
FIG. 1. (Color online) (a) Two-dimensional map of simulated STS of a (10, 0) CNT encapsulating a Cs atom and its model structure. (b) Two-dimensional map of simulated STS of a (10, 0) CNT encapsulating an iodine trimer (I_3) and its model structure. The Fermi level is set to zero. The orange and brown spheres located in the middle of CNT represent cesium and iodine, respectively.

not uniformly distributed on the CNT. Like the local DOS (LDOS) in Figs. 1(a) and 1(b), according to the Mulliken population analysis, the total electron density along the tube axis has a decay pattern. Regardless of the structural optimi-
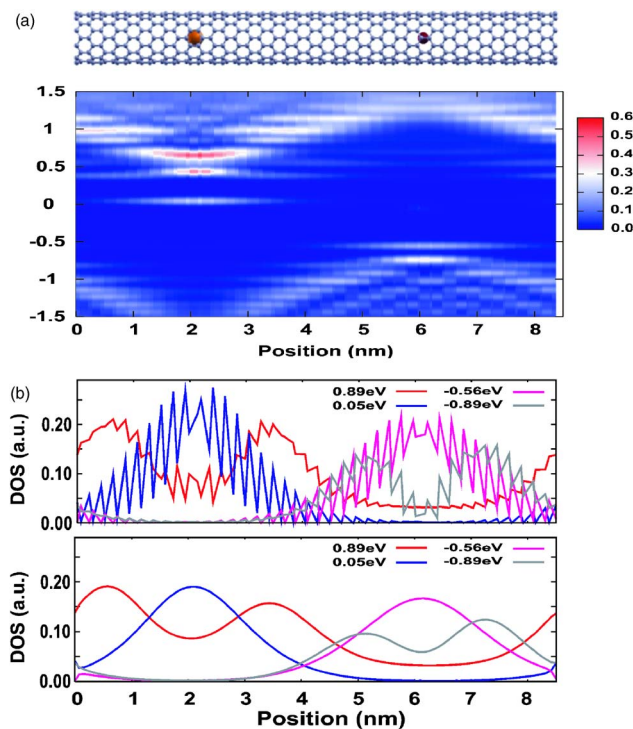

FIG. 2. (Color online) (a) Two-dimensional map of simulated STS data of a (10, 0) CNT encapsulating Cs and I and its model structure. The horizontal cuts of the STS map in several energies are shown in (b). The curves are shown as smooth curves again for visual clarity.
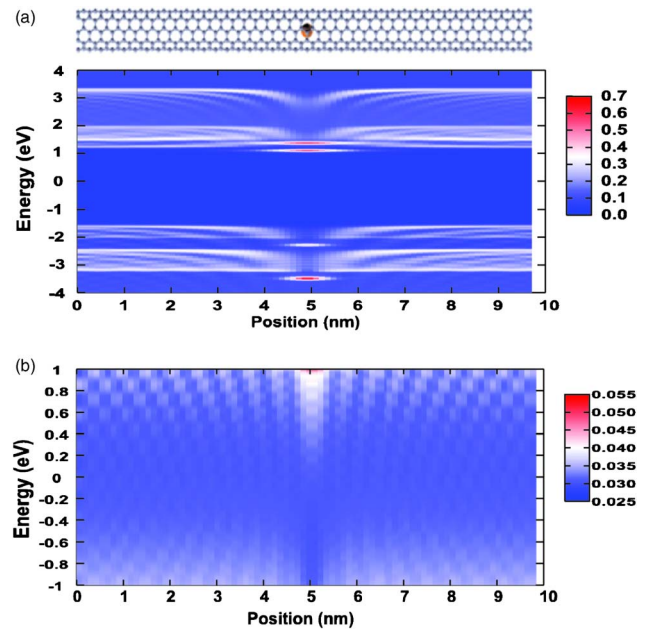

FIG. 3. (Color online) Two-dimensional map of simulated STS data of a (5, 5) CNT encapsulating a Cs atom and its model structure are shown in (a). The enlarged STS map is shown again in (b) to see the detailed structure of the DOS near the Fermi level.

zation (relaxation), this feature is shown. We conclude that local mechanical deformation of the single-walled nanotube is not very important for the modulation of the LDOS.

We also consider the case where two different kinds of charge dopants are encapsulated together inside the CNT. We put Cs and I atoms with the distance of 4 nm. As shown in Fig. 2(a), donorlike and acceptorlike states are shown near Cs and I embedded sites, respectively. The several horizontal cuts of Fig. 2(a) are shown in Fig. 2(b). The smooth curves are shown for visual clarity. The potential from Cs^+ and I^- ions makes the VBM and CBM oscillate like sinusoidal waves with the size of the band gap preserved. It is clearly shown that the local shift of the potential in the cesium site is opposite to that in the iodine site. In addition to the bound states in the gap region, we can see the quantum well states by the dopant ion in both valence and conduction bands. The confined states in Fig. 2(a) are located at the upper left and lower right regions. The states farther from the Fermi level have more nodes along the tube axis in their wavefunctions.

Finally, we investigate the effect of encapsulated charge dopants on the metallic armchair CNT. We select an armchair (5, 5) CNT which has robust metallic properties by the symmetry. In the simulated STS image shown in Fig. 3(a), there are states (−3.5, −2.2, and +1 eV) which have localization characters. To see the detailed spatial change of the DOS near the Fermi level, the enlarged picture of Fig. 3(a) is shown in Fig. 3(b). Considering horizontal cuts in Fig. 3, the spatial oscillations of the DOS are shown. We find that the screening amplitude and frequency are both dependent on energy. The positive charge (Cs^+) has the screening length of ~0.5 nm and there are the residual screening patterns over the radius. It demonstrates that the free-electron screening length in one-dimensional metallic structures is longer than in three-dimensional metals.[19]

By the Fourier transform for the spatial oscillation patterns, some features are found as follows: in k space, all peaks in the Fourier-transformed patterns map onto linear π

and π^* bands of the armchair CNT near the Fermi level. Below the Fermi level, both two linear π and π^* bands contribute to the screening. Above the Fermi level, however, only the π band contributes to the screening of the Cs^+ ion. We note that the wave functions of the π states do not have a phase variation in the circumferential direction in the armchair CNT while the wave functions of π^* electrons are more complicated to match and to interact with the orbitals of Cs because of the phase variation along the circumferential direction. This phase variation of π^* states in the circumferential direction is prominent in the unfilled (conduction) band.

In summary, effects of charge doping to the electronic structure of CNT have been investigated with first-principles calculations. Halogen and alkali metal atoms produce acceptorlike and donorlike states in the gap, respectively. Our work shows that the charge transfer by the dopant[20] and the generation of gap states greatly affect the electrical property of the CNT. In addition to the bound states in the gap region, we find the quantum confined states by the dopant ion in both valence and conduction bands. As in quantum harmonic oscillators, the number of nodes in those states increases as energy increases. Dopant-encapsulated metallic armchair CNTs show the spatial oscillations of its DOS near the Fermi level which is related with the linear bands crossing at the Fermi level.

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