Electronic structures of capped carbon nanotubes under electric fields

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We have investigated the electronic structure of capped carbon nanotubes under electric fields by density functional calculations. The calculated effective work function of the capped armchair nanotubes decreases linearly with increasing electric fields, whereas that of the metal tip decreases quadratically. We analyzed the density of states, highest occupied molecular orbitals (HOMO’s) and lowest unoccupied molecular orbitals (LUMO’s) for various charged states under electric fields. While the HOMO and the LUMO are not localized at the cap for a neutral state, the HOMO and LUMO of a negatively charged state are localized at the cap, particularly under electric fields. This localization plays an important role in the field emission. The Mulliken charge population shows that the charge accumulation is not dependent on the local atomic geometry but on the sharpness of the tip.

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I. INTRODUCTION

The carbon nanotubes (CNT’s) are promising materials for field emitters due to their unique structures and prominent stability. The high aspect ratio of the CNT tip with a small diameter can lower the threshold voltage. The chemical and mechanical stabilities of CNT’s may provide the field emitters with little tip degradation. In addition, the CNT tips have shown very good field emission stability compared to metallic emitters. Recently, a large size, CNT-based field emission display (FED) with full color has been demonstrated.

The field emission currents from CNT tips have been interpreted in terms of the Fowler-Nordheim equation, which fails in high field region. These current saturations at high fields have been explained by the attribution of gas adsorption. Several groups reported electronic structures and localized states at CNT tips. They reported that the local density of states at the tip showed sharp localized states that were correlated with the presence of pentagonal defects. Han and Ihm studied the role of the localized states in the field emission of CNT’s with various tip geometries. Adessi and Devel pointed out that the emission current from CNT’s originated from the Fermi sea and/or the localized states. Little is known, however, for the relationship between the electronic structures and field emission properties of CNT’s.

In this report, we present the density functional calculations for the electronic structures of the capped single-walled CNT’s. Especially, we focus on the changes of the charge densities at highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) under electric fields. We also study various charged states with or without electric fields. The Fermi level shifts downwards (upwards) in positively (negatively) charged tubes, which is similar to the p-type (n-type) doping in semiconductors. The Mulliken charge populations show that the field emission is not dependent on the atomic geometry of the tip but on the sharpness of the tip. We will further show that charge populations on HOMO and LUMO are strongly dependent on the applied electric fields and charged states.

II. THEORETICAL APPROACHES

In this study, we considered single-wall (5,5) and (9,0) nanotubes with a capped edge. The diameters of armchair and zigzag tubes are 6.8 and 7.0 Å, respectively, which are similar to those of C60. The armchair (5,5) nanotube is modeled by five layers of carbon rings (50 carbon atoms) along the tube axis. One end of the tube is capped with C30 and the dangling bonds at the other end are saturated by hydrogen atoms in order to emulate an infinite tube. We tested the convergence in the energy and charge density with seven and nine tube layers. Charge densities were slightly changed, but the symmetries were clearly reserved. The rest of the calculations were performed with a five-layers model. The zigzag (9,0) nanotube is similarly constructed, again with six layers of carbon rings (54 carbon atoms) along the tube axis and further capped by C30. Hydrogen atoms again saturate the dangling bonds at one end. Two carbon layers at the bottom as well as the hydrogen atoms are fixed during the whole simulation.

Our total energy calculations and corresponding structure optimizations are based on the density functional formalism within the local density approximation (LDA) and the generalized gradient approximation (GGA), as implemented in the DMOL3 code. The exchange-correlation energy in LDA is parametrized by the Perdew-Wang scheme, and Becke’s corrected exchange functional is adopted in GGA. All-electron Kohn-Sham wave functions are expanded in a local atomic orbital basis set, which is advantageous for Mulliken charge calculations. In the double-numerical basis set, the 2s and 2p carbon orbitals are represented by two wave functions each, and a 3d type wave function on each carbon atom is used to describe the polarization. No frozen core ap-
proximation is used throughout the calculations. For accurate binding energy calculations, GGA calculations are done whenever necessary after geometrical optimization by the LDA. The forces on each atom to be converged during each relaxation are less than 10^{-2} a.u.

The ionization potential (electron affinity) is defined as the energy difference between a system with a +1 (-1) charge and the original system with zero charge. The armchair (5,5) tube has a pentagon at the top of the cap surrounded by five hexagons, whereas the zigzag (9,0) tube has a hexagon at the top of the cap surrounded by three pentagons and three hexagons alternately. The optimized geometry of a capped (5,5) tube in a neutral state shows that the top pentagon has equivalent bond lengths of 1.44 Å, whereas the bond lengths of hexagon at the top of a capped (9,0) tube are 1.39 and 1.43 Å alternately. The constant electric field is applied parallel to the tube axis.

III. RESULTS AND DISCUSSION

Figure 1 shows the binding energy as a function of an electric field for various charged states of an armchair (5,5) tube. For a given charged state, the binding energy is proportional to the square of the magnitude of an electric field, and hence the nonlinear polarization effect is negligible within this field. Without applied electric field, the tube is stabilized by having $-2e$, as shown in Fig. 1(b). This phenomenon is similar to that of $C_{60}$ and attributed to the strong electron affinity of carbon species. Alkali metal atoms, therefore, can be easily accommodated in the tube by donating their electrons to the tube, thus change the transport properties and reduce resistance of tubes.^{17} The ability of electron capture could depend on the local geometry and the number of carbon atoms in the system. In our case, we use 50 carbon atoms in addition to the 30 cap atoms. This may change slightly the number of electrons to be captured in the system.

![Graph](image1)

FIG. 1. (a) Binding energy of a capped (5,5) nanotube carrying charge $Q$, as a function of the strength of the applied electric field. (b) Binding energy of a capped (5,5) nanotube as a function of the charge $Q$.

![Graph](image2)

FIG. 2. (a) Schematic of defined effective work function $\Phi_{\text{eff}}$. As $\Delta\Phi$ increases linearly with the applied electric field, $\Phi_{\text{eff}}$ decreases. (b) Effective work function of a capped (5,5) nanotube, as a function of the strength of the applied electric field.

<table>
<thead>
<tr>
<th></th>
<th>IP (eV)</th>
<th>EA (eV)</th>
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<tbody>
<tr>
<td>Capped (5,5) CNT LDA</td>
<td>6.83</td>
<td>2.84</td>
</tr>
<tr>
<td>GGA</td>
<td>6.67</td>
<td>2.66</td>
</tr>
<tr>
<td>$C_{60}$ LDA</td>
<td>7.74$^a$</td>
<td>2.78$^a$</td>
</tr>
<tr>
<td>Experiment</td>
<td>7.6±0.2$^b$</td>
<td>2.65±0.02$^c$</td>
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$^a$Reference 19.
$^b$Reference 20.
$^c$Reference 21.
FIG. 3. (a) DOS of a capped (5,5) armchair tube in a neutral state ($Q=0$) under various applied electric fields. (b) DOS of a capped (9,0) zigzag tube in a neutral state ($Q=0$) under various applied electric fields. (c) DOS of a capped (5,5) armchair tube at zero field strength ($F=0$ V/Å) with various charges. (d) DOS of a capped (5,5) armchair tube with various charges under an electric field of 1 V/Å. The Fermi level is set to zero in all figures.
compared to that of C\textsubscript{60}. Table I shows the ionization potential (IP) and electron affinity (EA) of a capped (5,5) nanotube, giving similar results to those of C\textsubscript{60}. These values may depend on the number of atoms in the tube wall.\textsuperscript{18}

Although the (5,5) armchair tube is metallic, the capped armchair tube is semiconducting with a finite size of HOMO-LUMO gap, which is similar to C\textsubscript{60}, as suggested in the previous calculations.\textsuperscript{22} This suggests that the field emission from capped tubes may be interpreted by a semiconducting model rather than by a conventional metallic model. Saturation in the field emission currents which was observed in most carbon nanotubes may be explained by the presence of a cap in CNT's, because the current saturation is also observed in semiconductors.\textsuperscript{23} Figure 2(a) shows a schematic of definition of effective work function $\Phi_{\text{eff}}$, which is defined as the difference of the energy between the Fermi level and the LUMO, i.e., half the band gap in case of a semiconductor. The difference between the LUMO and the vacuum level $\Delta \Phi$ would vary when the strength of the applied electric field is changed. Figure 2(b) shows that $\Phi_{\text{eff}}$ decreases linearly with an increasing electric field, in good contrast with quadratic behavior in a metallic model.\textsuperscript{24} The effective work function approaches zero at a high electric field, and electrons can be emitted more easily.

Figures 3(a) and 3(b) show the density of states (DOS) of capped (a) armchair and (b) zigzag nanotubes as a function of the field strength in a neutral state. The DOS of a capped armchair tube at the Fermi level increases with field strength, whereas the DOS of a capped zigzag tube at the Fermi level is rather insensitive to the field strength. This may originate from the difference between metallic and zero-gap semiconducting tubes.\textsuperscript{25} The bond length changes are negligible in the presence of electric fields up to 1.5 V/Å.

Figure 3(c) shows the DOS of charged armchair tubes at zero field strength. Added charges will fill up the LUMO first, shift the Fermi level into the unoccupied states, and stabilize the tube more strongly by shifting the valence bands into deeper energies, as shown in the first two panels of Fig. 3(c). These agree well with the binding energy stabilization in charged states, as shown in Fig. 1(b). It is interesting to see that additional charges contribute uniformly to the whole occupied states and the bandwidth is contracted. Extraction of charges from the tube lowers the Fermi level into the occupied states, as shown in the bottom two panels of Fig. 3(c). The trend of the Fermi level shift of a capped zigzag tube is similar to that of a capped armchair tube.

The DOS at the Fermi level is not changed much by the external field of 1.0 V/Å for negatively charged states, as shown in Fig. 3(d), but the DOS near the Fermi level is increased by filling the HOMO and LUMO localized at the cap, as will be discussed later. For positively charged states, the DOS at (and near) the Fermi level increases under the field, but the HOMO and LUMO are not localized at the cap. In order for the change of DOS to contribute to the field emission currents, such states have to be localized at the cap. This will be discussed in the next paragraph.

Figure 4 shows change of HOMO's and LUMO's for various charged states under the applied electric field. For neutral states, the HOMO and LUMO charges are localized at the

FIG. 4. HOMO and LUMO of a capped (5,5) armchair nanotube. The left column shows local charge densities under no applied electric field and the right column shows those under an electric field of 1 V/Å. (a) A capped (5,5) nanotube in a neutral state ($Q = 0$). (b) A capped (5,5) nanotube in a charged state of $Q = -2e$. (c) A capped (5,5) nanotube in a charged state of $Q = 2e$. 

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Fig. 5. The Mulliken charge population of a capped (5,5) armchair and a capped (9,0) zigzag tube. The charges are averaged for each layer indexed in the figure. The lower graph is the change of the Mulliken charges when an electric field of 1 V/Å is applied.

When \( Q = -2e \) is added, the LUMO (Ref. 26) is filled and localized at the cap as shown in Fig. 4(b). This is similar to the \( n \)-type doping. With an electric field of 1 V/Å, both the HOMO and LUMO are localized at the cap, which is consistent with the DOS increase in the occupied states near the Fermi level. These states can contribute directly to the field emission currents. For charge extraction of \( Q = 2e \) as shown in Fig. 4(c), the HOMO is localized at the cap, whereas the LUMO is localized at the side wall, which is opposite to the case of \( Q = -2e \). This is similar to the \( p \)-type doping. The first level from the LUMO is localized at the cap, which can contribute again to the field emission currents.

For negatively charged states, the HOMO and LUMO are localized at the cap under an electric field. Because the local field can be enhanced easily at the cap by the local field enhancement factor, these electrons can be easily emitted by the external electric field. For positively charged states, the HOMO and LUMO are not always localized at the cap under an electric field. These states are not affected much by the external electric field.

Figure 5 shows the Mulliken charge population of both tubes. The charges are averaged for each layer indexed in the figure. More charges are accumulated near the top of the cap when the field is applied, regardless of the position of the pentagon at the cap, although the tendency of accumulating the charge is stronger in zigzag tubes than in armchair tubes. This suggests that the charge accumulation is mainly determined by the sharpness of the tip, not by its detailed atomic structure. Very recently Kuzumaki et al. reported from their experiment that the electron emission from a closed nanotube is not necessarily from pentagonal sites, but from the sharp tips. 27

IV. SUMMARY

We have performed density functional calculations of electronic structures of capped carbon nanotubes under electric fields along the tube axis. We found that the effective work function of a capped armchair nanotube decreases linearly with increasing field strengths, in good contrast with the quadratic behavior observed in a typical metal tip. This suggests that the capped nanotubes can be interpreted in terms of a semiconductor model rather than metallic one.

The DOS at the Fermi level increases with field strengths in armchair nanotubes, whereas it is not affected by the change of field strengths in zigzag nanotubes. This may be attributed to the differences in the nature of metallic and semiconducting nanotubes.

For negatively charged states, DOS at the Fermi level is not much changed by the external field, but the DOS near the Fermi level is increased by filling the HOMO and LUMO localized at the cap. These electrons can be easily emitted by the external electric field, contributing to the field emission current. For positively charged states, the DOS at (and near) the Fermi level increases under the field, but the HOMO and LUMO are not always localized at the cap. These states are not affected much by the external field. The Mulliken charge populations show that the field emission is not dependent on the atomic geometry of the tip but on the sharpness of the tip.

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13 We also tested calculations with a double numeric polarized basis set, which includes an additional p orbital of hydrogen atom, and the most complete set available in the code. The binding energy difference was less than 0.1% for LDA and GGA calculations.
15 The ionization potential changes with the number of tube layers. For instance, with nine layers, the ionization potential reduces by about 6%. We estimate these values to be valid with an error of approximately 10% with large layers.
22 The LUMO in the negatively charged state was originally HOMO in the neutral state. We still follow this notation from the definition of the Fermi level.