Electronic Structure and Field-Emission Characteristics of Open-Ended Single-Walled Carbon Nanotubes

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The field-emission mechanism of open-ended single-walled carbon nanotubes (SWNTs) is studied. Owing to electronic effects that directly alter the bonding mode and remarkably influence the work function, an open-ended SWNT has much better field-emission properties than a closed SWNT; owing to geometrical effects that slightly influence the work function and the amplification factor, an open-ended SWNT with relaxation has higher threshold voltage and higher current density compared to one without relaxation. It is suggested that adjusting the localized electronic states of the emitting regions, by electronic and geometrical means, could improve the field-emission properties of carbon nanotubes.

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Along with the development in fabricating, processing, and manipulating techniques for large-area highly ordered arrays of carbon nanotubes [1], it becomes possible that both single-walled carbon nanotubes (SWNTs) and multiwalled carbon nanotubes (MWNTs) are used as ultimate field emitters in the near future. The experiment [2] showed that field-emission properties of open-ended MWNTs obtained by laser evaporation or oxidative etching are dramatically enhanced compared with capped MWNTs, and a corresponding hypothesis that a linear carbon chain of sp-bonded carbon atoms unraveled from the edge of an open-ended MWNT by the force of the electric field was proposed. However, the field-emission pattern of the open end for the MWNT showed that electron emission seems to occur from the circular edges of graphite sheets [3]. Meanwhile, theoretical studies [4–6] focused on electronic structure and localized electronic states at tips have been reported for carbon nanotubes. Carroll *et al.* [4] found the presence of sharp resonant states in the local density of states (LDOS) near the ends of capped carbon nanotubes results in weak acceptor states in field emission. Han *et al.* [5] claimed that emission effects of flat-cut open-ended tubes are weaker compared with capped tubes that contradict the experiments [2,3] and the theoretical results by Adessi *et al.* [6].

Therefore, the field-emission mechanism of open-ended carbon nanotubes is unknown until now, which seriously restricts their applications. Based on the integrative analysis of structure, both geometrical and electronic structure, and the field-emission characteristics of tubes, we suggest that in open-ended carbon nanotubes, field-emission properties are dominated in substance by geometrical and electronic effects. In this Letter, we will clarify these two kinds of effects in essence and estimate their relative importance in field emission.

In our calculations, a finite-length cylindrical carbon cage consisting of 168 carbon atoms is chosen to represent an armchair C(6,6) open-ended carbon nanotube, where one mouth is opened and the other is terminated by hydrogen atoms to avoid the boundary effect. The geometrical structure is shown in Fig. 1b. Linear combination of atomic orbitals for molecular orbital (LCAO-MO) cluster method using the discrete variational scheme within the framework of local density approximation is employed [7]. The numerical free-atom variational basis sets selected are $2s2p$ atomic orbitals for C atom and $1s$ for H atom, respectively. In order to examine electronic effects on field emission of an open-ended SWNT, we select a closed SWNT, which is represented by the same dimension finite-length cylindrical carbon cage that both ends are terminated by hydrogen atoms, as a reference (shown in Fig. 1a).

We use the total energy minimization to obtain the equilibrium C-C bond length of hexagonal network in the carbon cage (1.463 Å), which is in accord with the practical case (1.44 Å) [8]. By analyzing the C-C bonding mode along the tube, we notice the significant difference between the behaviors of atoms located at the mouth and at the body. The number of the nearest neighbors (only 2) for the mouth atom is less than that for the body atom (3), and carbon atoms at the mouth are unsaturated with

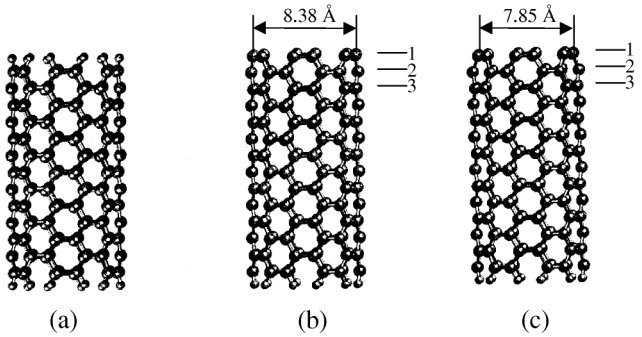

FIG. 1. Geometrical structures of closed (a) and open-ended single-walled carbon nanotubes before relaxation (b) and after relaxation (c). Numbers 1, 2, and 3 correspond to the atomic layers at the mouth, the first neighbor, and the second neighbor, respectively. Hydrogen atoms, represented by tint spheres, saturate the dangling bonds at the ends.

12 dangling bonds. Therefore, for carbon atoms at the mouth, besides two σ bonds and one π bond formed by hybridizing $2s$ and $2p$ atomic orbitals, the remaining valence electrons are in "no-bonding" states and the interaction between the corresponding atomic orbitals is far weaker than the rigid chemical bond. Using the total energy minimization to optimize the geometrical structure of an open-ended SWNT, we find that during relaxation, carbon atoms at the mouth shift uniformly to the core along the radial, with the diameter of the mouth varying from 8.38 to 7.85 Å, and the contraction ratio is up to 6.35%, whereas less atomic movement occurs along the longitudinal axis, and the shrinking ratio is less than 0.5%. The geometrical structure of this cage after relaxation is shown in Fig. 1c. This deformation characteristic of an open-ended SWNT not only is in good agreement with the morphology of perfect tip assumed in the experiments [9], but also indicates that the valence electrons in no-bonding states are localized as similar emitted electrons in the tip emission. Figure 2 shows the charge-density difference plots of closed and open-ended SWNTs before relaxation and after relaxation. From this figure, we find that the interaction mode between carbon atoms at the mouth varies from the repulsion (closed) to the attraction (open-ended) owing to "no-bonding" valence electrons (electronic effects); this interaction is far less than σ and π bonds and slightly strengthens the C-C bonding (geometrical effects). Obviously, electronic effects are dominant and geometrical effects lie in a subordinate position in the bonding of the emitting region for the open-ended carbon nanotube.

The field-emission characteristics of carbon nanotubes at low currents can be analyzed by the Fowler-Nordheim (FN) equation. Only ϕ and β in the expression of the slope p (i.e., $a\phi^{3/2}d/\beta$) of the FN equation constitute the link between structure and field-emission properties of carbon nanotubes. For field-emission materials, the work function ϕ of the emitting region is a very important parameter in judging its field-emission properties.

Recently, Groning *et al.* [10] obtained the work functions of 3.7 eV for SWNTs and 5.0 eV for MWNTs in the studies on field-emission properties of nanotube thin films. Suzuki *et al.* [11] reported the work function of 4.8 eV for SWNTs bundles by use of ultraviolet photoemission spectroscopy. Herein, we attempt to estimate the work functions ϕ of various electronic states in carbon nanotubes by the use of the first-principles calculations. Both experiments [1] and theoretical studies [4] showed that in carbon nanotubes, only electrons localized at the tip are emitted due to the unique tubular geometrical structure closed by the small radius tip and the same directions of the tube and the electric field. Therefore, it is important to establish the concept of localized states (i.e., "tip states"), which faithfully represents the electronic structure localized at one special spatial location (i.e., the tip), in the limit cluster. Despite the metallic behavior in the electric conductivity [12], armchair SWNTs have the same bonding characteristics [13] as those of graphite sheet. The nature of the covalent bond of C-C determines that the valence electrons localize only in the vicinity of the corresponding carbon atoms. Thus, the tip states are related only to the interaction behavior of the valence electrons localized at the tip. Within the framework of LCAO-MO, molecular orbitals (MO) Ψ_j to the one-electron Hamiltonian can be approximated by a linear combination of localized atomic orbitals and delocalized atomic orbitals ϕ_i from the various atoms that compose the molecule (or cluster),

$$\Psi_j = \sum_{i=\text{localized}} C_{ij}\phi_i + \sum_{i=\text{delocalized}} C_{ij}\phi_i , \qquad (1)$$

where C_{ij} is the mixing coefficient. It is easy to distill the localized electronic states at one spatial location of an SWNT according to the components of atomic orbitals localized at the same spatial location. The difference in potential energy of an electron between the vacuum level and the highest occupied molecular orbital in the localized states is defined as the corresponding localized work function. In our calculations, the vacuum level is set to zero, so the localized work function at one spatial location corresponds to the tunneling energy barrier of emitted electrons stayed at the same location. We use this method to calculate the conventional work function for a perfect tip of C(5,5) nanotube (5.08 eV), which is close to the experimental values [10,11].

First, we explore electronic effects on field emission in an open-ended carbon nanotube. We find that the existence of no-bonding valence electrons in an open-ended SWNT results in a remarkable variation of the work function of SWNTs from 5.44 eV (closed) to 4.86 eV (open-ended). Dyke *et al.* [14] had demonstrated that the field amplification factor β of the tip is mostly related to the geometrical structure of emitter. For a closed SWNT and an open-ended SWNT without relaxation, their amplification factors β are the same owing to the same geometrical structure. The slope p of the open-ended nanotube in the FN plot increases up to 15.6% compared with the closed nanotube, which indicates field-emission properties of tubes are remarkably enhanced. Recently, many important experiments under real conditions [15] showed that

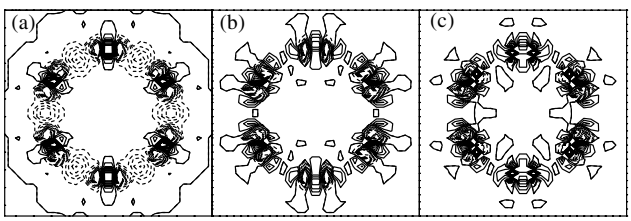

FIG. 2. Contour plots of charge-density difference at the tube mouth for closed (a) and open-ended SWNTs before relaxation (b) and after relaxation (c). Solid (dotted) contours denote contours of increased (decreased) density [in units of 0.003 $e/(\text{a.u.})^3$].

field-emission properties of carbon nanotubes dramatically vary with the variation of localized electronic states at the tips owing to foreign molecules adsorption and desorption. This further reveals that electronic effects on field emission of tubes are very significant.

Second, we explore geometrical effects on field emission of the open-ended carbon nanotube. With the approach as mentioned above, we can easily distill the localized electronic states corresponding to the carbon layers at the mouth, the first neighbor, and the second neighbor, and calculate the corresponding work functions, yielding 4.86 eV (mouth) and 5.25 eV (first neighbor) before relaxation, and 4.95 eV (mouth) and 5.20 eV (first neighbor) after relaxation. The slope p for the mouth atoms in the FN plot decreases up to 2.8% during relaxation, and the slope p for the first-neighbor layer atoms increases 1.6%, which indicates that the structural change slightly affects field-emission properties. The work function of the second-neighbor carbon layer does not vary during relaxation. The variation of energy levels for an open-ended SWNT during relaxation is shown in Fig. 3. We can see the types of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), labeled as 39 A1 and 29 B2, respectively, do not vary, but the corresponding energies decrease during relaxation. The energy of molecular orbital 18 A2 corresponding to the first-neighbor carbon layer alters from -5.25 eV (before relaxation) to -5.20 eV (after relaxation). These variations are in accordance with the variations of the calculated localized work functions.

Based on the analyses as above, we know that geometrical effects on field-emission properties are far less important than electronic effects. In consideration of the same directions of the electric field and the tube axis in applications, it is easily found that besides carbon atoms at the mouth, carbon atoms located at the first-neighbor layer also contact with the vacuum along the direction of the electric field in an open-ended SWNT after relaxation, and the number of carbon atoms and emitted electrons involving field emission dramatically increases. So in an open-ended SWNT, the threshold voltage and current density slightly increase owing to geometrical effects. The energy gap between HOMO and LUMO varies from 0.02 to 0.12 eV after relaxation, and is far smaller than that of a closed SWNT (0.69 eV) [13]. We can suggest that electronic effects significantly reduce chemical stability, but geometrical effects slightly enhance chemical stability in open-ended SWNTs because the smaller HOMO-LUMO gap means lower chemical stability.

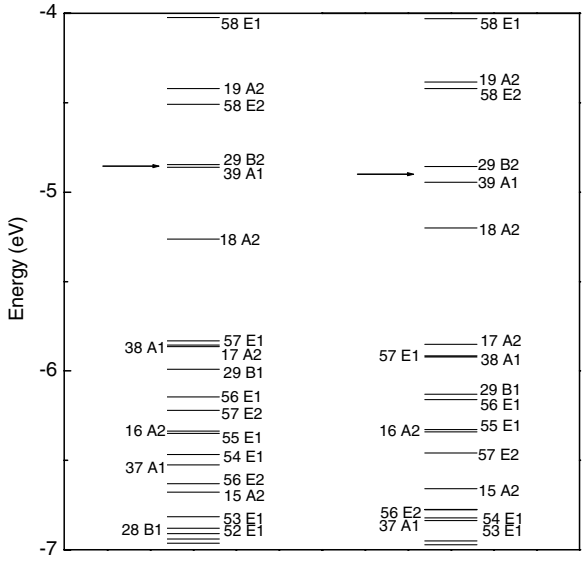

FIG. 3. Distributions of energy levels near the Fermi level in open-ended SWNTs before relaxation (left) and after relaxation (right). Arrow represents the Fermi level.

Figure 4a displays the calculated DOS of closed and open-ended SWNTs without and with relaxation. Compared with the DOS of a closed SWNT, the DOS of open-ended SWNTs exhibit significantly different features: (i) the deep valley corresponding to the minimum DOS value moves from the Fermi level to the lower energy level, and (ii) the first DOS peak profile below the Fermi level significantly increases. The first feature of DOS indicates that chemical stability of an open-ended SWNT remarkably reduces, which is consistent with the variation of the energy gap between HOMO and LUMO of open-ended and closed nanotubes. In a closed SWNT, $2p$ valence electrons of all carbon atoms have the uniform contributions to DOS at the Fermi level [13], whereas, in open-ended SWNTs, $2s$ and $2p$ valence electrons of carbon atoms at the tube mouth contribute most to DOS at the Fermi level, as shown in Figs. 4b, 4c, and 4d. The fact that the minimum DOS deviates from the Fermi level as shown in Fig. 4b is associated with the electronic states localized at the mouth ("dangling" bond), and indicates that donor or acceptor states are easily yielded in open-ended carbon nanotubes, which are propitious to field emission. The different contributions to DOS at the Fermi level for the different carbon layers as shown in Figs. 4b, 4c, and 4d are consistent with the FEM experiments of MWNTs [16], which revealed that the spatial charge distribution of the emitting states of a single tube is nonhomogeneous. We observe a small distinction between the LDOS of an open-ended SWNT before relaxation and that after relaxation, which directly reflects geometrical effects. After relaxation, the contributions from carbon atoms at the mouth to the DOS at the Fermi level and adjacent levels decrease, those from the first-neighbor carbon layer increase, and those from the second-neighbor carbon layer remain unchanged. This is consistent with the variation of geometrical structure and the variation of the work function for each layer during this relaxation.

In conclusion, we clarify geometrical effects and electronic effects on field emission of open-ended single-walled carbon nanotubes. The presence of no-bonding valence electrons at the tube mouth not only

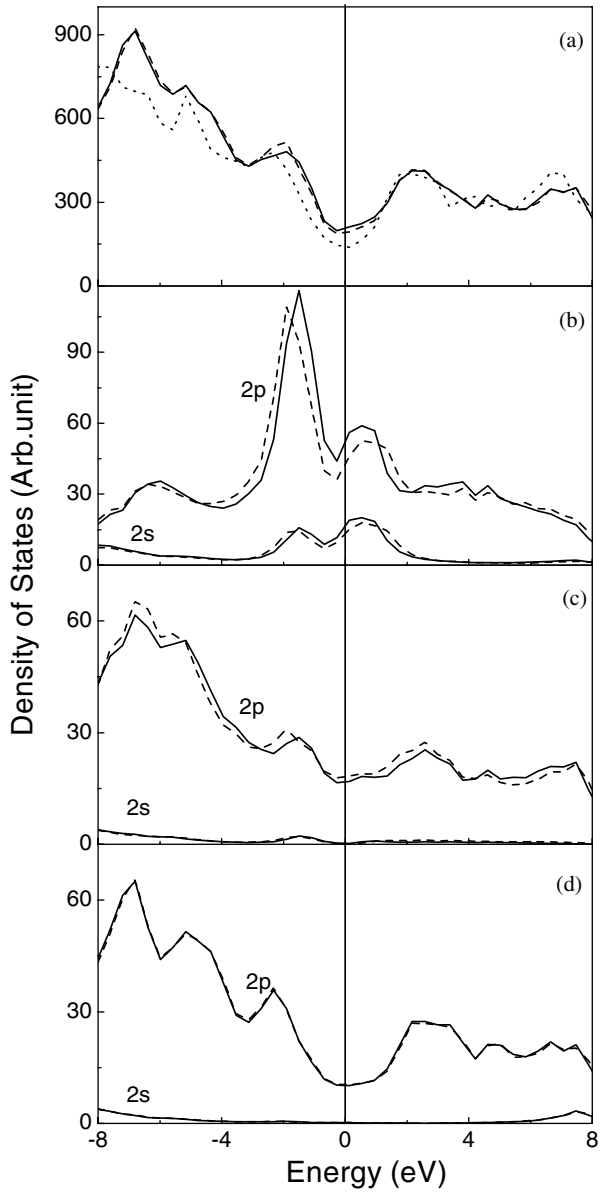

FIG. 4. (a) Density of states for closed and open-ended SWNTs. Solid, dashed, and dotted lines correspond to an open-ended SWNT before relaxation, an open-ended SWNT after relaxation, and a closed SWNT, respectively. (b),(c),(d) correspond to the local density of states for the carbon layers at the mouth, the first neighbor, and the second neighbor in open-ended SWNTs before relaxation (solid lines) and after relaxation (dashed lines), respectively.

induces the variation of the electronic structure at the mouth, the decrease of the work function, and the reduction of chemical stability of the tube, but also strengthens the bonding between carbon atoms at the mouth. Electronic effects on emission properties are more significant than geometrical effects for open-ended SWNTs. Thus, we can speculate that adjusting the localized electronic states of the emitting region for the carbon nanotube would be a main and new way to improve field-emission properties. In detail, besides modifying the geometrical structure of a SWNT by increasing defects in its tip or opening its end, substituting carbon atoms at the tip with foreign atoms that have more valence electrons, such as nitrogen atom, may improve field-emission properties of the carbon nanotube.

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