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Field emission properties of double-wall carbon nanotubes

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Abstract
Using a first-principles method, we study field emission properties of double-wall carbon nanotubes with various end geometries and combinations of inner and outer walls. The open double-wall nanotubes exhibit substantial contribution to the emission current from the extended π states. These states are insensitive to the detailed tip structure or the presence of foreign adsorbed molecules and the resulting emission current is expected to be stable under moderate vacuum environment. The mechanical stiffness also increases significantly compared to the single-wall nanotube, ensuring prolonged device lifetime under high-field operating conditions of the field emission display.

1. Introduction

The carbon nanotube (CNT) is a promising nanomaterial with unique physical properties [1]. Its geometry and chemical properties are ideal for an electron emitter with a low threshold voltage and long lifetime [2] and a wide range of applications have been suggested, e.g., field emission displays (FEDs), miniature x-ray sources, and cold cathode components of microwave power tube amplifiers [3–5].

The reliability of field emission devices made of CNTs largely depends on the long term stability of emission currents under a moderate vacuum condition as well as the structural stability in a rapidly switching AC field. Many experiments as well as computational studies show that molecules such as O_2 and H_2O affect the structure of the tip of the single-wall carbon nanotube (SWCNT), leading to a large fluctuation and degradation of the emission current [6, 7]. The problem is less serious with the multi-wall carbon nanotube (MWCNT), but its smaller aspect ratio undermines the emission performance compared to the SWCNT. Recently, experimental conditions to grow preferentially double-wall carbon nanotubes (DWCNTs) have been identified [8]. While maintaining an aspect ratio similar to that of the SWCNT, the DWCNTs may also achieve the improved current stability dictated by MWCNTs [9]. For further progress toward DWCNT-based FED, it is important to understand the emission mechanism of DWCNTs and their mechanical response to strong AC electric fields. In this paper, we present first-principles calculations on the field emission characteristics of DWCNTs with various tip structures to shed light on the field emission mechanism of DWCNTs.

2. Computational method and model system

Numerical calculations are carried out based on the *ab initio* pseudopotential method to obtain the electronic structure and equilibrium geometries of DWCNTs. The local density approximation is employed for the exchange–correlation energy [10] and the Troullier–Martins type pseudopotentials [11] are used. We employ pseudo-atomic orbitals [12] in expanding wavefunctions and the external electric field is simulated by a saw-tooth potential. The electronic structure of the emission tip under the electric field is obtained and the field emission current is evaluated by examining the time evolution of the wavefunctions. This method has been applied to the field emission phenomena of other types of carbon systems [13–15]. Compared to a tight-binding approach [16], the electronic tunnelling is directly simulated to calculate the emission current.

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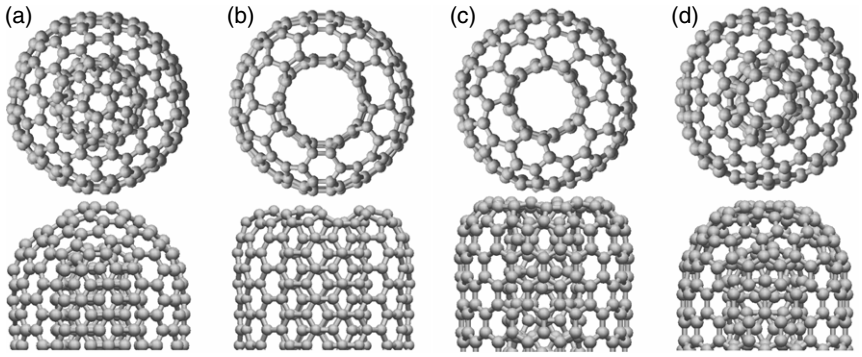

Figure 1. The top and the side view of the atomic model of DWCNT tips. The actual lengths in the calculation (∼30 Å) are much longer than those appearing in the figure. All dangling bonds of carbon atoms at the bottom are passivated by hydrogen atoms (not shown here). (a) c-(5, 5)@(10, 10) model with the closed domes at the tip. (b) b-(5, 5)@(10, 10) model. The bridge atoms connect edges of each SWCNT. (c) b-(4, 4)@(16, 0) model. (d) c-(4, 4)@(16, 0) model.

We choose four representative types of DWCNTs for detailed studies (see figure 1). The first and second models consist of the (5, 5) and (10, 10) SWCNTs with closed caps (figure 1(a)) or the bridge atoms connecting two open edges (figure 1(b)). We denote them as c-(5, 5)@(10, 10) and b-(5, 5)@(10, 10), respectively. These two models involve only metallic SWCNTs. The third model consists of the metallic (4, 4) SWCNT inside the semiconducting (16, 0) SWCNT. As before, we consider both bridged (figure 1(c)) and open tips (figure 1(d)) and they are called b-(4, 4)@(16, 0) and c-(4, 4)@(16, 0), respectively. We note that the open models in figures 1(b) and (c) are representative tip structures when ambient molecules bombard and break open the cap structure. One can also conceive a structural combination of a semiconducting SWCNT inside a metallic one. (The DWCNT made of two semiconducting tubes is not considered because it does not conduct well and is not suitable as an electron emitter.) However, in this case, nearly perfect screening of the outer metallic SWCNT will prohibit the electrons in the inner semiconducting SWCNT from being accelerated by external electric fields. Therefore, the emission current of this model should be the same as that of a single metallic SWCNT and we will not consider this case further here.

3. Field emission properties

For c-(5, 5)@(10, 10) shown in figure 1(a), the analysis on the charge distribution under an applied electric field shows that electrons on the (5, 5) nanotube are almost unaffected by the field because of the metallic screening of the (10, 10) nanotube (see figure 2). This indicates that the DWCNT with a closed metallic nanotube as an outer wall exhibits essentially the same emission mechanism as a metallic SWCNT. The additional current channel provided by the inner (5, 5) tube contributes little to the emission because the electrons on the inner tube should hop into the extremity (dome-shaped cap) of the outer (10, 10) tube in order to contribute to the current. On the other hand, b-(5, 5)@(10, 10) in figure 1(b) shows a quite different emission mechanism in comparison with that of c-(5, 5)@(10, 10). In figure 3, the Fowler–Nordheim (FN) plot is shown for b-(5, 5)@(10, 10), decomposed by the character of emitting states. The FN plot for b-(5, 5)@(10, 10) is almost linear, as expected for the conventional metallic tip, and the

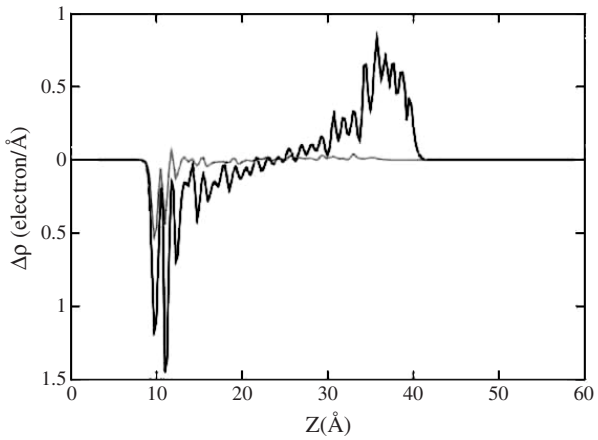

Figure 2. The calculated charge redistribution of c-(5, 5)@(10, 10) under an applied electric field of 0.7 V Å^{-1}. The grey and the black curve correspond to the redistributed charge of the inner (5, 5) and outer (10, 10) SWCNT respectively.

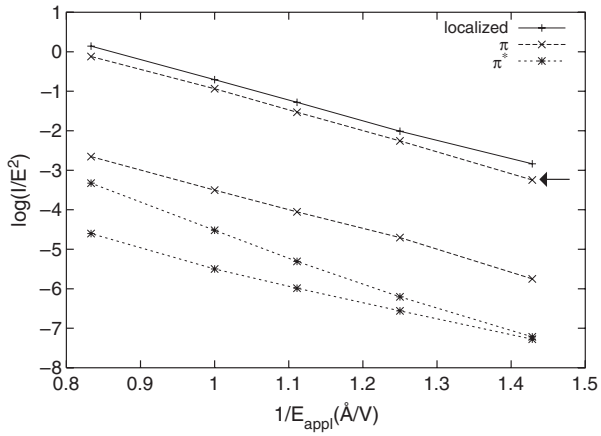

Figure 3. The calculated I–V characteristics of b-(5, 5)@(10, 10). The current from the π state of the outer (10, 10) nanotube is indicated by an arrow.

relative contribution between emitting states does not change much as E_{appl} is varying. It turns out that ∼40% of the total current comes from the extended π states of the DWCNT and ∼50% from the states localized at bridge atoms connecting

inner and outer nanotubes. The large reduction of currents from π^* states compared to π states is attributed to the rapid phase modulation around the circumference of the nanotube which suppresses the coupling of the π^* states to the vacuum states beyond the energy barrier [13].

The significant contribution of the π state is in stark contrast with the case of the closed SWCNT where the localized state dominates the emission current [13, 17]. The large current from the extended π state of the open DWCNT implies an improved current stability over the closed nanotubes since the current-carrying property of the extended state is rather insensitive to the presence of foreign molecules at the tip. Unlike the closed nanotube, the open tip of b-(5, 5)@(10, 10) exposes the π states to the region of high electric fields and increases the tunnelling probability. On the other hand, although localized states have the largest amplitudes at the high field region, the phase of the wavefunction of localized states changes rapidly from one bridge site to another. This azimuthal phase variation reduces emission currents of the localized states because it weakens coupling to the vacuum states [13]. These factors result in an amount of current from π states comparable to that of the localized states in b-(5, 5)@(10, 10). If we could produce an ideal open SWCNT, a large contribution of the extended state to the current would occur for the same reason as above. In practice, however, the edge structure of the open SWCNT is much less stable than the open DWCNT where the bridge atoms saturate dangling bonds.

In b-(4, 4)@(16, 0), we find a tendency different from that of b-(5, 5)@(10, 10). In figure 4, the density of states is decomposed with respect to the inner (5, 5) nanotube, the outer (16, 0) nanotube, and the bridge atoms. We find that the extended π state in the inner nanotube (figure 4(a)) is pinned near the Fermi level. On the other hand, the extended state of the outer semiconducting (16, 0) nanotube (figure 4(b)) is found to move deeply below the Fermi level as E_{appl} increases so that its tunnelling probability decreases substantially. This is due to the incomplete screening of the semiconducting nanotube. The emission current from the π state of the metallic (4, 4) nanotube is comparable to that of the localized state at the bridge atoms, similar to b-(5, 5)@(10, 10).

In the last model considered in figure 1(d), the metallic (4, 4) SWCNT is enclosed by the capped semiconducting (16, 0) SWCNT with the cap geometry shown in figure 1(d). This model turns out to have enhanced currents from the localized state on the outer cap whose energy position approaches the Fermi level as E_{appl} increases. The emission from the inner metallic tube is negligible since the electric field is substantially screened by the outer semiconducting tube.

4. Mechanical properties

Considering the strong local electric field applied on nanotubes in the FED (0.3–1.0 V Å^{-1}), the mechanical properties of the emitting tip are also important for the device durability. A nanotube that stands askew will bend upward by the electrostatic force acting on the induced charge at the tip of the nanotube. Because the electric field is switched on and off in the FED, the corresponding vibrational motion of nanotubes eventually leads to mechanical fatigue. In addition,

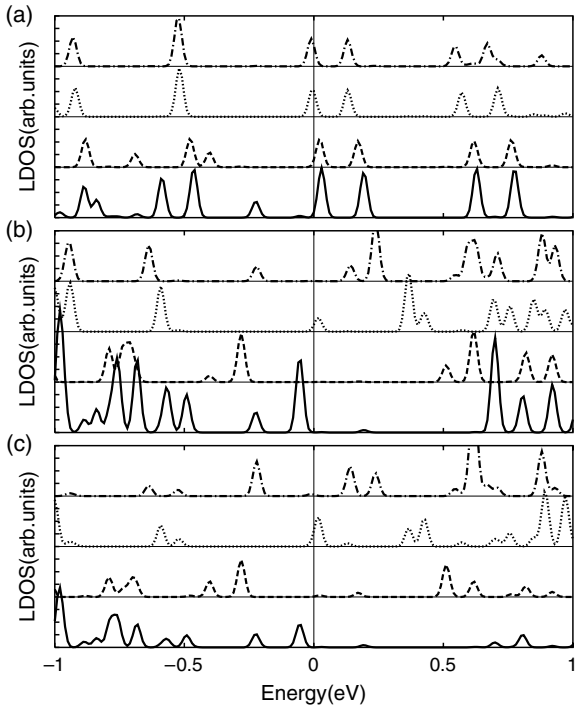

Figure 4. The local density of states (LDOS) of b-(4, 4)@(16, 0) at different applied fields projected on (a) the inner (4, 4) nanotube, (b) the outer (16, 0) nanotube, and (c) the brige atoms. The Fermi level is set to zero in the energy level. The solid, dashed, dotted, and dash–dotted curves represent the LDOS at $E_{\mathrm{appl}} = 0.0$, 0.3, 0.6, and 0.9 V Å^{-1}, respectively.

the uncontrolled displacement of the nanotube position by the electrostatic force may affect the sharpness of images on the phosphor screen.

The characteristic vibrational frequencies of typical nanotubes range from MHz to GHz [18], while the frequency of the AC electric field in a FED device is below 100 Hz. Thus one can assume that nanotubes are under the static electric field. In this situation, a nanotube bends like a needle-shaped conductor as the force is applied near the tip of the nanotube [19]. Resorting to the continuum model [20], one can describe the nanotube in the FED as a clamped cantilever of length l with an electrostatic force f applied on its tip. The displacement of the nanotube tip d is given by $d = \frac{fl^3}{3EI}$, where E is the Young modulus of the nanotube and I $(=\pi(r_{\mathrm{o}}^4 - r_{\mathrm{i}}^4)/4)$ is the areal moment of inertia of an elastic cylinder with outer and inner radii of r_{o} and r_{i}, respectively [20]. Under the typical condition of field emission, d is of the order of 10 nm. The larger outer radius r_{o} (or smaller inner radius r_{i}) and higher Young's modulus [21] of the DWCNT compared to those of SWCNTs indicate that the displacement of the DWCNT, d, is much smaller than that of the SWCNT. For example, the d of the (5, 5)@(10, 10) DWCNT is only $\sim 1/8$ of the corresponding value of the (5, 5) SWCNT.

5. Conclusion

In summary, our calculation demonstrates that the FE current from the DWCNT is more stable than that of the SWCNT because (i) in the case of the open DWCNT, the extended

character of the emitting states gives a relatively constant emission current irrespective of microscopic details of the tip structure or the possible adsorption of foreign molecules and (ii) the enhanced mechanical stiffness of the DWCNT makes the device more durable under rapid field switching.

Acknowledgments

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