

Field Emission of Carbon Nanotubes and the Electronic Structure of Fullerenes Encapsulated in Carbon Nanotubes

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ABSTRACT

We have performed first-principles calculations on the field emission of carbon nanotubes. The three-dimensional character of the current source, as well as the effect of the external electric field, are explicitly considered. The calculated electron-leakage by solving the time-dependent Schrödinger equation is quite linear in short time scale, giving the tunneling rate from the emitter to the vacuum. The total current fits the Fowler-Nordheim formula reasonably well. The magnitude of the current associated with each electronic state is found to exponentially depend on the energy level. We have also performed first-principles pseudopotential calculations for the electronic structure of fullerenes such as C_{82} encapsulated in single-walled carbon nanotubes. We find a charge transfer occurs between the carbon nanotube (CNT) and C_{82} , and states are produced by the hybridization of C_{82} and the CNT.

Keywords: field emission, carbon nanotube, carbon nanopeapod.

1 INTRODUCTION

Due to its high aspect ratio and the mechanical strength, the carbon nanotube [1] is regarded as a new material for the electron emitters to be used in the field emission display [2] as well as in the coherent electron source [3]. However, the emission mechanism of the nanotube is still not well understood and many unusual observations in the emission currents of carbon nanotubes remain to be explained [4], [5]. In the early study on the field emission from open carbon nanotubes [6], it was suggested that the carbon chains ravelling from the nanotube edge induce remarkable changes in the emission current. In that experiment, the current was greatly quenched when the laser was illuminated on the nanotube and it was suggested that the elimination of the carbon chains at the end of the tube was the main reason for the significant current reduction.

Theoretical estimates of the emission current are usually done in a semi-classical fashion based on the Fowler-Nordheim (F-N) theory. The potential around the tip

region is obtained by solving the classical electrostatics with the Laplace equation [7] or from the quantum mechanical calculations [8]. The transmission functions are then evaluated by using the one-dimensional semiclassical approach (e.g., WKB approximation) along a specific line in the emission direction [9]. The electronic structure of the emitter is reflected in the supply function, as a form of the density of state. Such a simplified model, however, is not appropriate for nanostructures. For instance, the boundary of the tip is not a well-defined physical quantity at the atomic scale and the potential obtained by solving the Laplace equation would not be valid for nanosize systems. In addition, the one-dimensional WKB calculation neglects any spatial variations of the wave function on the xy -plane (the emission is in the z -direction). Even for a flat metal plane, the suppression of the current from the d band compared to the s band has been well addressed in many works. [See Ref. 10 and references therein.] The situation becomes more complicated in the nanostructures where the xy -dimension of the tip is on the nanometer scale. It is also well-known that the total current changes significantly in the presence of the localized states induced by the adsorbates at the tip [10]. The contribution of the localized states increases for the nanostructures where the atomic size of the tip restricts the number of the conducting channels, but these localized states are not well described in the semi-classical approach.

2 FIELD EMISSION

In this article, we will first present the results of the first-principles calculation on the field emission of carbon nanotubes, addressing the above-mentioned relevance of the realistic computation. In our analysis of the field emission process, we do not make any simplifying assumptions on the geometry, potential distributions, or electronic states. We calculate the electronic structures of carbon nanotubes (under a given applied electric field) using the standard *ab initio* pseudopotential method [11] with the local density approximation. Troullier-Martins pseudopotentials in the separable form are used with a cutoff energy 40 Ry to ensure the reliable computational results. When computing the potential driving the field emission, we have used

pseudo-atomic-orbitals in the expansion of wave functions [12]. Suzuki-Trotter type split operator method [13] and the plane waves are used for tracing the electron motions. A saw-tooth type potential is applied for simulating the external electric field. Details have been presented elsewhere [14].

In a unit supercell, we have 12 carbon atoms forming a linear chain with two hydrogen atoms attached at both ends. The H atoms saturate the dangling σ -bonds in the bare carbon chain, eliminating states near the Fermi level. Therefore, the current sources near the Fermi level are all extended π -states. The vacuum space is 45 Å in length outside the carbon chain. The state right above (LUMO state) and below the Fermi level (HOMO state) are 3.9 and 5.8 eV below the vacuum level, respectively. Since the pseudo-atomic orbitals are slightly shrunk from the original atomic orbitals, the additional Coulomb energy may cause some error in the energy levels of each eigenstates.

At $t = 0$, the wave functions are confined within the emitter because the local basis set is used. Upon changing basis to plane waves at $t > 0$, the electron starts to leak out of the carbon chain and the electron density in vacuum begins to increase. In order to evaluate the rate of electron leakage, we integrate the electron density inside the carbon chain (ρ_{in}) over $z_0 < z < z_1$, with z_0 and z_1 effectively defining boundary planes that separate the carbon chain and the vacuum. The time increment Δt in the time-displacement operator ($e^{-iH\Delta t/\hbar}$) is set to 0.1 a.u. (1 a.u. = 0.0242 fs) and the operator is symmetrically decomposed up to the fourth order of Δt [15]. The integration boundaries z_0 and z_1 are fixed at 3Å outside the H atoms but the results are insensitive to the variations of z_0 by an order of angstrom.

Before $t = 50$ a.u., the electron-leakage is quite linear in time, giving the transition rate in the emission process. Shortly after $t = 50$ a.u., the tail of the wave function reaches the boundary of the supercell in our simulation where a large barrier is present because of the saw-tooth type potential. The interference between the outgoing and reflected waves is shown as small wiggles at $t = 80$ a.u. The reflected wave begins to flow backward into the carbon chain around $t = 110$ a.u. Finally, the resonance occurs near the end of our simulation (Rabi oscillation) and large changes in ρ_{in} are observed. To avoid such a computational artifact, we take the slope around the $t = 50$ a.u. as the transition rate of the state. It is found that the initial time region showing the linear behavior can be extended by adopting a longer supercell, consistent with the above analysis. The current for each state is evaluated by multiplying the electron charge, the transition rate, and the occupation number. Each level is doubly degenerate due to the rotational symmetry of the carbon chain. The magnitude of the current contributed by each state is exponentially de-

pendent on the energy level. Due to the exponential decay of the current to the low energy side, it turns out to be sufficient to consider only the states within ~ 2 eV below the Fermi level.

3 CARBON NANOPEAPODS

We then calculate the electronic structure of fullerenes encapsulated in carbon nanotubes. Since the discovery of CNTs in 1991 [1], a lot of efforts have been exerted to encapsulate many kinds of molecules inside the CNTs by various methods such as chemical insertion, physical insertion, and arc encapsulation [16]–[18]. A few papers reported the observation of the single-walled carbon nanotubes (SWNTs) with a chain of fullerenes (or endohedral metallofullerenes) inside, the so-called carbon nanopeapods [19]–[21]. Various fullerene molecules were found to be packed with a regular intermolecular distance of ~ 1 nm in SWNTs through High-Resolution Transmission Electron Microscopy and electron diffraction pattern [22]. Recently, it was observed that parts of the nanotubes appear brighter than other areas when topographies of metallofullerene nanopeapod (Gd@C₈₂@SWNT) are imaged by the STM [23]. In these systems, the diameter of most SWNTs is around 1.4 nm. If the diameter of the CNT encapsulating fullerenes is smaller than that of inserted fullerene plus twice the van der Waals distance, it is possible that there is strain on the carbon nanotube and fullerenes, or charge redistribution can be brought about by the hybridization of the encapsulated fullerene and CNT states. Most significantly, the carbon nanotube encapsulating the metallofullerenes exhibits spatially modulation of the band gap along the tube axis [23].

We choose the C₈₂@(12,8) nanotube and the C₈₂@(17,0) nanotube because the nanopeapods observed by J. Lee *et al.* [23] were all semiconducting CNTs of about 1.4 nm in diameter. We have performed first-principles pseudopotential calculations using a localized basis set within the local density approximation (LDA). To consider only the interaction between the fullerene and the nanotube, we assume that the distance between fullerenes is much longer than the typical van der Waals distance (~ 3.4 Å).

The density of the states (DOS) of the nanotubes with the fullerenes inside are shown in Fig. 1. Because the distance between fullerenes is much longer than the typical van der Waals distance (~ 3.4 Å), the DOS here is essentially that of the isolated fullerene encapsulated in the tube without the interaction between fullerenes. Figure 1(a) shows the DOS of C₈₂ encapsulated in a (12,8) carbon nanotube, and (b) shows that of C₈₂ encapsulated in a (17,0) nanotube. Comparison between the two indicates that the size of the energy gap (~ 0.5 eV) and other electronic structures are more or less similar. The states associated with C₈₂ are located

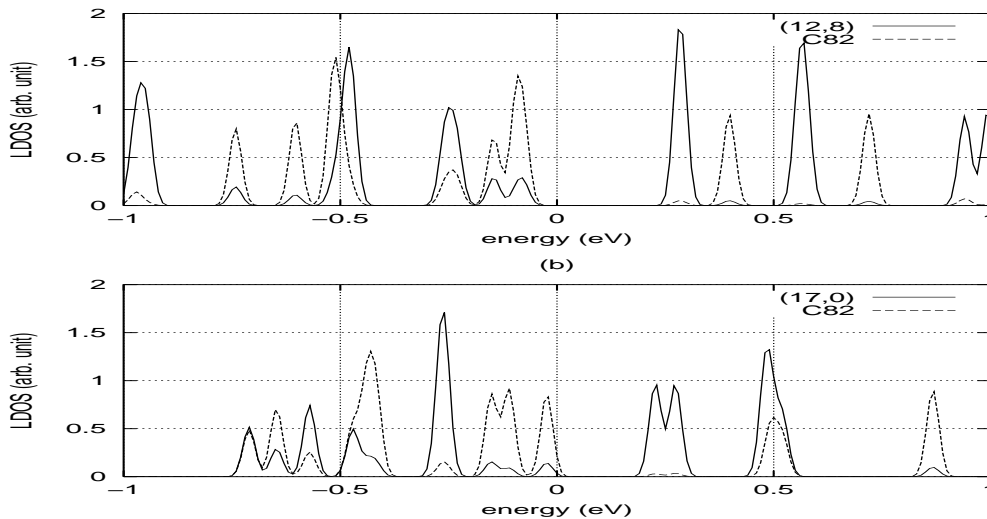


Figure 1: Density of States of (a) $C_{82}@CNT(12,8)$ and (b) $C_{82}@CNT(17,0)$.

just below the Fermi level (zero of the energy) in both cases as indicated in dashed lines (between -0.2eV and 0). Since the $(17,0)$ tube has about the same diameter as the $(12,8)$ tube, the similarity of the gap is expected for unstrained nanotubes. However, a nontrivial result of our calculation is that the gap changes very little by the insertion of a relatively large-sized fullerene, C_{82} , into the $(12,8)$ or $(17,0)$ nanotube. According to the theory for nanotubes under large elongation along the tube axis, (n,m) nanotube experiences an increase of the gap when $n - m = 3k + 1$ is satisfied (n , m , and k are all integers). A $(12,8)$ tube falls into this criterion. On the other hand, the nanotube should exhibit a decrease of the gap when $n - m = 3k - 1$ is satisfied. Our calculations of the relaxed geometry show that the strain is very small (much less than 1% in either the axial or circumferential direction) and the energy gap changes by a small amount for both $(12,8)$ and $(17,0)$ nanotubes.

We find a charge transfer from the carbon nanotube to C_{82} . The charge transfer is expected to influence the band gap. The substrate metal (usually gold) also gives rise to charge transfer which at least partially explains the experimental band gap modulation.

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