First-principles study on electron field emission from nanostructures

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A first-principles approach is introduced to calculate electron field emission characteristics of nanostructures, based on the nonequilibrium Green function technique combined with the density functional theory. The method employs atomic-like basis orbitals with large confinement radii and lithium anode to describe the electron density in the vacuum between the nanostructure tip and the anode, so takes the presence of emitted current into account. The simulation results on a capped single-walled carbon nanotube reproduce the experimental trend closely, in particular, the current saturation and the deviation from the Fowler-Nordheim behavior.

Electron field emission (FE) has been one of active research areas owing to its theoretical, as well as commercial, significance.1 In recent years, various nanostructures, including carbon nanotubes, metal oxide nanowires and nanoneedles, have been synthesized, and among many applications areas, they have emerged as promising candidates for electron emitters due to their very high aspect ratios.2–7 Actually, it has been demonstrated that single-walled carbon nanotubes (SWNT) provide low turn-on voltages and brightness values of an order of magnitude higher than typical conductors such as copper and silver.2–7 Given these experimental results, it is important to develop theoretical methods which can calculate and analyze FE characteristics of any nanostructures accurately.

The first model for FE from metal surfaces was proposed by Fowler and Nordheim in 1928, which assumes that under an external electric field electrons in the metal tunnel through a one-dimensional (1D) potential barrier into the vacuum.8 The emitted current, when graphically expressed on ln[I/E −2] versus E−1 scales, where I is current and E is electric field, exhibits a linear relationship, which is known as the Fowler-Nordheim (FN) plot. This model has been widely used by experimentalists to interpret the performance of electron emitters like the nanostructures.2–7 However, the full applicability of the FN model to the FE from the nanostructures is not obvious: electron states in the nanostructures are not similar to that in the metal, and the nanostructures are not an infinitely wide surface, but three-dimensional (3D) structures. Thus, a more general and accurate treatment than the FN model is required, and among various approaches first-principles methods are the most adequate for this goal.

There have been some first-principles methods to calculate the FE characteristics of the nanostructure emitters. Han and co-workers calculated the many-body wave function of the emitting nanotube using a pseudopotential-based time-dependent density functional theory approach.9,10 However, in order to calculate transmission functions they used a 1D potential barrier. Next, Khazaei et al. developed an approach to calculate the FE properties based on first-principles local density of states and effective potentials.11 Although it has been used in several theoretical works on the FE from various nanostructures,12–15 it also uses a 1D potential barrier and the WKB approximation to calculate the tunneling current. Recently, Yaghoobi and co-workers proposed a method based on a real-space first-principles Hamiltonian in the nonequilibrium Greens function (NEGF) and Fisher-Lees transmission formulation, which took the 3D nature of the problem into account.16 However, their first-principles Hamiltonian and NEGF are constructed in the absence of electronic current.

To the best of our knowledge, a first-principles approach based on the electron density and the Hamiltonian determined self-consistently in the presence of electronic current, has not been reported to date. Here, for the first time we present a first-principles method for calculating the FE characteristics of nanostructures using the NEGF technique combined with the density functional theory (DFT),17–19 which allows the nonequilibrium conditions to be taken into account.

In FE experiments using a nanostructure as an electron emitter, the nanostructure is grown on a cathode electrode and placed in front of an anode at some distance. As it has been shown that most of the nanostructure remains equipotential under an external field and potential drop occurs mainly very close to the tip of nanostructure,20 the FE characteristics of the nanostructure can be determined by the region that encapsulates the nanostructure tip and vacuum. Therefore, it is reasonable to simulate only a small section close to the tip of nanostructure, which allows us to study the FE using fully first-principles approaches. However, such a short section of the nanostructure would not reproduce the strong field enhancement that the entire nanostructure would have due to its high aspect ratio. Although in order to compensate for the lack it is common to use an electric field value that already contains the effect of field enhancement,16 typically several hundred times stronger than the applied external field,21 we will not introduce such parameters in the simulation.

Our method employs the state-of-the-art quantum transport algorithms based on the DFT and the NEGF combined with the two-probe model (electrode-
used confinement radii of basis orbitals are $2\sim$ but there exists electronic current, because the commonly
uum between the nanostructure tip and the anode, where the electron wave function and the electron density in the vac-
FE problem, one challenge is how to describe the electronic density in the vacuum, by decreasing the energy shift $\delta \varepsilon$
so that basis set is sufficient to describe the electron density.
The two-probe system the emitted current can be calcu-
loted numerical eigenfunctions $\varphi(l)$ of the atomic pseudopotential $V_l(r)$ for an energy $\varepsilon_l + \delta \varepsilon_l$ chosen so that the first node occurs at $r_l^f$:&&&&&&&&&&&&&&&&
\begin{align}
\left(-\frac{1}{2r} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l(r)\right) \varphi_l(r) & = (\varepsilon_l + \delta \varepsilon_l) \varphi_l(r),
\end{align}
with $\varphi_l(r_l^f) = 0$. When we apply this package to the FE problem, one challenge is how to describe the electron wave function and the electron density in the vacuum between the nanostructure tip and the anode, where there are no atoms and thus there are no basis functions, but there exists electronic current, because the commonly used confinement radii of basis orbitals are $2\sim 3$Å. To solve this problem, we extend the scope of basis orbitals so that basis set is sufficient to describe the electron density in the vacuum, by decreasing the energy shift $\delta \varepsilon$. In the two-probe system the emitted current can be calculated by the Landauer-Büttiker formula:&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&
mized capped nanotube as input structure, the current-voltage (I - V) characteristics were calculated and the results are shown in Fig. 2 with a FN fit for comparison. The corresponding plot on FN scales is also shown in the inset figure, which obviously deviates from a straight line and exhibits a non-FN behavior. The current saturation behavior, which has been previously observed experimentally in single-walled carbon nanotubes, is quite evident.

Insight can be gained into this saturation behavior by examining the transmission spectrum (Fig. 3). In the figure shaded areas represents the integrated transmission in the bias window, which is referred to the energy interval from the chemical potential of the left electrode to that of the right electrode. The higher integrated transmissions in the bias window, the higher emitted current. It is clearly seen that the integrated transmission in the bias window increases with bias voltage increasing at low bias, resulting in the pseudoeponential increase of emitted current. But at high bias the integrated transmission remains nearly unchanged, although the bias window gets wider with bias voltage increasing, which explains the current saturation behavior. Our results suggest that the saturation behavior of emitted current may be common properties of nanostructure-based electron emitters, as observed experimentally in single-walled carbon nanotubes, and multi-walled carbon nanotubes, and other sharp emitters like nanowires as well.

In conclusion, we introduced a general first-principles approach for calculating electron FE characteristics of any kind of nanostructures, based on the DFT combined with the NEGF technique. The method employs basis orbitals with large confinement radii sufficient to describe the electron density in the vacuum between the nanostructure tip and the anode, and takes the presence of emitted current into account. The simulation results on a capped single-walled carbon nanotube reproduce the experimental trend closely, in particular, the current saturation and deviation from the Fowler-Nordheim behavior.

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