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First principles calculation of field emission from carbon nanotubes with nitrogen and boron doping

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ABSTRACT

We investigate the field emission properties of nitrogenated and boronated carbon nanotubes using time-dependent density functional theory, where the wave function propagation is performed using the Crank–Nicholson algorithm. We extract the current–voltage characteristics of the emitted electrons from nanotubes with different doping configurations. We found that boron doping alone either impedes, or slightly enhances, field emission. Nitrogen generally enhances the emission current, and the current is sensitive to the location of the nitrogen dopant in the nanotube. Doping with both nitrogen and boron will generally enhance emission, and the closer the nitrogen dopant is to the tip, the higher is the emitted current. The emitted charge cloud from nitrogen-doped carbon nanotubes, however, diffuse more than that from pristine ones, our simulations show the emergence of a branching structure from the charge cloud, which suggests that nitrogenated carbon nanotubes are less convenient for use in precision beam applications.

1. Introduction

Field emission has been one of the active research areas owing to its theoretical, as well as commercial, significance [1]. Unique field emission properties were discovered in carbon nanotubes owing to their high aspect ratio and mechanical and chemical stability, making them the best candidate for flat-panel displays and atomic force microscopy probes [2–4]. Among the number of nanostructures investigated for field emission, carbon nanotubes proved, both theoretically and experimentally, to possess the strongest field emission characteristics.

Nitrogen and boron are among the most common dopants encountered in carbon nanotubes [5]. Nitrogen-doped carbon nanotubes were studied experimentally by several groups [6–9], reporting generally improved field emission characteristics. However, the strength of the emission current, as well as the onset field, were reported to be influenced by the substrate used in fabricating the nitrogenated carbon nanotube [9], processing method [8] and post-processing [7]. While nitrogen doping of carbon nanotubes, as was indicated by, for example, Doytcheva et al. [8]is close to that of metallic emitters, boron doping either impedes emission or has minimal effect on emission. Sharma et al. [10] suggested that, based on their experimental investigation, boron-doped carbon nanotubes are more convenient for applications in flat-panel display devices where they are packed in large arrays or parallel emitters, while nitrogen-doped carbon nanotubes, owing to their high field emission quality [11], can be used in narrow beam applications. Zhang et al., based on a theoretical study, concluded that doping with both nitrogen and boron will generally enhance emission [12].

Theoretical work by Qiao et al. [13] and experimental work by Chan et al. [14] concluded that boron doping decreases the tunneling probability in comparison with pristine carbon nanotubes. Owens [15], based on theoretical computations, expected that both boron and nitrogen doping will not enhance field emission based on the fact that they increase the ionization energy of carbon nanotubes. However, although this is true in the case of boron doping, the ionization potential was not a correct indicator for field emission quality. Theoretical work on the field emission from boron-doped carbon nanotubes, however, have reported conflicting results [13], and there is a need to understand the details of the emission process and the variable factors to which emission current in boron-doped carbon nanotubes would be sensitive. We believe that this work will shed more light into the microscopic nature of field emission from doped carbon nanotubes and the role of electron donation or acceptance in enhancing or impeding field emission.

In this letter, we simulate the process of field electron emission from the doped carbon nanotubes by applying the methodology

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adopted in Ref. [16], where the current is simulated by the evolution of charge from the tip structure through the integration of the time-dependent Kohn–Sham equation [17]. This method, which utilizes time-dependent density functional theory (TDDFT), was applied by several other authors [18–21]. Other methods include the application of the Kubo formalism [22], the transfer matrix formalism [23] and Landauer–Buttiker formalism [1], all of which depend upon the solution of a self-consistent problem and the estimation of tunneling current. TDDFT, however, is of greater value for the simulation of physical processes in dynamical systems [17], and the field emission process is no exception. TDDFT has been applied for studying laser-induced control of chemical reactions [24], subtle optical properties of biological chromophores [25], molecular dissociation [26], as well as other fine properties that have manifested the utility of TDDFT in shedding light at a picosecond-level of detail on the interaction between the electric field and the charge cloud and the, more broadly, the influence of dangling bonds and impurities in enhancing or impeding the amount of charge evolution.

2. Computational details

We summarize our calculation procedure as follows (more details of the procedure are presented in Ref. [16]). We performed density functional theory computation using the local density approximation for exchange and correlation potential by Pedrew and Zunger [27]. Then, we solved the time-dependent Kohn–Sham equations by propagating the wave function using the Crank–Nicholson method. Then, following each propagation step, the amount of charge remaining in the emitter region at time t for a particular wave function corresponds to the electric charge remaining, which is given by

$$Q_n(t) = \int_0^{z_0} \iint |\psi|^2 \, d\mathbf{x} \tag{1}$$

and in terms of the life time τ_n of state n,

$$Q_n(t) = e^{-t/\tau_n}, \tag{2}$$

which implies linear behavior of $Q_n(t)$ in the short time interval. From this formula, the current generated by a wave function is given by

$$I_n = e\frac{dQ_n(t)}{dt} \approx -\frac{1}{\tau_n} \tag{3}$$

in the short time range. The total current is given by

$$I = e\sum f_n \frac{dQ_n(t)}{dt}.$$

In order to compute the charge remaining in the lower portion of the simulation box, we integrate that lower portion each time-step for each wave function. At the beginning of the simulation, the charge is typically 1 (which works as a check for normalization consistency of the propagator used). Charge starts to decrease as time elapses, until it reaches a minimum point after which it starts increasing (due to reflection of the wave back from the upper surface of the simulation box). The integration is performed by simply summing the product of unit volume boxes of the mesh used in Octpus within the region concerned.

3. Results and discussion

In case of doping with a single dopant atom, we consider the following nitrogen and boron doping configurations: the dopant replacing a carbon atom in the top ring; the dopant replacing a carbon atom in the second ring; the dopant replacing a carbon atom in the third ring. The different positions are shown in Fig. 1, and a diagram showing the simulation box is showing Fig. 2. We also study nanotubes doped with the two different dopants at various positions, where one dopant is kept at the tip while the other is placed at one of the lower rings.

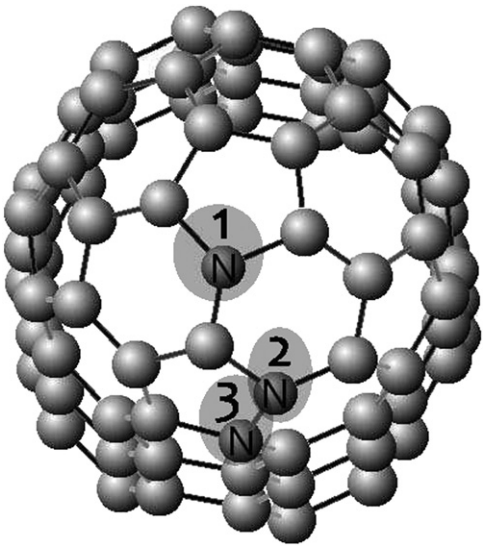

Fig. 1. Relative positions of nitrogen (or boron) dopant on the carbon nanotube tip. Note that the position of the dopant is labeled by the respective number used in Table 1 highlighted by a light gray circle.

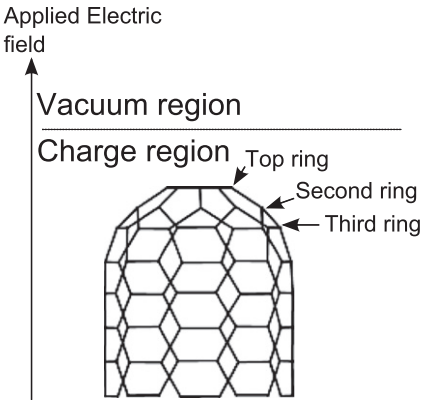

Fig. 2. The simulation box, showing the direction of the applied electric field, and the two regions: vacuum region (above the dotted line) and the charge region (below the dotted line). Charge leaves the charge region into the vacuum region, and our calculations are based upon computing the total charge contained inside the charge region (about the lower 66% portion of the simulation box).

The symbols in Table 1 above are as follows: N1: Nitrogen dopant replacing a carbon atom at the top ring. N2: Nitrogen dopant replacing a carbon atom at the second ring below the tip. N3: Nitrogen dopant replacing a carbon atom at the third ring below the tip. B1: Boron dopant replacing a carbon atom at the top ring. B2: Boron dopant replacing a carbon atom at the second ring below the tip. B3: Boron dopant replacing a carbon atom at the third ring below the tip. NBn: Placing the nitrogen dopant at the top while the boron dopant is placed at the nth ring. BNn: Placing the boron dopant at the top while the nitrogen dopant is placed at the nth ring.

In order to understand the mechanism whereby a dopant enhances or impedes emission, we present in Fig. 3 the evolution of charge in the three cases (pristing, nitrogen-doped and boron-doped) followed by Figs. 4 and 5 the charge evolution graphs for both the N1 and B2 configurations.

Fig. 4 indicates the occurrence of a strong propagation of the wave function into the vacuum region (the empty space above the tip of the nanotube). The influence of the nitrogen atom, however,