Field emission properties of N-doped capped single-walled carbon nanotubes: A first-principles density-functional study


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The geometrical structures and field emission properties of pristine and N-doped capped (5,5) single-walled carbon nanotubes have been investigated using first-principles density-functional theory. The structures of N-doped carbon nanotubes are stable under field emission conditions. The calculated work function of N-doped carbon nanotube decreases drastically when compared with pristine carbon nanotube, which means the enhancement of field emission properties. The ionization potentials of N-doped carbon nanotubes are also reduced significantly. The authors analyze the field emission mechanism in terms of energy gap between the lowest unoccupied molecular orbital and the highest occupied molecular orbital, Mulliken charge population, and local density of states. Due to the doping of nitrogen atom, the local density of states at the Fermi level increases dramatically and donor states can be observed above the Fermi level. The authors’ results suggest that the field emission properties of carbon nanotubes can be enhanced by the doping of nitrogen atom, which are consistent with the experimental results. © 2007 American Institute of Physics.

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I. INTRODUCTION

Since their discovery in 1991,1 carbon nanotubes (CNTs) have drawn particular attention due to their unique geometrical structures and novel physical properties.2 As a kind of quasi-one-dimensional material, CNTs are considered as field electron emitters,3 nanoheterojunction,4 scanning tunneling microscopy tip,5 and structural reinforcement fibers.6 It is well known that the electronic structures of CNTs can be significantly changed by adsorption,7 encapsulation,8 and doping,9,10 and consequently the physical and chemical properties can be modified. With the development of synthesis techniques of CNTs, various kinds of doped CNTs have been fabricated.11,12 By incorporating other elements within the hexagonal lattice, the applications of CNTs can be realized more easily. For example, Li- and K-doped single-walled carbon nanotube (SWCNT) bundles have been reported to enhance conductivity and hydrogen storage capacity.13 The resistivity of an individual B-doped multiwalled carbon nanotube (MWCNT) was measured, which was found to be reduced at room temperature as compared with pristine CNT.14 Therefore, the doping of CNTs with other chemical elements is a practical and feasible way to modify the physical and chemical properties of CNTs.

Among the proposed applications, field emission displays with CNTs cold cathodes are the most promising and considered as the next-generation flat-panel displays.15 Compared with conventional metallic field emission tips, CNTs as field emission electron source have many advantages: unusually high aspect ratio (long tube length and small curvature radius on the tips), high chemical stability, low extracting field, high current density, as well as long operating time. The application of CNTs to field emitters3 is based on the electrical properties of CNTs, which strongly depend on the microscopic electronic structures of CNTs. Thus, the control of the electronic structures of CNTs is of great technological importance, and doping CNTs with other elements is the best way to accomplish this goal. Nitrogen atom (contains one electron more than carbon atom) is the most common candidate of n-type dopant for carbon materials, which can modify the electronic structures of CNTs by introducing donor states near the Fermi level. N-doped CNTs have been synthesized by several groups,16 and the existing experimental investigations indicate that N-doped CNTs show enhanced electron field emission and special emission properties.17-19 It is found that N-doped CNTs exhibit higher current density and stable electron field emission at lower turn-on voltage when compared to pristine CNTs.20

Most field emission investigations of CNTs have been performed using the Fowler-Nordheim (FN) tunneling theory,21 which has been successful in describing the field emission of microsized metallic tips. However, some experiments22 reveal that the FN theory is not sufficient for a full understanding of the field emission of CNTs. For example, the nonlinear I-V characteristics of the FN plots at high current range are often observed, which suggests that the FN formula should be modified. The intrinsic mechanism of the field emission of CNTs is different from that of the conventional metallic tips, and is more complicated. Therefore, theoretical studies are required to understand the field emission properties of such a quasi-one-dimensional nano-
material. First-principles calculations have been successfully used to identify the electronic structures and electronic properties of CNTs. The electronic structures at CNTs tips and field emission behaviors of CNTs have been reported. On the other hand, compared with pristine CNTs, the field emission properties of N-doped CNTs are also investigated. Nitrogen doping introduces unsaturated dangling bond states at the tip of CNT and increases the emission current, which is due to the shift in the energy level of localized states to the Fermi level. At the same time, the actual emission current depends strongly on the doping configuration of CNT, which is related to the doping position of the extrinsic atom. Although several reports have demonstrated the enhanced field emission properties of N-doped CNTs, no clear relationship has experimentally been built between nitrogen atoms and the electronic structures of doped CNTs under applied electric field. Furthermore, the mechanism of the enhanced field emission by the doping of nitrogen atoms is not well clearly revealed, which requires further investigations.

The aim of this work is to develop structural models for nitrogen doping in capped (5, 5) SWCNTs. The different doping positions of nitrogen atom are chosen. We present first-principles density-functional theoretical (DFT) simulation to determine the optimized geometrical structures and the electronic structures of N-doped CNTs. The results provide accurate values of work function and ionization potential (IP) of N-doped CNT. Especially, we present the evidence to reveal the role of nitrogen atom in enhancing the field emission properties, in terms of energy gap between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), Mulliken charge population, and local density of states (LDOS).

II. THEORETICAL DETAILS

To obtain the exact and detailed information about the geometrical structures and electronic structures of N-doped CNTs, a two-step procedure of quantum mechanical calculation was carried out. The doped CNT was first optimized to get the most stable geometrical structure. After that, electronic property calculation was performed. All the calculations were carried out using first-principles DFT code provided by DMOL3 code (module from MATERIALS STUDIO 3.1, software package of Accelrys Inc. installed on SGI Origin 300 server). The local density approximation (LDA) was employed to optimize the geometrical structures of the doped CNTs during self-consistent field iterations, with the Perdew-Wang parametrization of the local exchange-correlation energy. The generalized gradient approximation (GGA) was adopted to calculate the total energy and various electronic properties of the doped CNTs with the Perdew-Burke-Ernzerhof correlation gradient correction. The all-electron Kohn-Sham wave functions were expanded in the local atomic orbital (double numerical polarization) basis set with orbital cutoff of 5.5 Å. Self-consistent field procedure was done with a convergence criterion of $10^{-5}$ a.u. on the energy and electron density. In general, LDA provides quicker calculations, and GGA provides more reliable results. Especially, for any calculations involving comparison of energies, GGA is recommended. The use of LDA is known to underestimate the band gap and overestimate the binding energy significantly. In this work, the calculated band gaps between HOMO and LUMO and binding energies of C60 are 1.665 and 506.7 eV for the LDA calculation and 1.683 and 450.8 eV for the GGA calculation. The band gap from GGA calculation is closer to the estimated band gap of 1.7 eV of C60. These results indicate that the use of GGA for energy calculations is more reliable.

In our study, finite-length capped (5, 5) SWCNTs with nitrogen substitutional atom were considered. The diameter of armchair (5, 5) CNT is 6.8 Å, which is similar to that of C60, and the average bond length is 1.42 Å. The capped CNT (80 atoms, due to the limited computational resources) was represented by five layers of carbon rings along the tube axis with one end capped by half of C60. The doped CNT was the capped CNT with direct substitution of one carbon atom by one nitrogen atom in the hexagonal lattice, which can lead to different doping positions of the doped CNTs. In all of the doped CNTs, the dangling bonds at the other end of the capped CNTs were not saturated by hydrogen atoms, which is different from other calculations because the difference in electronegativity between hydrogen and carbon atoms imparts an artificial dipole moment to CNT, which may affect the field emission properties. Two carbon layers at the bottom were fixed during whole simulations in order to mimic the presence of a long CNT below the tip in actual experiments. Pristine CNT was also considered in order to compare with the doped CNTs.

III. RESULTS AND DISCUSSION

A. Geometrical structures and heat of formation

The geometrical structure of (5, 5) CNT used in the calculation is shown in Fig. 1. The numbers denote the different atomic layers of CNT, and the letters denote the different doping positions of the substitutional nitrogen atom in each atomic layer. It means that there are five different configurations for N-doped CNTs, which have nominal formulas...
C$_7$N. Although there are also other defective configurations for N-doped CNT, such as bridge or rocket configurations used in previous work, the perfect $sp^3$ position of the nitrogen atom in CNT atomic network is the most important configuration. The initial doped structure is relaxed when the minimum energy is reached, and the most stable structure is obtained. In fact, the different sizes between carbon atom and nitrogen atom will affect the lattice locally. It means that the implant of nitrogen atom into CNT will introduce topological defect into the perfect hexagonal lattice, which plays an important role in the field emission. This would also happen if we have nitrogen atom substituting carbon atom in bulk diamond. The C–N bond length of the doped CNT with respect to the different doping positions is listed in Table I. For the doped CNT, there is an inward local structural distortion along the radial direction due to the shortened C–N bond length (the averaged bond length is 1.40 Å).

In order to study the field emission properties of CNTs, a uniform electric field was applied along the CNT axis. In real field emission conditions, the applied electric field near CNT tip is highly anisotropic and inhomogeneous, and the electric field lines converge radially toward the CNT tip. The use of uniform electric field along the CNT axis is just for simplicity. We ignore the electric field gradient along CNT axis, and suppose CNT is in a uniform electric field. This simplicity is not very critical. Various values of electric field have been applied in previous studies of the field emission properties of CNTs. In our study, electric fields of 0.5 and 1 eV/Å are applied along the CNT axis, because the values are comparable with the electric field at which CNT field emission currents can be measured in experiments. The structural changes are rather small under the applied electric field.

Figure 2 shows the results for the heats of formation of N-doped CNTs at different doping positions with and without the applied electric field. Total energy as well as atomic chemical potential are used to determine the heat of formation of the system, according to the following formula:

$$H = E(C_{n-1}N) - \frac{n-1}{n}E(C_n) - \mu,$$

where $n$ represents the number of carbon atoms in pristine CNT, $E(C_{n-1}N)$ is the total energy of the doped CNT, $E(C_n)$ is the total energy of the corresponding pristine CNT, and $\mu$ is the chemical potential of nitrogen atom. In our study, $\mu$ is calculated as the total energy per atom of the N$_2$ molecule. The heat of formation is the energy required to dissociate the nitrogen atom from CNT and take it far away. Therefore, negative heat of formation means that the formation of the doped CNT is favorable. The calculated results indicate that N-doped CNTs remain stable in the presence of the applied electric field. As shown in Fig. 2, for N-doped CNT, the most preferable doping position appears at the fourth layer, which is the link between the cap and the body of CNT. Ahn et al. calculate the energy of the localized states relative to the Fermi energy of decide the preferable doping position. They only consider the local distortion or defects induced by nitrogen atom, which leads to that the favorable doping position they obtained is different from what we calculated using heat of formation.

B. Field emission properties

As for the quasi-one-dimensional structure CNT, the field emission process can be described as follows: the valence electrons localized at discrete energy levels being emitted from CNT tip and passing through the potential barrier to the vacuum under the applied electric field. Although (5, 5) armchair CNT is metallic, capped armchair CNT cluster exhibits semiconducting property with a finite value of energy gap between LUMO and HOMO, which is similar to C$_{60}$. The metallic tube body is good for electron transport, and the semiconducting cap is good for electron emission.

The LUMO–HOMO energy gaps are shown in Fig. 3 for pristine and N-doped CNTs with and without the applied electric field. For N-doped CNTs, the LUMO–HOMO energy gaps decrease significantly when compared with pristine CNTs. The reduction of the LUMO–HOMO energy gap means the increase in the probability of electron excitation to
will be filled with electrons transferring from other states, coupled. When the electric field is applied, the coupled states as the localized states and the extended states, could be the states with different azimuthal angular momentum, such as the states with different azimuthal angular momentum, such as the localized states and the extended states, could be coupled. When the electric field is applied, the coupled states will be filled with electrons transferring from other states, and then the electrons will be leaked out completely. The coupled states have a contribution to the enhanced field emission properties of N-doped CNT.

The LUMO, and then more electrons tend to escape from the surface of CNT to the vacuum. This suggests that the doping of nitrogen atom in CNT can enhance the field emission properties. It can also be seen that the doping position of nitrogen atom can affect the energy gap. As shown in Fig. 3, for N-doped CNTs the energy gaps of the fourth- and the fifth-layer-doped CNTs decrease gradually with increasing the applied electric field. It results in an excellent doping-induced enhancement of field emission properties when nitrogen atom is doped at the link position. The formation of the energy gap is mainly due to the existence of the semiconducting cap, and this suggests that the field emission from capped CNT may be interpreted by a semiconducting model rather than by a conventional metallic model.

The charge densities of HOMO and LUMO of pristine and fourth-layer-doped CNTs under 0.5 eV/Å electric field are shown in Fig. 4. The HOMO and LUMO of other doped CNTs are similar and not plotted here. For pristine CNT, the HOMO is localized at the sidewall of CNT, which refers to the extended states, and the LUMO is localized on the tip of CNT, which refers to the localized states on the CNT cap. For N-doped CNT, we can see from Figs. 4(c) and 4(d) that the HOMO and LUMO are localized at both the cap and the body of the CNT. These kinds of states are called “coupled states” with mixed properties of both the localized states and the extended states. The coupled states cannot be found in pristine CNT and can only be found in N-doped CNTs, which is due to the presence of nitrogen atom. The doping of nitrogen atom breaks the rotational symmetry of CNT so that the states with different azimuthal angular momentum, such as the localized states and the extended states, could be coupled. When the electric field is applied, the coupled states will be filled with electrons transferring from other states, and then the electrons will be leaked out completely. The coupled states have a contribution to the enhanced field emission properties of N-doped CNT.

The work function is a critical quantity in understanding the field emission properties of CNT. The work function of CNT emitter can be derived directly from the I-V characteristic of the FN model. Recently, several investigators have attempted to estimate the work function of CNTs by experimental measurements. Groning et al. combine the measurements of the field emitted electron energy distribution and the I-V characteristic to determine the work function at the field emission site. The work function of SWCNT bundles is 4.8 eV by ultraviolet photoemission spectroscopy. The MWCNTs have a work function of 4.6–4.8 eV by in situ transmission electron microscopy. The work function of N-doped MWCNT has also been measured by Doytcheva et al. and Gohel et al. As to the theoretical prediction, the work function \( \phi \) is defined as \( \phi = \varphi - \mu \), corresponding to the energy needed to take an electron from the Fermi level \( \mu \) to the vacuum level \( \varphi \). As for the quasi-one-dimensional structure CNT, due to its unique geometrical characteristics, the work function \( \phi \) is the minimum energy required for one electron to be removed from the CNT tip to the vacuum. Due to the semiconducting properties of the capped (5, 5) armchair CNT as mentioned above, the Fermi level is placed at the midgap of HOMO and LUMO. The work function \( \phi \) is defined as the potential energy difference on the tip of the CNT for one electron between the Fermi level and the vacuum level. This is different from the conventional metal surface definition of the work function.

The work functions of pristine and N-doped CNTs with and without the applied electric field are shown in Fig. 5. The work function of pristine CNT without the applied electric field is 5.05 eV, which shows great agreement with the value of 5.05 eV obtained by the photoelectron emission method and the value of 5.10 eV by field-ion microscopy. We can see that the work functions of N-doped CNTs decrease drastically with the substitution of carbon atom by nitrogen atom. On the other hand, the work functions of pristine and N-doped CNTs all decrease when the electric...
field is applied. The reduction of the work function means the enhancement of the field emission properties of CNT. This confirms that the presence of nitrogen atom indeed improves the field emission properties of CNT, which is in agreement with the experimental results.\textsuperscript{17} In particular, the work function of N-doped CNT can be reduced to as low as 2.87 eV under 1 eV/Å applied electric field. It is found that the work functions $\phi$ of N-doped CNTs under the applied electric field are related to the doping positions of nitrogen atom. It seems that the best doping position is in the fourth and fifth layers for our calculations. We believe that this finding may be helpful in the design of field emission devices, which make use of N-doped CNTs. Very recently, Ahn et al.\textsuperscript{24} have reported the field emission enhancement of N-doped CNTs and find that the most favorable doping position is the second layer by calculating the field emission current. We think that emission current and work function are two separate parameters and are incomparable. The emission current is the amount of charge flowing out of the CNT tip per unit time, which is also related to the emitting area, while the work function is the minimum energy required to emit one electron, which is related to the turn-on voltage in the field emission experiments. Doytcheva et al.\textsuperscript{18} have measured the work function of individual N-doped CNTs, which is sensitive to the temperature and shows a lower value at lower temperature. This is due to the impurity molecules adsorbed on the cap of CNT, which can locally enhance the emission, as what has been reported in previous investigation for pristine SWCNTs.\textsuperscript{41}

In order to explain the effects of doping nitrogen atom on the enhanced field emission properties, we have calculated the first IP of pristine and N-doped CNTs. The IP is obtained by evaluating the energy difference between the neutral CNT and its corresponding +1 charged CNT cation. The +1 charged CNT has essentially the same geometrical structure as the neutral CNT, because the "hole" left by an emitted electron can be immediately recombined with an incoming electron from the CNT body.\textsuperscript{7} The calculated IPs of pristine and N-doped CNTs with and without the applied electric field are shown in Fig. 6. It is known that the lower the IP, the easier to emit an electron and the higher the field emission current at a given operating voltage. The presence of nitrogen atom in CNT reduces the IP significantly, as expected. In the absence of an applied electric field, a 0.88–1.02 eV reduction in the IP is observed. Similarly, the IP of N-doped CNT is lowered by 0.54–0.84 eV under 0.5 eV/Å electric field, and is lowered by 0.23–0.55 eV under 1 eV/Å electric field, as compared with pristine CNT. We can note that the reduction of IP due to the doping of nitrogen atom is correlated to the increase in the HOMO level, which is listed in Table II. The increase in the HOMO level means that it is easier for an electron to be emitted from CNT to the vacuum level. These results indicate that the doping of nitrogen atom can enhance the field emission properties of CNT.

Also, we calculate the electron affinities (EAs) of pristine CNT. The EA is defined as the energy difference between the $-1$ charged CNT anion and its corresponding neutral CNT. Without the applied electric field, the EA of pristine CNT is 3.44 eV. Some investigations have shown that CNT is stabilized by having two to four extra electrons.\textsuperscript{30,42} This phenomenon is attributed to the strong EA of CNT. Therefore, when nitrogen atom is incorporated into CNT, it is easy for nitrogen atom to substitute carbon atom in hexagon network by donating its electron to CNT, which results in the charge redistribution along the CNT axis and variation of the electronic structures as well. Figure 7 exhibits the result of Mulliken population analysis of the second-layer-doped CNT with the presence of 1 eV/Å applied electric field.

\begin{table}
\centering
\caption{HOMO energy levels (eV) for pristine and N-doped CNTs with and without the applied electric field.}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\multicolumn{2}{|c|}{Doping layer} & 1 & 2 & 3 & 4 & 5 \\
\hline
E (eV/Å) & Pristine & & & & & \\
\hline
0 & −5.65 & −4.69 & −4.68 & −4.56 & −4.64 & −4.64 \\
0.5 & −4.57 & −3.97 & −3.90 & −3.81 & −3.71 & −3.71 \\
1 & −3.52 & −3.29 & −3.22 & −3.11 & −2.94 & −2.93 \\
\hline
\end{tabular}
\end{table}

FIG. 6. The IPs of pristine and N-doped CNTs with and without the applied electric field. The abscissa denotes the doping layer of CNT, and the layer “zero” denotes pristine CNT.

FIG. 7. Mulliken population analysis of the second-layer-doped CNT with the presence of 1 eV/Å applied electric field. The position of the nitrogen atom is indicated by an arrow.
the doping position. A small peak is observed in the LDOS see from Fig. 8 the electronic states at both sides of the Fermi level. We can responsible for the electron field emission, we only focus on LDOS for CNT with one substitutional nitrogen atom in the applied electric field are shown in Fig. 8, and the LDOS for CNT is also shown in (b). The Fermi level is set to zero.

The LDOSs at the first two layers for pristine, second-layer-doped, and fourth-layer-doped CNTs under 0.5 eV/Å applied electric field. The LDOS (dashed line) for the nitrogen atom in second-layer-doped CNT is also shown in (b). The Fermi level is set to zero.

FIG. 8. LDOS at the first two layers for (a) second-layer-doped (solid line) and fourth-layer-doped (dotted line) CNTs and (b) pristine (solid line) and second-layer-doped (dotted line) CNTs under 0.5 eV/Å applied electric field. The LDOS (dashed line) for the nitrogen atom in second-layer-doped CNT is also shown in (b). The Fermi level is set to zero.

The nitrogen atom carries negative charges, and for the three nearest carbon atoms each carries a little positive charge, which is due to the negative charged nature of the nitrogen atom. The doping of nitrogen atom can aggregate more electrons at the doping position. With the increase of the applied electric field, the electron congregation becomes more obvious. In essence, the extra electron on the tip of CNT will concentrate in the conduction band, and consequently the Fermi level can be shifted toward the vacuum. This will lower the potential barrier of CNT tip and make the field emission more easily.

The LDOSs at the first two layers for pristine, second-layer-doped, and fourth-layer-doped CNTs under 0.5 eV/Å applied electric field are shown in Fig. 8, and the LDOS for the nitrogen atom in the second-layer-doped CNT is shown as well. In contrast, Zhang et al.9 have only reported the LDOS for CNT with one substitutional nitrogen atom in the first layer. As the states in the vicinity of the Fermi level are responsible for the electron field emission, we only focus on the electronic states at both sides of the Fermi level. We can see from Fig. 8(a) that the LDOS is almost not affected by the doping position. A small peak is observed in the LDOS for nitrogen atom above the Fermi level (at 0.05 eV) in Fig. 8(b), which indicates that nitrogen atom is partly hybridized with carbon atom. The nitrogen atom possesses an unpaired electron, which seems to actively participate in hybridization with the carbon atom nearby. The higher peak localized at 0.25 eV above the Fermi level in the LDOS for N-doped CNT can be assigned as donor states of the doped CNT, which is due to the doping of nitrogen atom. The prominent deep valley of the minimum LDOS above the Fermi level shifts to the lower energy level when nitrogen atom is doped into CNT, implying that the Fermi level shifts toward the conduction band, and the potential barrier reduces as well. Consequently, for N-doped CNT, the corresponding emission probability of electrons increases when compared with that for pristine CNT. It can be seen that the value of LDOS for the doped CNT at the Fermi level is found to be about 43 times larger than that of pristine CNT, which implies that additional states appear at the Fermi level. The value of LDOS at the Fermi level directly affects the chemical reactivity. The higher LDOS at the Fermi level can be ascribed to the doping of nitrogen atom, and thus enhances the chemical reactivity. The additional states at the Fermi level are able to act as tunneling states, and electrons near the Fermi level will be emitted easily to the vacuum. In summary, our above theoretical calculations show that the field emission properties of CNT can be enhanced by the doping of nitrogen atom, which is in agreement with what has been observed in the field emission experiments.17

IV. CONCLUSIONS

The first-principles DFT can be used to calculate the geometrical structures and the field emission properties of pristine and N-doped capped (5, 5) SWCNTs. The doped CNTs with one carbon atom substituted by one nitrogen atom at different positions are remarkably stable under the field emission conditions. The doped capped CNT exhibits semiconducting property with a finite value of energy gap between LUMO and HOMO. The energy gap of the doped CNT decreases significantly when compared with pristine CNT. The “couple states” are found in N-doped CNT, which have a contribution to field emission. Upon nitrogen atom substitution, the work function decreases dramatically, indicating the enhancement of the field emission properties. Similarly, as it is expected, the IP of N-doped CNT reduces significantly due to the doping of nitrogen atom. The reduction of IP is correlated to the increase in the HOMO level. The doping of nitrogen atom into CNT will donate its extra electron to CNT, which results in the Mulliken charge redistribution. Due to the doping of nitrogen atom, the value of LDOS at the Fermi level increases dramatically and the Fermi level shifts toward the conduction band. Donor states can be observed above the Fermi level, and the additional states at the Fermi level are able to act as tunneling states. Our results provide the possible field emission mechanism and suggest that the doping of nitrogen atom can enhance the field emission properties of CNTs, which will open new avenues in the field emission devices.

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29 Under the same computational conditions, the dipole moments of first-layer-doped CNT increase by 30% and 50% under 0.5 and 1 eV/A applied electric fields due to the saturation of the dangling bonds, which overestimates the role that the dangling bonds play in the field emission of N-doped CNTs. Hence, we do not use hydrogen saturation in this work.