# Effects of B and N dopings and $H_2O$ adsorption on structural stability and field emission properties of cone-capped carbon nanotubes*

Wang Yi-Jun(王益军), Wang Liu-Ding(王六定)†, Yang Min(杨 敏), and Yan Cheng(严 诚)

*School of Science, Northwestern Polytechnical University, Xi'an* 710129, *China*

(Received 22 June 2011; revised manuscript received 8 August 2011)

The effects of B and N dopings and $H_2O$ adsorption on the structural stability and the field emission properties of cone-capped carbon nanotubes (CCCNTs) were investigated by using the density-functional theoretical calculation. The adsorption of $H_2O$ can increase the structural stability and decrease the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO gap) of the CCCNTs. The strength of total electric field on the top of the $H_2O$-adsorbed CCCNTs is larger than that of the B-doped and the N-doped CCCNTs, electrons will be emitted primarily from the $H_2O$-adsorbed CCCNTs at the same applied voltage. Therefore, the $H_2O$ adsorption can lower the threshold voltage for the CCCNTs. While the B and the N dopings produce opposite effects. The HOMO–LUMO gap of the N-doped CCCNTs is the widest among all the gaps of the CCCNTs.

**Keywords:** carbon nanotubes, nitrogen doping, boron doping, $H_2O$ adsorption

**PACS:** 73.63.Fg, 79.70.+q, 31.15.ae **DOI:** 10.1088/1674-1056/20/11/117304

## 1. Introduction

Carbon nanotubes (CNTs) have been considered as a very promising electron field emission material because of their very low threshold voltage and high emission current density.[1−3] It is well known that a suitably chemical doping and the adsorption are effective ways to alter and adjust the microstructure and the field emission properties of CNTs.[4] For example, the threshold voltage of B-doped CNTs is lower than that of pristine CNTs,[5,6] and the density of states (DOS) at the Fermi energy level ($E_F$) increases due to the B doping.[7] The work function of N-doped CNTs is lower than that of pristine CNTs.[8] Furthermore, the $H_2O$ adsorption on the tip is another way to adjust the binding configuration and enhance the emission current of CNTs.[9−11]

Since the electrical properties of CNTs are very sensitive to their microstructures, the same treatment can lead to different electronic properties for CNTs with and without defects. For defect-free CNTs, the N doping could increase the emission current of achiral CNTs.[8] For CNTs with defects, it can change the metallic chiral CNTs into a semiconductor[12] and lower the CNTs' electronic transmission properties. In general, pristine cone-capped CNTs (CCCNTs) contain five or seven carbon ring defects, and the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO–LUMO gap) and the total energy are much smaller than those of defect-free $C_{30}$ hemisphere-capped CNTs.[13] Therefore, the field emission property and the structural stability of the former are significantly better than those of the latter. It is well known that most CNTs obtained from experiments contain some defects and the cone-capped CNTs are more common than the $C_{30}$ hemispherical-caped CNTs. As a result, it is important to study the performance of the doped and the adsorbed CCCNTs as the field emission materials. Up to now, the comparisons of B- or N-doped and $H_2O$-adsorbed CCCNTs have rarely been concerned, so it is still an open question and requires an in-depth investigation. In this work, we study the effects of B doping, N doping and $H_2O$ adsorption on the structural stability and the field emission properties of CCCNTs by using the first principle density-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 50771082, 60776822, and 11075135) and the Natural Science Foundation of Shaanxi Education Department, China (Grant No. 09JK807).

†Corresponding author. E-mail: wangld@nwpu.edu.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

functional theoretical (DFT) calculation We focus on the HOMO–LUMO gap of CCCNTs and elaborate on the effects of the above mentioned treatments on the field emission properties of CCCNTs.

## 2. Model and method

All the calculations were carried out by using the first-principle DFT provided by the DMOL$^3$ code.[14] The geometrical optimization was based on the local density approximation (LDA) during the self-consistent field iteration with the Perdew–Wang parameterization of the local exchange correlation energy. The generalized gradient approximation (GGA) was adopted to calculate the total energy and various electronic properties with the Perdew–Wang-91 (PW91) function.[8] The all-electron Kohn–Sham wave functions were expanded in the local atomic orbital basis set with an orbital cutoff of 4.5 Å. The self-consistent field procedure was done with a convergence criterion of $10^{-5}$ a.u. on the energy and the electron density.

In our simulation, the CCCNTs (140 atoms) were built by connecting (6, 6) CNTs and carbon nanocones of angle 38.9°. The 5-7-5 carbon ring defects inevitably emerged at the connection between the cone and the tube because of their different numbers of atoms there. The doped CCCNTs were built with a direct substitution of one carbon atom by one nitrogen or one boron atom at the cone tip. The adsorbed CCCNTs were formed with one $H_2O$ molecule adsorbed on the top (Fig. 1). For the purpose of studying the field emission properties of the CCCNTs, an uniform electric field ($E_{\rm appl}$) changed from 2.5 eV·nm$^{-1}$ to 4.0 eV·nm$^{-1}$ were applied along the CCCNTs axis.

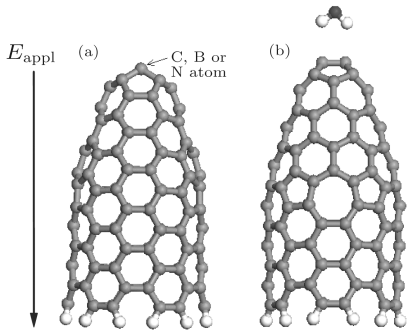



**Fig. 1.** CCCNTs model: (a) front view of pristine, B-doped and N-doped CCCNTs; (b) left view of $H_2O$-adsorbed CCCNTs. The arrow denotes the direction of $E_{\rm appl}$.

## 3. Results and discussion

### 3.1. Structural stability

The high structural stability of CNTs helps to prolong the lifetime of the field emission device. In order to examine the structural stability of CNTs, the binding energies have been computed for the systems having the same number of atoms. The binding energy is defined as the net energy required to decompose a molecule into free atoms. The binding energies of the pristine, the B-doped and the N-doped CCCNTs are calculated by using the Dmol$^3$ module. The binding energy of the $H_2O$-adsorbed CCCNTs except the $H_2O$ molecule has been estimated as the binding energy difference between a $H_2O$-adsorbed CCCNT and a $H_2O$ molecule.

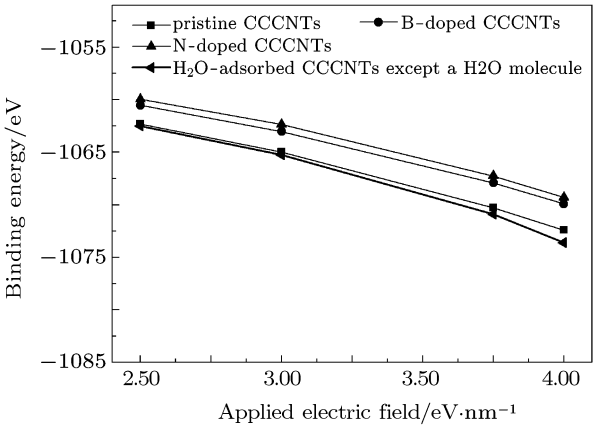



**Fig. 2.** Binding energy of four types of CCCNTs with $E_{\rm appl}$.

The binding energies are compared, as shown in Fig. 2. All the binding energies of the CCCNTs reduce with the increase of $E_{\rm appl}$, which implies that the structural stability of the system enhances accordingly. Under the same $E_{\rm appl}$, the structural stability of the B- and the N-doped CCCNTs is slightly lower than that of the pristine CCCNTs and that of the $H_2O$-adsorbed CCCNTs is the highest among all the CCCNTs. The basic reason for this is that the length of the C–B (C–N) bond is longer (shorter) than that of the C–C bond,[8] which will introduce an outward (inward) local structural distortion along the radial direction.[8] Therefore, the structural stability decreases for the B- and the N-doped CCCNTs. Because the $H^+$ ion in the $H_2O$ molecule and the electron in the delocalized $\pi$ orbital near the top of the CCCNTs attract each other and the adsorption energy of the $H_2O$-adsorbed CCCNTs increases with the increase of $E_{\rm appl}$ (Table 1), the structural stability of the $H_2O$-adsorbed CCCNTs is enhanced.

**Table 1.** Adsorption energy of $H_2O$-adsorbed CCCNTs with an applied electric filed.

| $E_{\rm appl}$/eV·nm$^{-1}$ | 2.50 | 3.00 | 3.75 | 4.00 |
|---|---|---|---|---|
| Adsorption energy /eV | 0.14 | 0.19 | 0.57 | 0.84 |

The adsorption energy ($E_{\rm adsorption}$) is defined as the energy required to detach the adsobate from the nanotube tip and place it at a distance far away from the tip. The $E_{\rm adsorption}$ under an applied electric field ($E_{\rm appl}$) is computed using the following expression:[7]

$$\begin{aligned} &E_{\rm adsorption}(E_{\rm appl}) \\ &= E_{\rm CCCNTs}(E_{\rm appl}) + E_{\rm H_2O}(E_{\rm appl}=0) \\ &\quad - E_{\rm H_2O\text{-}adsorbed\ CCCNTs}(E_{\rm appl}), \end{aligned} \tag{1}$$

where the three terms at the right side are the total energies of the pristine CCCNTs, the $H_2O$ molecule and the $H_2O$-adsorbed CCCNTs, respectively.

## 3.2. Electrical properties

In order to deeply investigate the effects of the B and the N dopings and the $H_2O$ adsorption on the field emission properties of the CCCNTs, the pseudo gap and the HOMO–LUMO gap of the four types of CCCNTs with $E_{\rm appl}$ are plotted in Figs. 3 and 4, respectively.

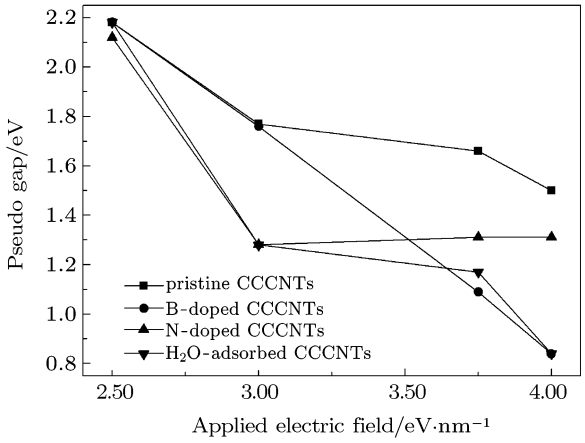



**Fig. 3.** Pseudo gap of four types of CCCNTs with $E_{\rm appl}$.

Under the same $E_{\rm appl}$, the pseudo gaps of the B- and the N-doped and the $H_2O$-adsorbed CCCNTs are narrower than that of the pristine CCCNTs, which indicates that the covalence bond of the former CCCNTs weakens and the metallicity of them increases.[15] It proves that the treatment of the B and the N dopings and the $H_2O$ absorption improves the metallicity of the CCCNTs.

Compared with the HOMO–LUMO gap of the pristine CCCNTs (Fig. 4), the gap of the $H_2O$-adsorbed CCCNTs decreases, whereas that of the doped CCCNTs increases. Then in the two kinds of systems, the electrons can jump over the HOMO–LUMO gap more easily or more difficulty, respectively. It is noticed that only the HOMO–LUMO gap (Fig. 4) and the pseudo gap (Fig. 3) of the N-doped CCCNTs increase with the increase of $E_{\rm appl}$, which means that the N doping obviously weakens the CCCNTs' metallicity under $E_{\rm appl}$. This phenomenon is different from that of the N-doped $C_{30}$ hemisphere-capped CNTs.[4] So it is opposite for the two types of CNTs with and without defect.

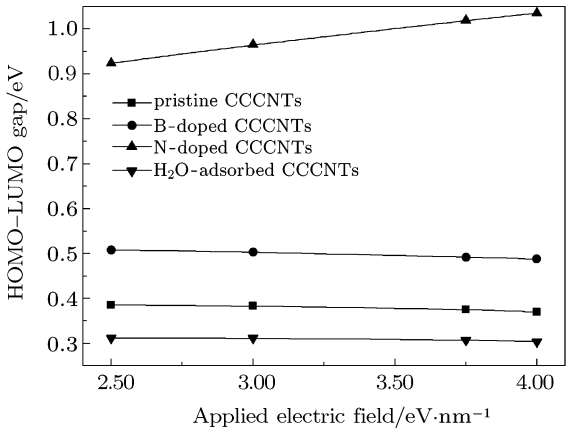



**Fig. 4.** HOMO–LUMO gap of four types of CCCNTs with $E_{\rm appl}$.

The local density of states (LDOS) at the first layer (the adsorbed system contains a $H_2O$ molecule) and the total density of states (TDOS) of the four types of CCCNTs under $E_{\rm appl}$ = 3.0 eV·nm$^{-1}$ are shown in Fig. 5. It can be seen that only the peak value near $E_{\rm F}$ of the LDOS leads to the increase of the TDOS for the N-doped and the $H_2O$-adsorbed CCCNTs (Fig. 5(a)). Moreover, the very high DOS values near the Fermi energy levels ($E_{\rm F}$) for all the systems clearly show that they are metallic (Fig. 5(b)).

Since the HOMO is even closer to $E_{\rm F}$ than the LUMO for the doped CCCNTs (Fig. 5(b)), their electron transport mainly depends on the HOMO,[16] which indicates that they can easily lose electrons. The large space between the LUMO and $E_{\rm F}$ leads to their even wider HOMO–LUMO gap. In particular, the HOMO–LUMO gap of the N-doped CCCNTs is the widest among all the systems. On the contrary, the LUMO of the $H_2O$-adsorbed CCCNTs is closest to $E_{\rm F}$ and its HOMO–LUMO gap is the narrowest among all the systems (Fig. 5(b)), which results in that the electron will easily be obtained from the system and then be emitted. Considering the relatively high value of DOS near $E_{\rm F}$ (Fig. 5(b)), the main probability for losing electrons lies in the HOMO of the N-doped CCCNTs and the main probability for getting electrons

lies in the LUMO of the $H_2O$-adsorbed CCCNTs.

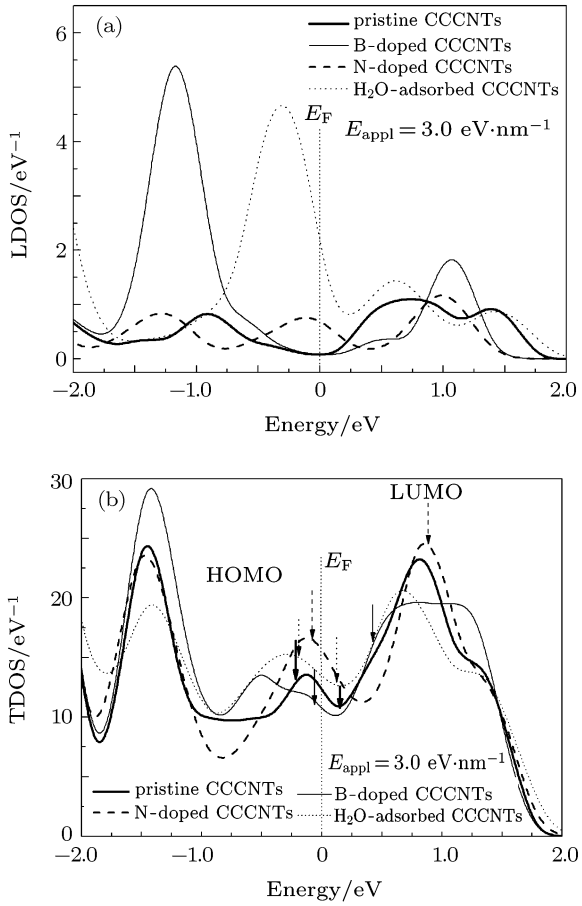



**Fig. 5.** (a) LDOS and (b) TDOS of four types of CCCNTs under $E_{\rm appl}$ = 3.0 eV·nm$^{-1}$. The arrows to the left and the right of $E_{\rm F}$ denote the sites of HOMO and LUMO, respectively. The $E_{\rm F}$ is set to be zero.

The top of the CCCNTs, where the maximum curvature of the surface lies, is the main electron field emission region. The electrical properties of the top are also a major factor affecting the DOS distribution near $E_{\rm F}$.[17,18] It is necessary to analyze the electrical property of the CCCNTs in terms of the microscopic structure. The top views of the Mulliken populations for the four types of CCCNTs under $E_{\rm appl}$ of 3 eV·nm$^{-1}$ are shown in Fig. 6. Because the electronegativity of B, C and N elements increases in an ascending order in the B- and the N-doped CCCNTs, the electrons gather at the C and the N atoms, which are the sites for the electron field emission. Then the local electric field pointing to the atom generates at the CCCNTs' top and the corresponding electrostatic force prevents the ortho-electrons from moving to the emission site, which shows that the HOMO–LUMO gap of the B- and the N-doped CCCNTs is even wider. Because the $H^+$ cation in the $H_2O$ molecule attracts the electrons in the $\pi$ orbital at the tube top and the top-down local electric field generates, the corresponding electrostatic force

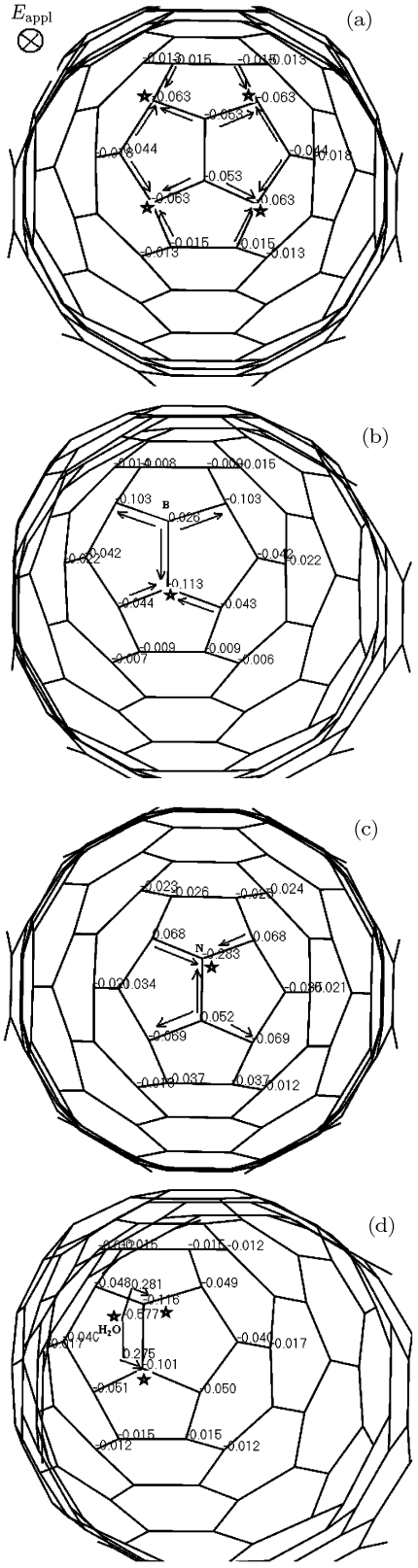



**Fig. 6.** Top view of the Mulliken population for (a) pristine, (b) B-doped, (c) N-doped and (d) $H_2O$-adsorbed CCCNTs at $E_{\rm appl}$ = 3 eV·nm$^{-1}$. The arrows denote the direction of the local electric field and the asterisks denote the site of field emission.

accelerates the shifting of the ortho-electrons to the tube top, which shows that the HOMO–LUMO gap of the $H_2O$-adsorbed CCCNTs is even narrower, so the $H_2O$ adsorption is propitious to while the B and the N dopings impede the field emission of the CCCNTs.

Due to the doping of the B or the N atom, the increase of the HOMO–LUMO gap may further enhances the surface barrier and the threshold voltage for the CCCNTs, however this inference needs further evidence from experiments.

# 4. Conclusion

The different effects of the B and the N dopings and the $H_2O$ adsorption on the structural stability and the field emission properties of the CCCNTs were investigated by using the density-functional theoretical calculations. We found that the $H_2O$ adsorption can increase the structural stability and decrease the HOMO–LUMO gap of the CCCNTs, while the B and the N dopings have the opposite effects. In particular, the HOMO–LUMO gap of the N-doped CCCNTs is the widest among all the gaps of the CCCNTs.

The N doping and the $H_2O$ adsorption can reduce the pseudo gap and increase the density of states near the Fermi energy of the CCCNTs, which leads to the increase of the metallicity and the emission current.

# References


[1] Meyyappan M 2005 *Carbon Nanotubes: Science and Applications* (California: CRC) p. 223

[2] Peng J, Li Z B, He C S, Chen G H, Wang W L, Deng S Z, Xu N S, Zheng X, Chen G H, Chris J E and Richard G F 2008 *J. Appl. Phys.* **104** 014310

[3] Yu S S, Zheng W T, Wen Q B and Jiang Q 2008 *Carbon* **46** 537

[4] Chen G D, Wang L D, An B, Yang M, Cao D C and Liu G Q 2009 *Acta Phys. Sin.* **58** 1190 (in Chinese)

[5] Charlier J C 2002 *Nano Lett.* **2** 1191

[6] Terrones M, Jorio A, Endo M, Rao A M, Kim Y A, Hayashi T, Terrones H, Charlier J C, Dresselhaus G and Dresselhaus M S 2004 *Materials Today* **7** 30

[7] Wang Y J, Wang L D, Yang M, Liu G Q and Yan C 2010 *Acta Phys. Sin.* **59** 4950 (in Chinese)

[8] Wen Q B, Qiao L, Zheng W T, Zeng Y, Qu C Q, Yua S S and Jiang Q 2008 *Physica* E **40** 890

[9] Maiti A, Andzalm J and Tanpipat N 2001 *Phys. Rev. Lett.* **87** 155502

[10] Gao R P, Pan Z W and Wang Z L 2001 *Appl. Phys. Lett.* **78** 1757

[11] Tang D S, Ci L J, Zhou W Y and Xie S S 2006 *Carbon* **44** 2155

[12] Wei Y, Hu H F, Wang Z Y, Cheng C P, Chen N T and Xie N 2011 *Acta Phys. Sin.* **60** 027307 (in Chinese)

[13] Wang Y J, Wang L D, Yang M and Yan C 2011 *Acta Phys. Sin.* **60** 077303 (in Chinese)

[14] Delley B J 1990 *Chem. Phys.* **92** 508

[15] Heer W A D, Chatelain A and Ugarte D 1995 *Science* **270** 1179

[16] Zhang H, Chen X H, Zhang Z H, Qiu M, Xu L S and Yang Z 2006 *Chin. Phys. Soc.* **55** 2986

[17] Shen L, Wang L, Yang H F, Liu X J and Liu H P 2009 *Chin. Phys.* B **18** 5277

[18] Shtogun Y V and Woods L M 2009 *Carbon* **47** 3252