Field emission properties of capped carbon nanotubes doped by alkali metals: a theoretical investigation*

Jin Lei(靳 磊)[a], Fu Hong-Gang(付宏刚)[a)b)†], Xie Ying(谢 颖)[b], and Yu Hai-Tao(于海涛)[b]

[a] *School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin* 150001, *China*

[b] *Key Laboratory of Functional Inorganic Material Chemistry of Ministry of Education, Heilongjiang University, Harbin* 150080, *China*

(Received 14 November 2011; revised manuscript received 23 December 2011)

The electronic structures and field emission properties of capped CNT55 systems with or without alkali metal atom adsorption were systematically investigated by density functional theory calculation. The results indicate that the adsorption of alkali metal on the center site of a CNT tip is energetically favorable. In addition, the adsorption energies increase with the introduction of the electric field. The excessive negative charges on CNT tips make electron emittance much easier and result in a decrease in work function. Furthermore, the inducing effect by positively charged alkali metal atoms can be reasonably considered as the dominant reason for the improvement in field emission properties.

Keywords: field emission, density functional theory, carbon nanotube, alkali metal

PACS: 79.70.+q, 31.15.es, 61.48.De, 71.20.Dg **DOI:** 10.1088/1674-1056/21/5/057901

1. Introduction

Owing to their remarkable emission stability and mechanical strength,[1,2] carbon nanotubes (CNTs) have been applied in field emission display devices and molecular sensors.[3,4] Among these applications, one of the core problems is how to produce lower threshold voltage and stronger field emission current at low electric field strength.[5] Previous studies have shown that tuning the structures, such as the radius,[6] geometry,[7−10] packing density,[11,12] and polar molecule adsorption,[13−15] is the most common and effective way to improve the field emission performance of CNT systems. Han and co-workers investigated the capped CNT (10, 10) system and found that the emission current caused by the localized states at the tip is about 10 times larger than that caused by extended metallic states.[7] Kim and co-workers pointed out that the improvement in field emission properties is attributed to the enhancement of the density of state (DOS) near the Fermi level and localized states at the CNT tip.[8] Moreover, by means of XPS experiments, Ha and Lee suggested that the remarkable improvement in field emission properties for K-doped CNTs should be attributed to the adjustment of local electronic states at the emitting regions.[13]

Several separate experimental and theoretical investigations have demonstrated that the modification of metal atoms on CNT surfaces can significantly change the field emission performance,[13,15] and the interactions between CNT and metal atoms can be very different when the valence shell structure of a specific metal is considered. By changing the electric negativity and shell structures of metal atoms, the interactions between metals and CNT surfaces are expected to change. In addition, the electronic structures and field emission properties should therefore also be changed in response to such variations, providing an effective method for modulating the macroscopic properties of the systems.[16] As this issue is rather important and yet less reported at present, relevant investigations seem very urgent.[17,18] Therefore, the present investigation is aimed at providing an application of the first-principle technique to study the geometry and electronic structures of alkali metal atom (AMA) doped CNTs and to clarify the effect of the valence shell on field emission properties. The results are hoped to provide some insights into the relationship between the structures and macroscopic

*Project supported by the Key Program of the National Natural Science Foundation of China (Grant Nos. 21031001 and U1034003), the National Natural Science Foundation of China (Grant Nos. 20971040 and 21173072), and the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (Grant No. 708029).

†Corresponding author. E-mail: fuhg@vip.sina.com

© 2012 Chinese Physical Society and IOP Publishing Ltd

properties of AMA/CNT systems.

2. Theoretical details

The DMol^3 package[19] was employed to perform the density functional theory calculations. The generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) form[20] was adopted for the treatment of exchange-correlation energy, the real-space global cutoff radius was 5.5 Å, and the functions were described by a double numerical plus polarized (DNP) basis set. The metallic armchair carbon nanotube (5, 5) (CNT55) was selected as the model system, in which a symmetric cap (half of C_{60}) is attached at one end of the CNT and the other end is saturated by hydrogen atoms, as illustrated in the insets (a) and (b) of Fig. 1. The alkali metal atoms were placed perpendicularly above the tip of the CNT55 at three different positions (center, bridge, and top sites), and the constructed models were then used as initial geometries for consequence optimization processes. An additional uniform electric field, ranging from 0 V/Å to 0.5 V/Å, is applied along the CNT axis, and the direction is from vacuum to tip.

In the present investigation the adsorption energy ($E_{\rm ad}$) is defined as

$$E_{\rm ad} = E_{\rm Total} - (E_{\rm CNT} + E_{\rm Metal}), \qquad (1)$$

where $E_{\rm Total}$ and $E_{\rm CNT}$ are the total energies of the CNT55 systems with and without AMA adsorptions, respectively, and $E_{\rm Metal}$ is the total energy of the AMAs. The work function, a crucial physical quantity for field emission applications, is the minimum energy that is required to move an electron from the Fermi level into the vacuum region. Experimentally, this can be characterized by field-ion microscopy and photoelectron emission spectroscopy,[21,22] while theoretically the work function (Φ) can be defined as

$$\Phi = \phi - E_{\rm F}, \qquad (2)$$

where ϕ and $E_{\rm F}$ are the vacuum and Fermi levels of the investigated system, respectively.

3. Results and discussion

3.1. Geometry and adsorption energy

The optimization results indicate that the adsorption of alkali metal on the center site is energetically favorable. All further calculations were performed on the basis of the optimized center site model.

The adsorption energies of AMAs/CNT55 under different electric field strengths are shown in Fig. 1. When the electric field is absent (E = 0 V/Å), the adsorption energy of Cs/CNT55 (−2.272 eV) is more negative than that of Li/CNT55 (−1.795 eV), Na/CNT55 (−1.258 eV), K/CNT55 (−1.798 eV), and Rb/CNT55 (−1.941 eV), indicating that the absolute interaction between Cs atoms and the CNT surface is the strongest. The adsorption energy variation trend is in good agreement with that in the AMAs/graphite systems.[8,23]

Figure 1 also shows that the adsorption energy of the Li/CNT55 system is almost unchanged as the electric field strength is enhanced. However, for the other four AMAs/CNT55 systems, the situation is different and the values increase with electric field strength. The unusual property for Li/CNT55 can be attributed to the smaller radius of Li with respect to other AMAs, i.e., the inner electrons bear a stronger electrostatic attraction by the nucleus, leading to a smaller transformation of the electron cloud and an insensitive response to the applied electric field. Furthermore, we can also note that, except for Li/CNT55, the adsorption energies of AMAs/CNT55 decrease with shell number at arbitrary electric field strengths.

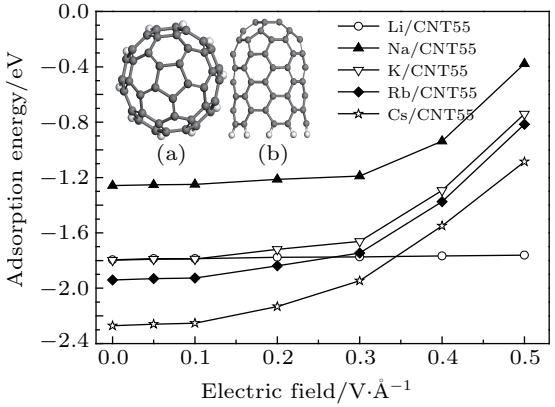


Fig. 1. The adsorption energies ($E_{\rm ad}$) of AMAs-doped CNT55 with and without external electric field. The insert is the top view (a) and side view (b) of the models.

3.2. Field emission properties

Figure 2 depicts the relationship between the work function and electric field strength for different AMAs/CNT systems. At zero bias, the work function of pristine CNT55 is 4.562 eV, which is close to the result of the PEEM experiment (4.73 eV)[22]; but the value decreases to 3.542 eV when the applied electric field is 0.5 V/Å, indicating that the emission of the electron to vacuum region is much easier under higher electric field strength.

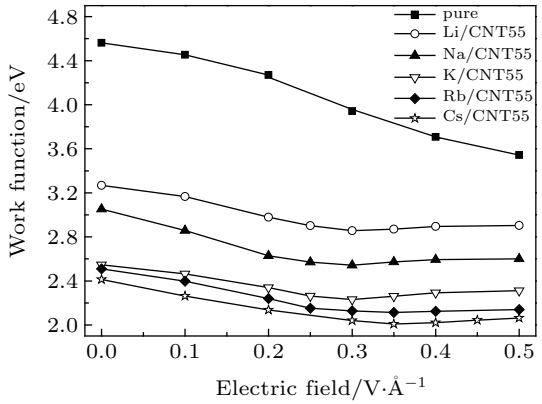


Fig. 2. Work function dependence of electric field strength for pure and AMA-doped CNT55 systems.

It can be identified that the work function of a system is significantly reduced because of the modification of the AMAs. Under a given electric field, the work functions of AMAs/CNT systems decrease monotonically with electron shell number, which indicates that the enhancement of metallicity can effectively reduce the threshold voltage. Moreover, for a specific AMAs/CNT system, the work function drops linearly at first and then almost keeps unchanged when the electric field is beyond 0.3 V/Å. The results clearly suggest the existence of an upper limit for the applied electric field. The special behaviors can be attributed to the structural changes in the AMAs/CNT systems under different electric fields. As confirmed in Fig. 1, when the applied electric field is larger than 0.3 V/Å, the adsorption energies of the AMAs/CNT systems increase drastically, which means that the interactions between the AMAs and CNT surface are significantly weakened. As a result, the distances between AMAs and CNT surface increase and the charge transfer between them is reduced to a large extent. A previous experiment showed an obvious reconstruction under a high electric field strength, which is widely known as the field evaporation phenomenon.[24] Therefore, both the experiment and our present theoretical prediction indicate that the excessively high electric field is unsuitable. To further elucidate the results, DOS and Mulliken population analyses are employed in the following discussion.

3.3. Density of states and Mulliken charge population

Figure 3 shows the DOSs of the pure CNT55 and Li/CNT55 systems. For the Li atom, the half-occupied 2s state changes significantly due to its interaction with CNT55, and some electrons therefore transfer to the CNT55 surface. It can be further confirmed that after modification with Li atoms, the DOSs of CNT55 shift towards the negative region, and some newly formed states appear at the Fermi energy (0 eV). Since the accumulation of electrons at the newly formed states is favorable to the enhancement of the field emission properties of corresponding systems, the energy that is required to move an electron from the Fermi energy to the vacuum region is significantly reduced. As a result, the threshold voltage decreases, as confirmed by the calculated work functions in Fig. 2. Besides the Li/CNT55 system, similar characteristics can also be observed in other AMAs/CNT55 ones.

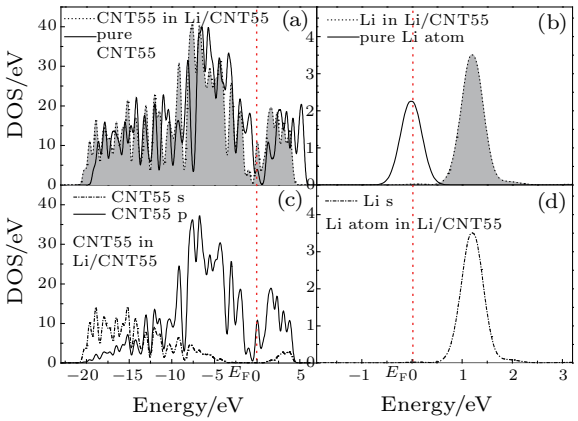


Fig. 3. DOSs of (a) CNT55 with (shadowed area) and without (solid line) Li modification and (b) pure Li (solid line) and Li in Li/CNT55 (shadowed area). the DOSs of CNT and Li in Li/CNT55 are shown in (c) and (d). The dashed line indicates the position of the Fermi energy.

To clarify the effect of the electric field, a Mulliken population analysis is applied. Figure 4 shows the Mulliken charges of the AMAs/CNT55 systems with different electric field strengths. For convenience, some of the labels are depicted in Fig. 4(a), in which layers 1–4 represent the cap, while the remaining layers compose the stem. As showed in Fig. 4(b), when the applied electric field strength is enhanced, the Mulliken charges of the four top layers of CNT55 increase monotonically. In consideration of the variation trend of work function, it can be deduced that the accumulation of negative charges at the cap of CNT55 is very crucial for the enhancement of field emission properties, which is coincident with the former research.[25–27]

When the AMAs are attached to the CNT cap, the situations are very different. Under zero bias, all the metal atoms are found to be positively charged, and the charges of the CNT cap become more negative. Figure 4(c) shows that the difference is very obvious. For layer 1, the charges of pure CNT and

Li/CNT55 are −0.024 e and −0.234 e, respectively, and the values of other AMAs/CNT55 are 18 times larger than those of pure CNT55. It can be found that the charges of layers 2–4 also follow a similar trend. Because the total charges of the four topmost layers and the eight topmost layers are almost identical, the charge summation of the four topmost layers, which can be applied as a criterion for further analysis, plays a determinate role for the macroscopic properties of the AMAs/CNT55 systems. Qiao's group[25] studied the field emission properties of CNT adsorbed by H_2O using the first-principles technique. They concluded that the existence of localized states at the cap of CNT do affect the threshold voltage. Besides the localized states, our results also indicate that the threshold voltage can be effectively modulated by changing the metallicity of the adsorption species.

Figure 4(d) shows the charge summation of the cap for AMAs/CNT55 systems under different electric fields. For Li/CNT55, the charge summation decreases at first and then increases when E is larger than 0.3 V/Å. The result explains the variation trend of the work function showed in Fig. 2 well. For other AMAs/CNT systems, similar characteristics are also confirmed. Furthermore, as the electron shell number increases, the charge summation of the systems is also changed accordingly, indicating that the

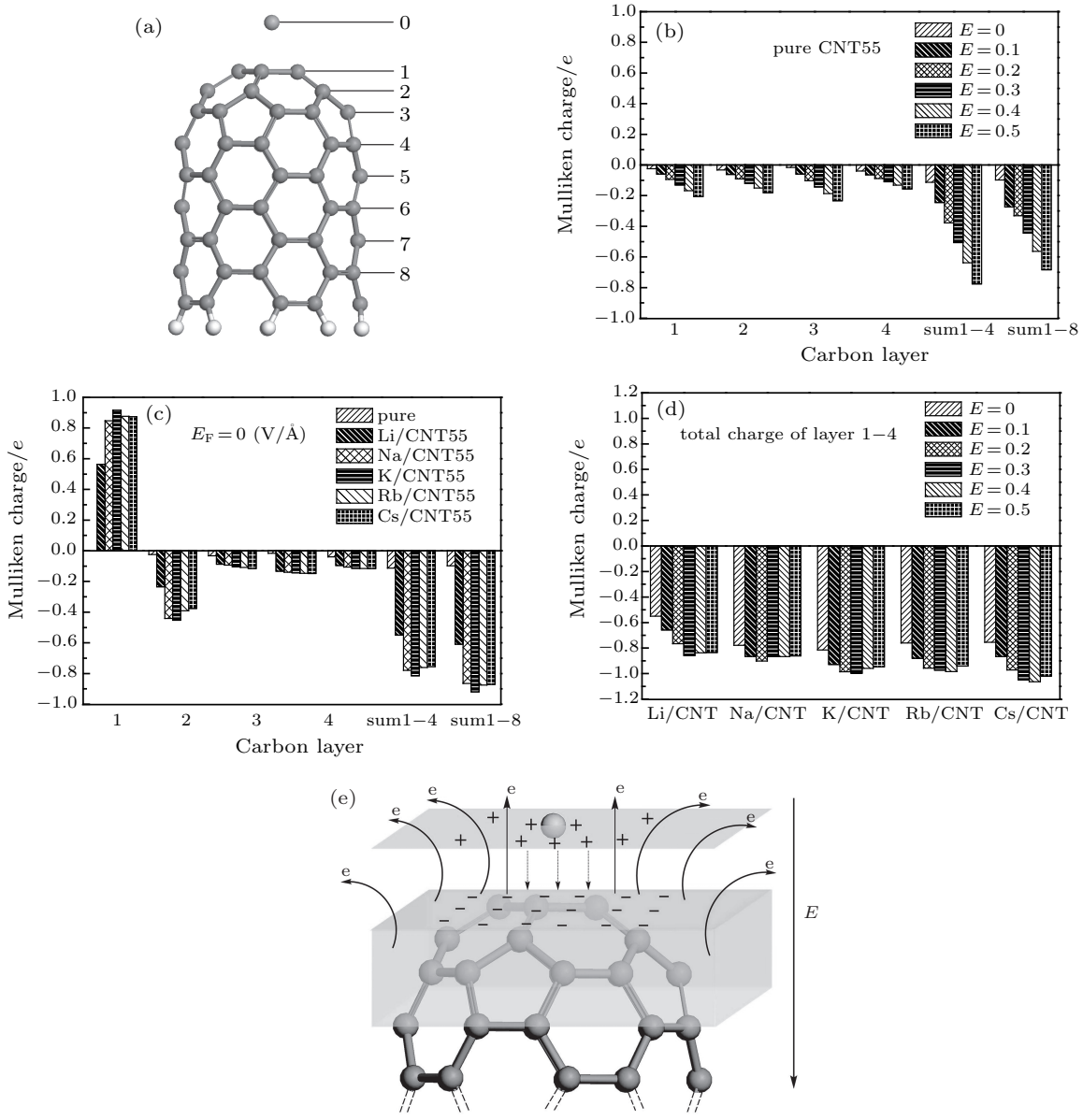


Fig. 4. (a) Layer model of CNT55. (b) Mulliken populations of pure CNT55 with an additional electric field. The Mulliken populations of AMAs/CNT55 without an electric field are shown in (c). The charge summation of 1–4 layers of AMAs/CNT55 as a function of the applied electric field is given in (d). (e) A schematic field-induced electron emission mechanism.

metallicity of the modification species does affect the field emission properties of AMAs/CNT systems. It should be pointed out that the special behaviors of AMAs/CNT systems are related to the electron accumulation at the CNT tip and the occurrence of an induced electric field due to the electron transfer from metal atoms to the CNT surface, as the schematic mechanism shows in Fig. 4(e).

4. Conclusions

We investigated the field emission properties of pure and AMAs-doped CNT55 systems by density functional calculations. The computational results show that the adsorption of metals on the center site is energetically favorable. Except for Li/CNT55, the adsorption energies of AMAs/CNT55 systems increase with increasing electric field strength. The work functions drop at first and then remain steady when $EF > 0.3$ V/Å, and the behavior can be well explained by the variations in Mulliken charge under an additional electric field. The DOSs and charge redistribution analyses suggest that the appearance of occupied electron states around the Fermi level in AMAs/CNT55 systems contribute significantly to field emission performance. Moreover, it is also identified that the occurrence of an induced electric field plays an important role for the improvement of field emission performance. The present calculations have confirmed that the modifications of AMAs on the CNT tip do affect the work functions of CNT systems, and the field emission properties can be modulated by tuning the metallicity of metals, which may provide some useful insights into the relationship between structures and macroscopic properties and will be helpful for further material design.

References

[1] Gotoh Y, Kawamura Y, Niiya T and Ishibashi T 2007 *Appl. Phys. Lett.* **90** 203107

[2] Khazaei M, Farajian A A and Kawazoe Y 2005 *Phys. Rev. Lett.* **95** 177602

[3] Teo K B K, Chhowalla M, Amaratunga G A J, Milne W I, Pirio G, Legagneux P, Wyczisk F, Pribat D and Hasko D G 2002 *Appl. Phys. Lett.* **80** 2011

[4] Jung H, Quy N V, Hoa N D and Kim D 2010 *J. Electrochem. Soc.* **157** J371

[5] Wang X Q, Wang M, He P M and Xu Y B 2004 *J. Appl. Phys.* **96** 6752

[6] Jonge N D, Allioux M and Doytcheva M 2004 *Appl. Phys. Lett.* **85** 1607

[7] Han S and Ihm J 2002 *Phys. Rev.* B **66** 241402(R)

[8] Kim C, Kim B, Lee S M, Jo C and Lee Y H 2002 *Phys. Rev.* B **65** 165418

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

[10] 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)

[11] Fujii S, Honda S I, Kawai H, Ishida K, Oura K and Katayama M 2008 *Diamond Relat. Mater.* **17** 556

[12] Wang Y J, Wang L D, Yang M, Yan C, Wang X D, Xi C P and Li Z N 2011 *Acta Phys. Sin.* **60** 077303 (in Chinese)

[13] Ha B and Lee C J 2007 *Appl. Phys. Lett.* **90** 023108

[14] Kim C, Choi Y S, Lee S M, Park J T, Kim B and Lee Y H 2002 *J. Am. Chem. Soc.* **124** 9906

[15] Durgun E, Dag S, V. Bagci M K Gülseren O, Yildirim T and Ciraci S 2003 *Phys. Rev.* B **67** 201401

[16] Zhao G P, Zhang Q, Zhang H, Qin L C and Tang J 2006 *Appl. Phys. Lett.* **89** 263113

[17] Zhou G, Duan W H and Gu B L 2004 *J. Chem. Phys.* **121** 12600

[18] Mpourmpakis G, Froudakis G E, Andriotis A N and Menon M 2007 *J. Phys. Chem.* C **111** 6593

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

[20] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865

[21] Balasubramanian K, Sordan R, Burghard M and Kern K 2004 *Nano lett.* **4** 827

[22] Suzuki S, Watanabe Y, Homma Y Fukuba S Y, Heun S and Locatelli A 2004 *Appl. Phys. Lett.* **85** 127

[23] Mpourmpakis G and Froudakis G 2006 *J. Chem. Phys.* **125** 204707

[24] Dean K A, Burgin T P and Chalamala B R 2001 *Appl. Phys. Lett.* **79** 1873

[25] Qiao L, Zheng W T, Wen Q B and Jiang Q 2007 *Nanotechnology* **18** 155707

[26] Sorescu D C, Jordan K D and Avouris P 2001 *J. Phys. Chem.* B **105** 11227

[27] Duan X F, Akdim B and Pachter R 2005 *Appl. Surf. Sci.* **243** 11