Materials Research Express

PAPER

Field emission characteristics of a nanotube-fullerene composite: a theoretical study

Shunfu Xu, Huaiwei Feng, Yuming Zhang, Weihui Liu, Chun Li and Guang Yuan

1 School of Architecture and Art, Weifang University of Science and Technology, Weifang 262700, People’s Republic of China
2 Department of Physics, Shandong Provincial University Laboratory for Protected Horticulture, Weifang, 262700, People’s Republic of China
3 Department of Physics, Shandong University of Science and Technology, Qingdao 266590, People’s Republic of China
4 Department of Physics, Institute of Information Science and Engineering, Ocean University of China, Qingdao 266100, People’s Republic of China

E-mail: xushunfu2009@gmail.com

Keywords: nanotube, fullerene, adsorption, work function, field emission

Abstract

First-principles calculations are used to investigate electronic and field emission characteristics of a nanotube-fullerene composite (a single-walled carbon nanotube (CNT) with a C_{20} molecule), which indicate that emission currents of the CNT-fullerene composite under external electric fields are roughly four times higher than those of original carbon nanotubes, and its pentagon on the apex is the highest probable positions for electron emission. Moreover, work functions of the CNT-fullerene composite decrease linearly with applied electric fields. The remarkable influence of lithium adsorption on electronic and field emission characteristics of the CNT-fullerene composite is also investigated. After lithium adsorption, the work functions of the CNT-fullerene composite decline evidently, while the emission currents increase polynomially. The emission currents of the adsorption system have been improved by two orders of magnitude (with an order of 10^{-4} A), and the lithium adatom above on the apex is the most probable position for emission.

1. Introduction

Nanomaterials such as carbon nanotubes (CNTs), graphene nanoribbon (GNR) and fullerenes are potential structures to meet the demands of future nanotechnology. In recent decades, carbon nanotubes [1] have attracted diverse interests as promising nanomaterial for new nanoelectronics because of their excellent performance. The applications of carbon nanotubes in field emission devices have been demonstrated in particular [2, 3].

The work functions of CNTs ranged from 4.30 to 5.05 eV [4–7], which are comparable with that of graphite [8–10]. And the single-wall CNTs have preferable field emission characteristics than those of other field emission materials [11].

Fullerenes [12, 13] are a series of hollow molecules made entirely of carbon atoms. The gas-phase C_{20}, which was prepared in 2000 [14], is the smallest molecule in this series. It obeys the Euler’s theorem and consists of 12 pentagons. Since then, application prospect of fullerenes in nanoelectronics and nanochemistry has been well validated.

The field emission characteristics could be modulated by an external electric field [15], metal dopings [16], and substrate orientations [17] for designing new electronic devices. Therefore, how to improve the field emission characteristics more effectively is significant for carbon nanotubes in practical application of field emission devices. It is well-known that Li atoms can be used as n-type dopants to reduce the work functions of many materials [18, 19]. Our previous work had also demonstrated that the work functions of CNTs with capped edges can be significantly improved by alkali-metal adsorption [20–22]. However, emission performances of CNT-fullerene composites were not discussed on the basis of first-principles calculations.
Here we present emission characteristics of a nanotube-fullerene composite (a single-walled carbon nanotube (CNT) with a C_{20} molecule) in the light of density functional theory (DFT). The outcome shows that the pentagon at the tip achieve the maximum current density under electric fields. The effect of Li adsorption on the CNT-fullerene composite is also studied.

2. Calculation details

Figures 1(a), (b) presents the calculation structures of the C_{20} molecule and the CNT-fullerene composite (a capped (5, 5) single-walled carbon nanotube within a C_{20} molecule (\((5, 5)\text{CNT} + \text{C}_{20}\)). Owing to constraints of computing capability, the CNT-fullerene composite consists of a six-layer (60 carbon atoms) trunk, a C_{20} molecule (20 carbon atoms) and 10 H atoms. The CNT-fullerene composite was designed by inserting the C_{20} molecule into the cap of the (5, 5) CNTs symmetrically, which resembles the C_{60}@MWCNT in experiments [23].

After structure relaxation, the structural changes were rather small. A Li adatom was located above the center of the apex of the CNT-fullerene composite \((5, 5)\text{CNT} + \text{C}_{20} + \text{Li}\).

Our research was performed under the PBE generalized gradient approximation (GGA) [24]. Tetragonal supercells comprised a vacuum thickness of 25/35 Å in X-axis/Z-axis to avoid corresponding deviation. Γ point approximation was used to sample the Brillouin zone. The structure was fully optimized with an energy cutoff of 400 eV. We exerted dipole and potential correction [25] on structure optimization. We have also considered factor of vdW force by using the DFT-D2 functional [26, 27]. Work function in this study was defined as

\[ W_F = V_F - E_F \]

which \(V_F\) represents vacuum level and \(E_F\) denotes Fermi level [28]. All structure optimization was carried out using the pwscl package, an open-source DFT software for first-principles calculations [29, 30] The emission current was achieved using formulas from Khazaei et al [31] integrating all the currents from all elements of the mesh.

3. Calculation results and analysis

After data postprocessing, adsorption of an adatom on the apex of the CNT-fullerene composite is 2.94 eV, which is higher than that of the capped (5, 5) CNT (1.16 eV). This result indicates that the Li adsorption on the CNT-fullerene composite is stronger than that on the capped (5, 5) CNT.

The work function of the capped carbon nanotube along Z-axis/X-axis direction (Z-\(W_F\)/X-\(W_f\)) in our calculations is 4.87/4.64 eV. However, the Z-\(W_F\)/X-\(W_f\) of the CNT-fullerene composite is 4.53/4.43 eV. The higher work functions arise from participation of the C_{20}. After Li adsorption, the Z-\(W_F\)/X-\(W_f\) of the CNT-fullerene decreases significantly (3.63/3.97 eV for the capped (5, 5) CNT), which has the same trend as Li adsorption on capped (5, 5) CNTs [28].

In order to facilitate the study of field emission performance, we did an overall consideration from related references [32–34] and choose uniform electric fields (\(E = -0.1, -0.2, -0.3, -0.4\) and \(-0.5 \text{ V Å}^{-1}\)). The structural changes after relaxation are rather small under above external fields. Figure 2 shows the Z-\(W_F\) of the
(5, 5) CNT, CNT-fullerene composite and the adsorption system (the (5, 5) CNT + C_{20} + Li) along Z-axis plotted against the external electric fields (The work functions under $−0.1$ to $−0.5$ V Å$^{-1}$ only have relative significance in investigating the difficulty level of emitting electrons and influence of electric fields on them).

As shown in figure 2, the Z-WF of the (5, 5) single-walled CNT, the CNT-fullerene composite and the adsorption system decline linearly with external fields. The linear dependence on electric fields indicates that the work functions of the CNT-fullerene composite can be simply manipulated by applied electric fields. The adsorption system has the lowest Z-WF among these materials under same external fields. In addition, our results show that the variations of W$_f$ are mostly due to the differences of vacuum levels under particular electric fields, while the differences of Fermi levels have only a very slight impact. To be precise, the Fermi/vacuum level difference of the (5, 5) single-walled CNT under $−0.5$ V Å$^{-1}$ is $+1.09/−4.27$ eV, and variation of work function is $−3.18$ eV. Moreover, other types of CNT-fullerene composites are presumed to have similar phenomenon as the CNT + C$_{20}$ composite.

Due to the influence of Li adsorption, electrons on the adatom are moved to the apex of the CNT-fullerene composite. Figure 3 presents differential charge density (DCD for short) on the CNT-fullerene composite and the adsorption system. The positive DCD (which represents acquisition of electrons) accumulates on the apex and the negative DCD (which represents loss of electrons) locates on the C$_{20}$ and the cap, showing charge transfer from the C$_{20}$ to the apex of the CNT. However, the positive DCD accumulates on the apex after Li adsorption, which produces a large $\pi$ molecular orbital on the cap. The redistribution of electric charge will heighten E$_f$ and decrease V$_f$, and further lower W$_f$. The DCD of the CNT-fullerene composite after Na/K/Rb/Cs adsorption may be similar to above DCD. Furthermore, the DCD after Na/K/Rb/Cs adsorption are presumed to be more evident in charge transfer and Fermi/vacuum level differences.

Figure 4 indicates the density of states (DOS for short) of the C$_{20}$, the single-walled carbon nanotube, the CNT-fullerene composite and the adsorption system, and figure 5 shows the DOS of the CNT-fullerene composite and the adsorption system under different fields ($−0.1$, $−0.3$ and $−0.5$ V Å$^{-1}$). According to figure 4, the pristine C$_{20}$ and capped (5, 5) CNT exhibits semiconducting behavior. The participation of C$_{20}$ heightens the DOS value near the E$_f$, transforming the CNT from pristine semiconducting properties into metallic properties. In addition, the adsorption system also shows metallic properties. Compared with figure 4 (under $0.0$ V Å$^{-1}$), the DOS of the CNT-fullerene composite and the adsorption system under different fields has no distinct change except for the Fermi levels. In figure 5(b), after adatom adsorption, the DOS moves along low-energy direction, indicating that more energy levels are occupied. These phenomena are in accordance with above-mentioned differences of the E$_f$.

Figure 6 shows projected density of states (PDOS) of an adatom and a C atom on the apex of the CNT-fullerene composite and the adsorption system. Most DOS value of the CNT-fullerene composite near the E$_f$ comes from the 2p orbitals of the C atoms. However, after Li adsorption, a number of electrons separated from the 2s orbital of the Li atom and move to the 2p orbitals of the C atoms. These phenomena are in accordance with DCD mentioned above. Moreover, the movement of electrons heightens Fermi level and depresses work function. Analogous behaviors are discovered are found for the adsorption system with different electric fields.
The field emission characteristics depend on many other factors including field enhancement factor, tunneling probability, electronic occupation of orbitals, and electron density on emission sites. Figure 7 illustrates 2D contour of electric field distribution of the capped $(5, 5)$ single-walled CNT, the CNT-fullerene

**Figure 3.** DCD (e/bohr$^3$) of (a) the CNT + $C_{20}$ system (b) the adsorption system. The isosurface value is ±0.0005 e/bohr$^3$. 

The field emission characteristics depend on many other factors including field enhancement factor, tunneling probability, electronic occupation of orbitals, and electron density on emission sites. Figure 7 illustrates 2D contour of electric field distribution of the capped $(5, 5)$ single-walled CNT, the CNT-fullerene
composite and the adsorption system under $-0.1 \text{ V} \text{ Å}^{-1}$. From this figure, we can clearly observe that the C atoms on apexes of the CNT and the CNT-fullerene composite play vital roles in electron emission owing to the strongest field. The field enhancement factor (FEF) of the CNT-fullerene composite (about 3165) is close to that of the pristine (5, 5) CNT (about 3212). The two values are comparable to the experimental results of single-wall carbon nanotube films [11]. Moreover, the Li adsorption has significant influence on distribution of electric fields and field enhancement factor of the CNT-fullerene composite (about 4078).

Figure 8 displays 2D pattern of tunneling probability (TP for short) of the capped (5, 5) single-walled CNT, the CNT-fullerene composite and the adsorption system under $-0.5 \text{ V} \text{ Å}^{-1}$, and the luminous positions in figure 8 are corresponding with larger values of tunneling probability. Some studies [35, 36] suggested that the
Figure 6. PDOS of the lithium atom and carbon atoms of the CNT + C_{20} system and the adsorption system.

Figure 7. 2D Contour of the electric field (V m^{-1}) distribution. (a) the pristine (5, 5) CNT under −0.1 V Å^{-1}, (b) the CNT-fullerene composite under −0.1 V Å^{-1}, (c) the CNT-fullerene composite with the Li adatom under −0.1 V Å^{-1}. Luminance represents different values of the electric field intensity.

Figure 8. Total TP pattern of (a) the pristine (5, 5) CNT under −0.5 V Å^{-1}, (b) the CNT-fullerene composite −0.5 V Å^{-1}, (c) the CNT-fullerene composite with the Li adatom under −0.5 V Å^{-1}. Luminance represents different values of the TP.
most probable emission sites located either on center pentagon or on neighboring atoms. Similarly, our first-principles results show that, under $-0.5 \text{ V Å}^{-1}$, not only the center pentagon at the center of apexes, but also the C atoms and their adjacent bonds at the apex are the highest probable positions for electron emission. Because Li adatom is ionized and the corresponding barrier height around the Li adatom is downgraded, the TP from the Li adatom is higher than that from the pentagons/hexagons. Therefore, the Li atom above the apex is of great importance in electron emission of the adsorption system.

We have also achieved 2D localized electron density (LED for short) of the CNT-fullerene composite and the adsorption system under applied electric fields, and figure 9 shows the 2D LED of the molecule orbitals associated with the largest emission currents. The LED in figures 9(a), (b) is mainly localized around the pentagon ring on the emission apex of the pristine (5, 5) CNT and the CNT-fullerene composite. Therefore, the pentagon owns both maximum TP and maximum LED, and then the molecule orbitals achieve the largest currents on the pentagon in figures 10(a), (b). In addition, molecule orbitals localized on the other pentagons/hexagons and sidewall result in smaller emission currents than that of the energy orbital mentioned earlier. The LED of the adsorption system in figure 9(c) is also localized around the pentagon on emission surface. Consequently, this molecule orbital approximately contributes largest emission current around the Li adatom figure 10(c).

According to the tunneling probability, the electronic occupation of orbitals, and LED for molecule orbitals, the total emission currents of the capped (5, 5) single-walled CNT, the CNT-fullerene composite and the adsorption system were achieved by integrating the currents from all molecule orbitals and all elements of the mesh, which are shown in figure 11. The currents of the CNT under external electric fields (with an order of $10^{-6}$ A) are is comparable to those values of carbon nanocones and carbon nanotubes [7, 37, 38] because of its smaller radius. The currents of the CNT-fullerene composite under the applied electric fields are roughly four times higher than that of the (5, 5) single-walled CNT.

We have made the Fowler-Nordheim plots. However, the corresponding curves are not linear. It maybe originate from the differences between experiments and theoretical calculations. The electric fields in experiments are so small ($E = 1 \sim 100 \text{ V μm}^{-1}$). Due to limitation of algorithm, we can not accurately simulated field emission performance of the CNT-fullerene composite under above fields.

After Li adsorption, the potential barrier around the emission spot of the CNT-fullerene composite is lowered, which make it possible to emit the electrons from low-energy molecule orbitals. The deep molecule orbitals would participate in field emission and make larger contributions to total current $I$. Therefore, the $I$ of the adsorption system have been improved by two orders of magnitude (with an order of $10^{-4}$ A). However, comparing with the emission currents from all individual states, it is unexpected that sometimes the contribution of the same molecule orbitals to the emission currents at strong fields is less than that at weak fields. Higher doping levels may obtain further increase in the emission current.
Therefore, the CNT-fullerene composite with Li adatoms is good candidates for field emission devices. Moreover, other types of CNT-fullerene composites are presumed to have similar conclusions as this kind of CNT-fullerene composite.

4. Summary

The field emission behaviors of the CNT-fullerene composite have been investigated by DFT calculations. The data reveal that the pentagon on the apex of the CNT-fullerene composite is the highest probable positions for electron emission. The electric currents of the CNT-fullerene composite under applied electric fields are obviously higher than those of original carbon nanotubes, and their work functions decline linearly with the external fields.

The influence of Li adsorption on field emission behaviors of the CNT-fullerene composite is also investigated. After adsorption, the semiconducting property of the CNT-fullerene composite is transformed into metallic property. The Li adatom on the apex is the most possible position for electron emission, and the
currents have been improved by two orders of magnitude. Therefore, the CNT-fullerene composite with Li adatoms can be new promising candidates for electron field emitters.

Acknowledgments

We thank the owners of XCrySDen and VESTA [39, 40]. This letter is benefited from National Natural Science Foundation of China (Grant No. 11804179), Shandong Provincial Natural Science Foundation (Grant No. ZR2019PA018), and Three-Platform Foundation of Department of Education (Grant No. 2018YY019, KJRC2019007).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest

The authors declare no conflict interest.

ORCID iDs

Shunfu Xu https://orcid.org/0000-0001-6755-2692

References

[1] Iijima S 1991 Helical microtubules of graphitic carbon Nature (London) 354 56–8
[2] Wang Q H et al 1998 A nanotube-based field-emission flat panel display Appl. Phys. Lett. 72 2912–5
[3] Bower C et al 2002 On-chip vacuum microtriode using carbon nanotube field emitters Appl. Phys. Lett. 80 3820–2
[4] Suzuki S et al 2001 Electronic structure at carbon nanotube tips studied by photoemission spectroscopy Phys. Rev. B 63 245418
[5] Gao R, Pan Z and Wang Z L 2001 Work function at the tips of multiwalled carbon nanotubes Appl. Phys. Lett. 78 1757–9
[6] Chen P et al 1999 Electronic structure and optical limiting behavior of carbon nanotubes Phys. Rev. Lett. 82 2348–51
[7] Xu Z, Bai X D, Wang E G and Wang Z L 2005 Field emission of individual carbon nanotube with in situ tip image and real work function Appl. Phys. Lett. 87 163106
[8] Shiraishi M and Ata M 2001 Work function of carbon nanotubes Carbon 39 1913–7
[9] Suzuki S, Bower C, Matanabe Y and Zhou O 2000 Work functions and valence band states of pristine and Cs-intercalated single-walled carbon nanotube bundles Appl. Phys. Lett. 76 4007–9
[10] Zhao J, Han J and Lu J P 2002 Work functions of pristine and alkali-metal intercalated carbon nanotubes and bundles Phys. Rev. B 65 193401
[11] Bonard J M et al 1998 Field emission from single-wall carbon nanotube films Appl. Phys. Lett. 73 918–20
[12] Buseck P R, Tsipursky S J and Hettich R 1992 Fullerenes from the Geological Environment Science 257 215–7
[13] Kroto H W et al 1985 C60: buckminsterfullerene Nature (London) 318 162–3
[14] Prinzbach H et al 2000 Gas-phase production and photoelectron spectroscopy of the smallest fullerene, C20 Nature 407 60–3
[15] Yu Y J et al 2009 Tuning the graphene work function by electric field effect Nano Lett. 9 3430–4
[16] Kwon K C et al 2012 Work-function decrease of graphene sheet using alkali metal carbonates J. Phys. Chem. C 116 26586–91
[17] Wang B, Gunther S, Winterlin J and Bocquet M L 2010 Periodicity, work function and reactivity of graphene on Ru(0001) from first principles New J. Phys. 12 043041
[18] Jin L, Fu H G, Xie Y and Yu H T 2012 Field emission properties of capped carbon nanotubes doped by alkali metals: a theoretical investigation Chin. Phys. B 21 057901
[19] Zheng B, Yu H T, Xie Y and Lian Y F 2014 Modulation of the work function of capped single-walled carbon nanotube by alkali-metal adsorption: a theoretical study ACS Appl. Mater. Inter. 6 19690–701
[20] Xu S F et al 2011 Modulation of the work function of capped single-walled carbon nanotube by alkali-metal adsorption: a theoretical study J. Phys. Chem. C 115 8928–33
[21] Liu W H, Xu S F, Yuan G and Li C 2012 Alkali–earth metal adsorption behaviors on capped single-walled carbon nanotubes based on first-principle calculations Diam. Relat. Mater. 29 59–62
[22] Liu W H, Xu S F, Yuan G and Xu Y 2013 Role of alkaline earth metals adsorption on capped single-walled carbon nanotubes based on first-principles calculations Physica B 408 46–50
[23] Tomi F et al 2004 Insertion of C60 into multi-wall carbon nanotubes—a synthesis of C60@MWNT Carbon 42 2735–77
[24] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8
[25] Neugebauer J and Scheffler M 1992 Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111) Phys. Rev. B 46 16067
[26] Grimme S 2006 Semiempirical GGA-type density functional constructed with a long-range dispersion correction J. Comp. Chem. 27 1787–99
[27] Barone V et al 2009 Role and effective treatment of dispersive forces in materials: polyethylene and graphite crystals as test cases J. Comp. Chem. 30 934–9
[28] Shan B and Cho K 2003 First principles study of work functions of single wall carbon nanotubes Phys. Rev. Lett. 94 236602
[29] http://quantum-espresso.org/
[30] Giannozzi P et al 2009 QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials J. Phys. Condens. Matter 21 39550

[31] Khazaei M, Farajian A A and Kawazoe Y 2005 Field emission patterns from first-principles electronic structures: application to pristine and cesium-doped carbon nanotubes Phys. Rev. Lett. 95 177602

[32] Qiao L et al 2007 Field emission properties of N-doped capped single-walled carbon nanotubes: a first-principles density-functional study J. Chem. Phys. 126 164702

[33] Mayer A, Miskovsky N M and Cutler P H 2002 Theoretical comparison between field emission from single-wall and multi-wall carbon nanotubes Phys. Rev. B 65 155420

[34] Liu F et al 2010 Metal-like single crystalline boron nanotubes: synthesis and in situ study on electric transport and field emission properties J. Mater. Chem. 20 2197

[35] Saito Y, Hata K and Murata T 2000 Field emission patterns originating from pentagons at the tip of a carbon nanotube Jpn. J. Appl. Phys. 39 L271–2

[36] Kuzumaki T et al 2004 The dynamic observation of the field emission site of electrons on a carbon nanotube tip Diam. Relat. Mater. 13 1907–13

[37] Qu C Q et al 2009 Electronic and field emission properties of carbon nanocones: a density functional theory investigation IEEE Trans. on Nanotech. 8 153–8

[38] Qu C Q et al 2010 Density functional theory study of the electronic and field emission properties of nitrogen- and boron-doped carbon nanocones Phys. Lett. A 374 782–7

[39] Kokalj A 2003 Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale Comput. Mater. Sci. 28 155–68

[40] Momma K and Izumi F J 2011 VESTA 3 for three-dimensional visualization of crystal volumetric and morphology data Appl. Crystallogr. 44 1272–6