Boron/nitrogen pairs Co-doping in metallic carbon nanotubes: a first-principle study*

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By using the first-principles calculations, the electronic structure and quantum transport properties of metallic carbon nanotubes with B/N pairs co-doping have been investigated. It is shown that the total energies of metallic carbon nanotubes are sensitive to the doping sites of the B/N pairs. The energy gaps of the doped metallic carbon nanotubes decrease with decreasing the concentration of the B/N pair not only along the tube axis but also around the tube. Moreover, the I–V characteristics and transmissions of the doped tubes are studied. Our results reveal that the conducting ability of the doped tube decreases with increasing the concentrations of the B/N pairs due to symmetry breaking of the system. This fact opens a new way to modulate band structures of metallic carbon nanotubes by doping B/N pair with suitable concentration and the novel characteristics are potentially useful in future applications.

Keywords: metallic carbon nanotubes, B/N pairs doping, energy gap, first-principles

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1. Introduction

Carbon nanotubes (CNTs)[1] have gained extensive attention due to their unique geometrical structures and novel physical properties, since their discovery in 1991. Much effort has been devoted to the preferential growth of semiconductor in the as-grown materials versus metallic nanotubes for large-scale device applications. It is well known that the introduction of donor/acceptor levels through substitutional doping in a material is an attractive alternative for controlling the electronic properties and conductivities of nanotubes. With the development of synthesis techniques, various kinds of doped CNTs[2−5] have been fabricated.

Nitrogen (N) and boron (B) atoms are the idea substitutional dopants in carbon materials as it has roughly the same atomic radius as C, and their binding with C is covalent and quite strong, comparing to that of host C–C bond.[6,7] The incorporation of N or B atoms into the carbon materials will influence the electronic and transport properties of C host by introducing extra carries and new scattering centres. For CNTs, mono doping by either B or N alone tends to produce metallic behaviour and the electronic properties mainly depend on doping concentration.[8,9]

Very recently, boron and nitrogen atom pairs co-doping CNTs have been synthesized directly using chemical vapour deposition.[10,11] It is shown that B and N alone are difficult to be doped into the C-SWNT lattice, and metallic CNTs are converted into semiconductors by B/N co-doping experimentally. So it is very interesting to investigate the effect of B/N pairs doping theoretically and understand the mechanism to interpret experimental observations.

Herein, density functional theory (DFT) calculation of the electronic structure and quantum transport properties of doped metallic armchair and zigzag single-walled nanotubes (SWNTs) with B/N existing as neighbouring atomic pair is reported. This choice is motivated by the recent fabrication of B/N pairs co-doping CNTs and the relative lack of the theoret-

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ical study. Several interesting computational results have been obtained: (i) when decrease the concentrations of the B/N pairs the energy gaps of the CNTs with doping B/N pairs decrease, not only along the tube axis but also around the tubes; (ii) the conducting ability of doped tubes decreases with increasing the concentrations of the B/N pairs, and the physical mechanism is given. Our results may present a new way to modulate band structure of metallic CNTs by doping B/N pairs suitably.

2. Calculation method and model

Using an *ab initio* code package, Vienna *ab initio* simulation package (VASP) the first-principles electronic structure calculations are performed.[12] The generalized gradient approximation (GGA)[13] and the Perdew–Burke–Ernzerhof (PBE) exchange–correlation function[14] are chosen. The energy cutoff for plane waves is 400 eV and each SWNT is separated by 10 Å (1 Å=0.1 nm) in vacuum. All geometry optimizations are performed using periodic boundary conditions, and Brillouin-zone intergrations are performed using a $1\times1\times5$ Monkhorst–Pach (MP) grid.[15] The tolerance for stopping structural optimization was 2.72×10^{-3} eV. A $1\times1\times21$ line-mode k-point grid has been chosen to calculate energy band.

Also, a first-principles transport calculations is carried out, using an *ab initio* code package, Atomistix ToolKit 2.0 (ATK),[16,17] which is based on real-space, nonequilibrium Green's function (NEGF) formalism and the density-functional theory (DFT). The calculation of the complete system can be obtained from two independent calculations of both electrode regions, and a two-probe calculation of the central scattering region. The electrode calculations are performed under periodical boundary conditions, with the unit cell being four atomic layers along the tube axis and the k-point grid being $1\times1\times50$. Self-consistent calculations are performed with a mixing rate set to 0.02, and the mesh cutoff of carbon atom is 1632.6 eV to achieve a balance between calculation efficiency and accuracy. The spin-unpolarized generalized gradient approximation (GGA) is used for the exchange–correlation functional.

3. Results and discussion

Two kinds of B/N pairs co-doping CNTs and several types of pristine/doped unit cells are shown in Fig. 1. Figures 1(a) and 1(e) illustrate the B/N pairs co-doping of armchair (5, 5) and zigzag (6, 0) CNT, respectively; figures 1(b)–1(d) and 1(f)–1(h) represent the pristine/doped unit cell of armchair (5, 5) and zigzag (6, 0) CNT including two different kinds of B/N co-doping sites. The C–C bond lengths are set to 1.42 Å, which had been tested in our previous work.[18] The grey, white, and black balls correspond to carbon, boron, and nitrogen atoms, respectively. Our main aim is to discuss the electronic structure and quantum transport properties of B/N pairs doping metallic armchair (5, 5) and zigzag (6, 0) SWNTs. In the elucidation of the electronic structure and quantum transport properties of doped metallic CNTs, we will focus on the following role: 1) the doping sites, 2) doping concentrations along the tube axis, 3) doping concentrations around the nanotubes.

First, one pair of adjacent C atoms of CNT is substituted with two atoms of B and N in the unit cell of metallic carbon nanotubes (MCNTs). For armchair (5, 5) CNT, there are two possible configurations with different doping sites of the B/N pair, as shown in Figs. 1(c) and 1(d). The free total energy of armchair (5, 5) CNT has been obtained: the energy of unit cell shown in Fig. 1(c) is −179.96 eV and the one in Fig. 1(d) is −178.60 eV, which means that the doping sites shown in Fig. 1(c) is the most favorable configuration. For zigzag (6, 0) CNT the favorable doping site is the configuration shown in Fig. 1(g) where the energy of unit cell is −211.19 eV but the one in Fig. 1(h) is −210.82 eV. Therefore, the unit cell shown in Figs. 1(c) and 1(g) are chosen as our doping models in this work.

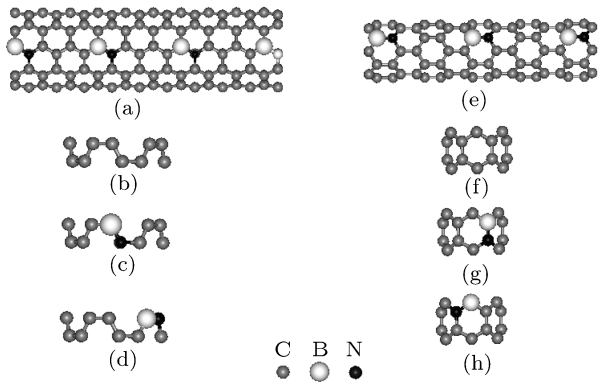


Fig. 1. Schematic view of the doped carbon nanotubes and the pristine/doped unit cells: (a)–(d) armchair (5, 5) CNT, (e)–(h) zigzag (6, 0) CNT. The grey, white, and black balls correspond to carbon, boron, and nitrogen atoms, respectively.

In the following, the sensitivity of electronic struc-

ture characters to B/N pair doping concentrations has been explored, and the band structures of armchair (5, 5) CNTs with the different axial concentrations of B/N pairs have been illustrated. Figure 2(a) clearly shows the band structures of armchair (5, 5) CNTs with the concentration of the B/N pairs of 0.407 Å^{-1}, corresponding to the super-cell size of 2.46 Å along the z axis, and figures 2(b)–2(d) show band structures of doped CNTs with various axial concentrations of B/N pairs: (b) 0.203 Å^{-1}, (c) 0.136 Å^{-1}, and (d) 0.102 Å^{-1}, respectively. Herein, the Fermi level is indicated with dashed line and the values of the energy gaps are shown. As can be seen in Fig. 2, the energy gaps are 0.2460, 0.2062, 0.1357 and 0.1303 eV respectively. The result implies that the band gap strongly depends on the doping concentration and decreases with decreasing of the concentration.

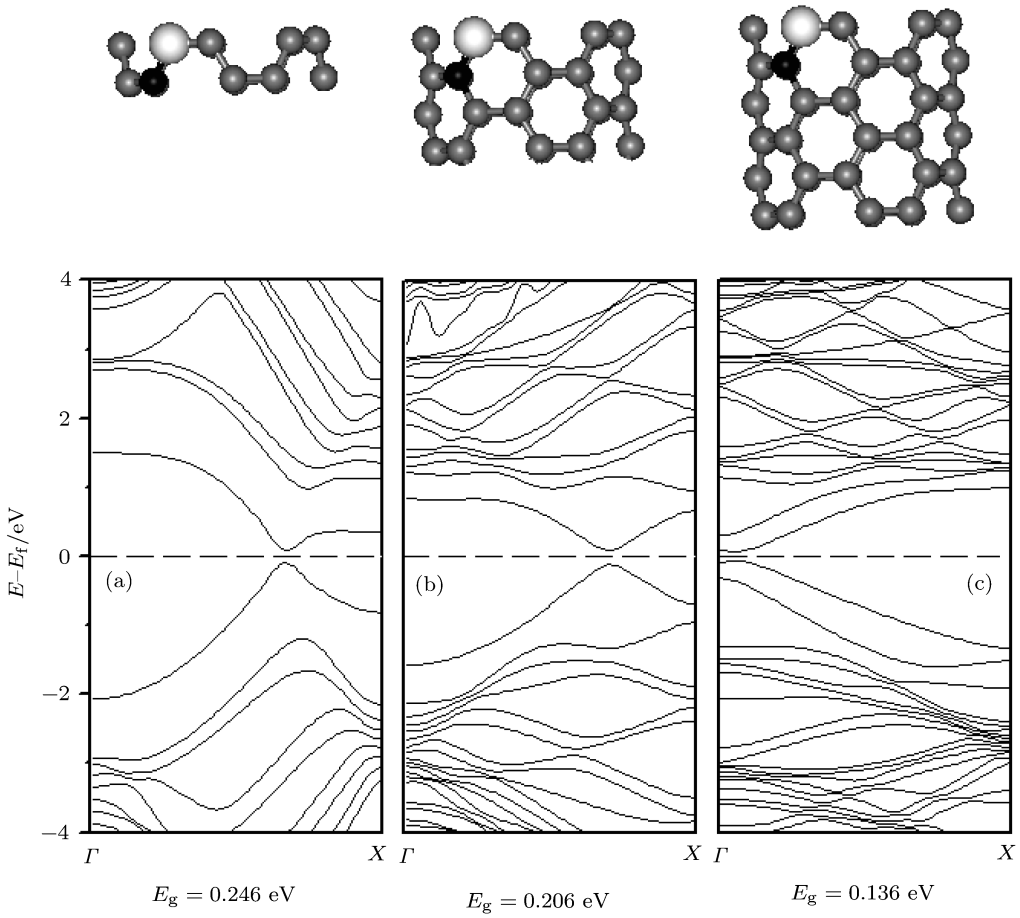


Fig. 2. Band structures of (a) armchair (5, 5) CNTs with the axial concentration of the B/N pairs of 0.407 Å^{-1}, corresponding to the super-cell size of 2.46 Å along the z axis. (b)–(d) doped CNTs with various axial concentrations of B/N pairs: (b) 0.203 Å^{-1}, (c) 0.136 Å^{-1}, and (d) 0.102 Å^{-1}. The Fermi level is indicated with dashed line and the values of the energy gaps are shown.

Next, the electronic structure characters of CNTs with the different concentration of B/N pair around the tube are studied. Figure 3 exhibits the band structures of pristine armchair (5, 5) CNTs without doped B/N pairs and doped CNTs with various circumferential concentrations of B/N pairs of 10% and 20%. A pristine armchair (5, 5) CNT is first employed, which has no energy gap at the Fermi level (Fig. 3(a)). In addition, the band structures of these B/N doped CNTs indicate that energy gaps of about 0.24 eV and 0.5 eV open at the Fermi level (Figs. 3(b) and 3(c)), which correspond to BN pairs concentrations of 10% and 20%, respectively. These results agree well with earlier studies that the band gap depends on doping concentrations.[12] For comparison, the band structure of metallic zigzag (6, 0) CNTs doped by B/N pairs around the tube is examined. There is no energy gap for pristine zigzag (6, 0) CNT (Fig. 4(a)). The band structures of these B/N doped CNTs show that energy gaps of about 0.05 eV and 0.57 eV opened at the Fermi level (Figs. 4(b) and 4(c)), which

correspond to B/N pairs circumferential concentrations of 8.33% and 16.66%, respectively. The study clearly reveals that the energy gap increases with increasing the concentration of B/N pairs co-doping into the tubes.

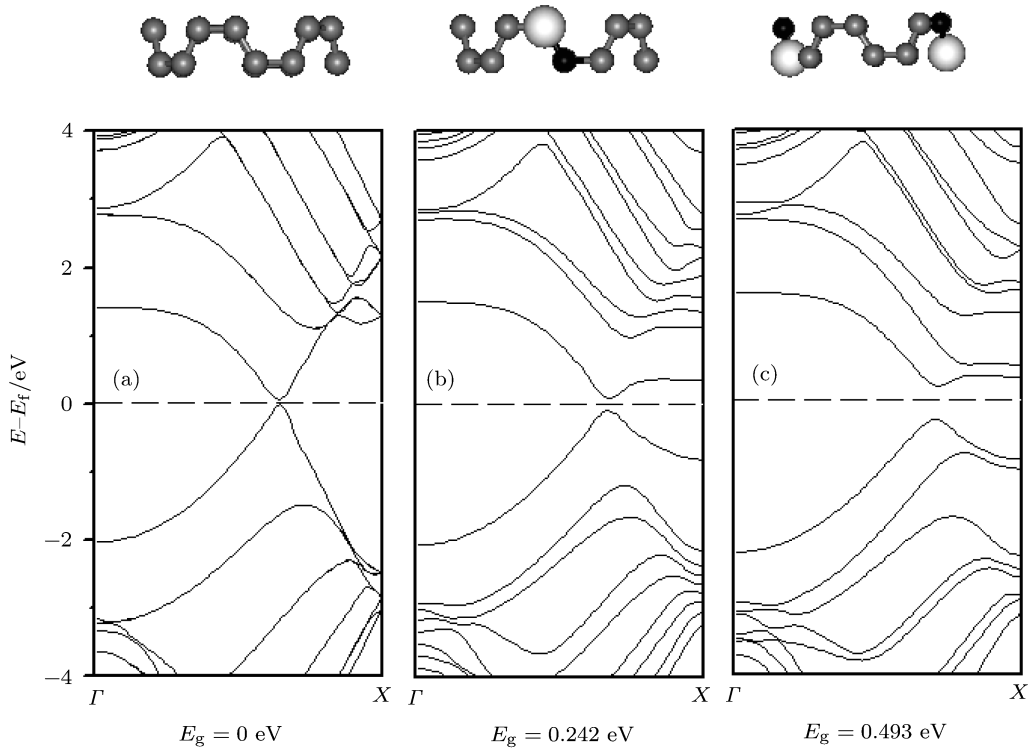


Fig. 3. Band structures of (a) pristine armchair (5, 5) CNTs without doped B/N pairs; (b)–(c) doped CNTs with various circumferential concentrations of B/N pairs: (b) 10%, and (c) 20% . The Fermi level is indicated with dashed line and the values of the energy gaps are shown.

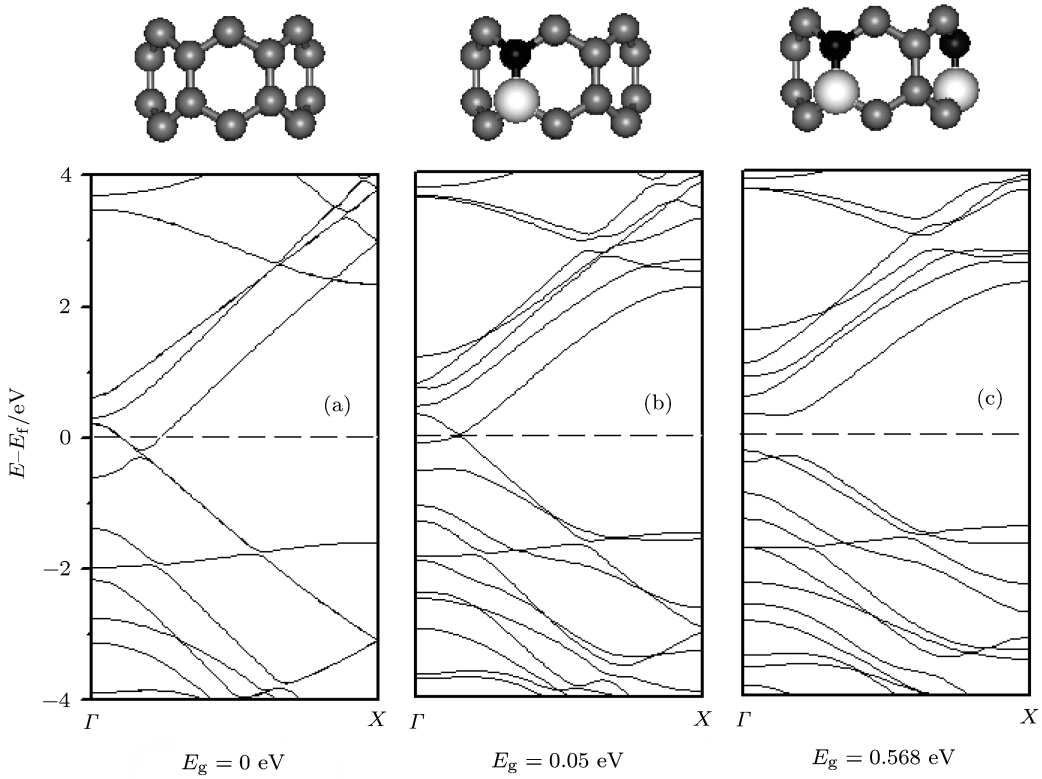


Fig. 4. Band structures of (a) pristine zigzag (6, 0) CNTs without doped B/N pairs; (b)–(c) doped CNTs with various circumferential concentrations of B/N pairs: (b) 8.33%, and (c) 16.66%. The Fermi level is indicated with dashed line and the values of the energy gaps are shown.

Finally, the quantum transport properties of doped metallic CNTs are explored. The I–V_{sd} curves and transmissions spectra of pristine/doped tube armchair (5, 5) CNTs with different circumferential concentrations of B/N pairs are presented in Fig. 5. From the I–V curves in Fig. 5(a), it is found that the pristine CNT with 0 eV energy gap exhibits pure metallic behaviour, and the transport properties of doped CNT deviate from metallic behaviour more greatly with increasing the doping concentration. It is clear that the current of the pristine CNT is higher than B/N pair doping CNT. The current values of the pristine and doped CNT under bias voltage 1.0 V are 155.6 μA and 82.4 μA, respectively, which means that the conducting ability of the doped tube decreases obviously. Additionally, figures 5(b) and 5(c) give the transmission spectra under bias voltage, 0 V and 0.5 V, respectively. Compared with the pristine tube, the conductance near Fermi level of the doped tube with 20% B/N concentration decreases notably (from $2.0G_0$ to $1.0G_0$ or so). Also, the irregular vibrating behaviour is shown in Figs. 5(b) and 5(c), which may origin from the quantum interference and quantum size effect in such nanostructure.[19,20] Our results of transport properties are in good agreement with the energy band structure analysis described above. These results indicate that B/N pairs doping in metallic CNT could be used to control the conductance effectively.

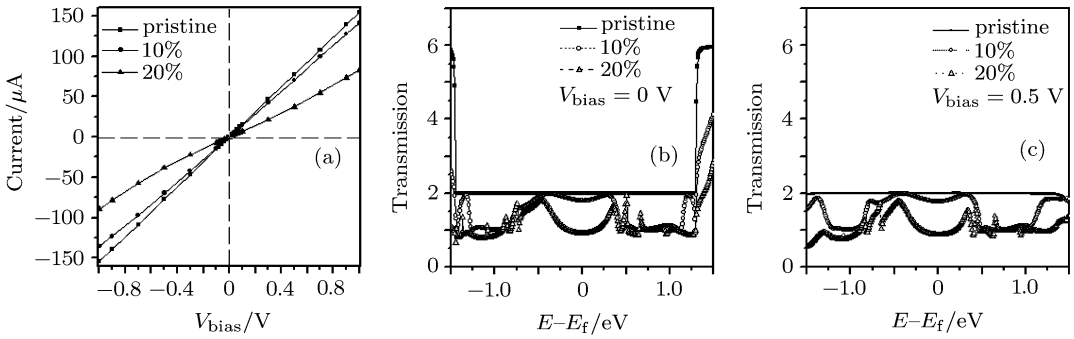


Fig. 5. The I–V_{sd} curves (a) and transmissions ((b)–(c)) of the B/N pairs co-doping armchair (5, 5) CNTs with different concentrations of B/N pairs, in which black circle, white circle ad triangle represent pristine tube, doped tube with the concentration of B/N pairs of 10% and 20%, respectively.

With the energy band theory and symmetry arguments, the B/N pairs co-doping mechanism for such system can be interpreted. Upon mono-doping by either B or N alone in either armchair or zigzag CNTs, the Fermi level is pushed down during B-doping (equivalent to p-type doping) and pushed up during N-doping (equivalent to n-type doping). Thus, CNTs with B or N doping alone tend to produce metallic behaviour through a shift of the Fermi level, and the amount of shift of the Fermi level decreases with he decrease in concentration of doping.[21] When two B and N atoms are substituted at neighbouring C–C sites (equivalent to B/N pairs doping), the system keeps the number of the valence electrons changeless. Our result also reveals that there is no shift of the Fermi level nearly after doping (not shown). For B/N pairs doping, the θ-bond formed between two dopant atoms is hetero-polar, which results in the local charge near the dopant atom and breaking the mirror symmetry of the tube and triggering a metal–semiconductor transition in some degree to generate an energy gap.

4. Conclusion

In summary, electronic band structure and transport properties of B/N pairs co-doping metallic armchair (5, 5) and zigzag (6, 0) CNTs with the first-principles quantum calculations have been investigated. Based on the energy calculations of the system, the most favourable configuration is obtained and optimized configurations are sensitive to the doping sites. In addition, it is found that the energy gaps of the CNTs strongly depend on doping concentration of B/N pairs. The energy gaps decrease with decreasing the concentration of the B/N pair not only along the tube axis but also around the tube. By showing the I–V characteristics and transmissions, our results reveal that the conducting ability of the doped tube decreases with increasing the concentrations of the B/N pairs. It is confirmed that the physical origin of the phenomenon may be that hetero-polar θ-bonds formed between two dopant atoms result in the local charge and the symmetry breaking of the tube, which trig-

gers a metal–semiconductor transition in some degree to generate an energy gap.

Thus far, although CNTs acting as semiconducting molecular wires have shown promise for future electronic devices, the coexistence of metallic and semiconducting CNTs in growth has made it notoriously difficult to scale up fabrication of CNT-based devices. Since it is possible to convert metallic CNTs to semiconductors effectively by doping B/N pairs with different doping concentration, the novel characteristics are potentially useful in the fabrication of devices based on CNTs, such as spintronic devices, field-effect transistors[20−23] and field emission source.[24]

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References

[1] Iijima S 1991 *Nature* **354** 56

[2] Terrones M, Ajayan M, Banhart F, Blase X, Carroll D L, Charlier J C, Czerw R, Foley B, Grobert N, Kamalakaran R, Redlich P K, Rühle M, Seeger T and Terrones H 2002 *Appl. Phys.* A **74** 355

[3] Xu H, Xiao J and Ouyang F P 2010 *Acta Phys. Sin.* **59** 4186 (in Chinese)

[4] Murata N, Haruyama J, Reppert J, Rao A M, Koretsune T, Saito S, Matsudaira M and Yagi Y 2008 *Phys. Rev. Lett.* **101** 027002

[5] Shlyakhova E V, Yudanov N F, Shubin Yu V, Yudanova L I, Bulusheva L G and Okotrub A V 2009 *Carbon* **47** 1701

[6] An B, Chen G D, Wang L D and Yang M 2009 *Acta Phys. Sin.* **58** 254 (in Chinese)

[7] Xu H F, Jia J F, Wang Z Y, Wei Y and Zhang L J 2010 *Acta Phys. Sin.* **59** 527 (in Chinese)

[8] Hu W K, Chu S Y, Munoz-Picone E, Boldu J L, Firth S, Franchi P, Roberts B P, Schilder A, Terrones H, Grobert N, Zhu Y Q, Terrones M, McHenry M E, Kroto H W and Walton D R M 2000 *Chem. Phys. Lett.* **323** 572

[9] Liu H X, Song J X, Zhang H M and Zhang Z Y 2010 *Chin. Phys.* B **19** 037104

[10] Wang W L, Bai X D, Liu K H, Xu Z, Golberg D, Bando Y and Wang E G 2006 *J. Am. Chem. Soc.* **128** 6530

[11] Xu Z, Lu W G, Wang W L, Gu C Z, Liu K H, Bai X D, Wang E G and Dai H J 2008 *Adv. Mater.* **20** 3615

[12] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169

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

[14] Perdew J P, Burke K and Ernzerhof M 1998 *Phys. Rev. Lett.* **80** 891

[15] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[16] Brand B, Mozos J L, Ordejón P, Taylor J and Stokbro K 2002 *Phys. Rev.* B **65** 165401

[17] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745

[18] Ouyang F P, Xu H and Fan T J 2007 *J. Appl. Phys.* **102** 064501

[19] Nöckel J U 1992 *Phys. Rev.* B **46** 15348

[20] Ladrón de, Guevara M L and Orellana P 2006 *Phys. Rev.* B **73** 205303

[21] Kahaly M U and Waghmare U V 2008 *J. Phys. Chem.* C **112** 3464

[22] Javey A, Guo J, Wang Q, Lundstrom M and Dai H G 2003 *Nature* **424** 654

[23] Park J Y 2007 *Nanotechnology* **18** 095202

[24] Qiao L, Wang C, Qu C Q, Zeng Y, Yu S S, Hu XY, Zheng W T and Jiang Q 2009 *Diamond & Related Materials* **18** 657