# The calculation of energy gaps in small single-walled carbon nanotubes within a symmetry-adapted tight-binding model*

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This paper studies in detail the electronic properties of the semimetallic single-walled carbon nanotubes by applying the symmetry-adapted tight-binding model. It is found that the hybridization of $\pi$–$\sigma$ states caused by the curvature produces an energy gap at the vicinity of the Fermi level. Such effects are obvious for the small zigzag and chiral single-walled carbon nanotubes. The energy gaps decrease as the diameters and the chiral angles of the tubes increase, while the top of the valence band and the bottom of the conduction band of armchair tubes cross at the Fermi level. The numeral results agree well with the experimental results.

**Keywords:** single-walled carbon nanotube, curvature effect, rehybridization of orbitals

**PACC:** 7125X, 7320A, 7360T

## 1. Introduction

As quasi-one-dimensional nanometer material, the carbon nanotube (CNT) that was discovered in 1991 by Iijima,[1] has been studied extensively both theoretically and experimentally.[2−7] A single-walled CNT (SWCNT) can be considered as a seamless cylindrical surface rolled up from a long strip of a graphite sheet. As the simplest case, the SWCNT is often taken as the ideal structure in numerical studies. For the large-diameter SWCNTs, the $\pi$ tight-binding ($\pi$-TB) model[6] predicts metallic or semiconducting properties, depending on the chiral vector $(n, m)$, where $n, m$ are integers. When the difference between $n$ and $m$ is a multiple of 3, the SWCNTs are metallic, while other tubes are semiconducting. This prediction was proved by the Odom's[3] and Wildöer's[4] experiments in 1998. However, when the 2s and 2p orbitals of a carbon atom were used as the basis set and the nonorthogonality of the atomic orbitals between neighbouring sites was taken into account by using the TB method, Hamada *et al.*[8] predicted the transition of the electronic energy band structure from metallic to semiconducting with the narrow energy gaps of 0.2 eV and 0.04 eV for the small diameter tubes (6, 0) and (9, 0), respectively. Such gaps are caused by curvature of the tube wall and are more remarkable when the diameters get smaller.[9] Using the $sp^3s^*$ TB model, Cao *et al.*[10] showed that the tubes (6, 0) and (9, 0) were narrow-gap semiconductors rather than metallic ones. With the Slater–Koster TB calculation, Chen *et al.*[11] pointed that tube curvature can produce an energy gap at the Fermi level for zigzag and chiral SWCNTs, and this effect decreases with the increase of both the diameter and the chiral angle. Gülseren *et al.*[12] discussed the large differences between the TB method and the first-principle calculations of the band gap values of small SWCNTs. For the zigzag tubes, the band gap formula $E_{\rm gap} = 1.99/d^2 + 140.9/d^4$ ($E$ in eV, $d$ in Å, 1 Å = 0.1 nm) was given by the Zólyomi *et al.*,[13] using the Vienna *ab initio* simulation package. Miyake *et al.*[14] studied the electronic structure of the CNT theoretically with the first-principles techniques using the local-density approximation (LDA) with the many-body correction. All of the $\pi$–$\sigma$ states hybridization effect, lattice relaxation effect and many-body effect due to electron interaction enhance the band gap. In 2001, with the technique of the scanning tunneling microscopy that is more accurate than previous experiments,[3,5] Ouyang *et al.*[15] measured the

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narrow-gaps of $0.080 \pm 0.005$ eV, $0.042 \pm 0.004$ eV, and $0.029 \pm 0.004$ eV for the small SWCNTs (9, 0), (12, 0), and (15, 0), respectively.

In this paper, the electronic properties of the semimetallic SWCNTs are presented in detail within a symmetry-adapted TB model.[16,17] When the overlaps of different orbitals of the atoms are taken into account, the method is called as symmetry-adapted nonorthogonal TB (SA-NTB) model, otherwise, the method is called as symmetry-adapted orthogonal TB (SA-OTB) model. Compared with the first-principle technique, the symmetry-adapted TB (SATB) model saves the machine time in calculating the energy band structures of the nanotubes, which makes it convenient to study the tubes in detail with large diameters and chiral angles. Using both the SA-NTB model and SA-OTB model, the electronic energy band structures are recalculated for the zigzag and chiral tubes which were previously predicted as metallic by the $\pi$-TB model.[6] The energy gaps become larger as the diameter decreases for the zigzag tubes. When the diameters of the tubes are similar, the energy gaps of the tubes are largest on the condition that the chiral angle of the tube is zero. The results show that the difference between the SA-NTB model and the SA-OTB model decreases as the diameter increases.

## 2. Model

The SWCNT is constructed by rolling up a graphene sheet along one lattice vector, which is defined as chiral vector $\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$, so that the beginning and the ending of the vector can join together. The $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the primitive lattice vectors of graphite sheet, and $n, m$ are a pair of integers to label general CNTs conveniently. The diameter and the chiral angle of the SWCNT can then be expressed as $d_{\rm t} = a_{\rm c-c}\sqrt{3(n^2+nm+m^2)}/\pi$ and $\theta = \arctan(\sqrt{3}m/(2n+m))$,[18,19] where $a_{\rm c-c}$ is the carbon–carbon–atom distance in a graphene sheet. With values of chiral angle $\theta$ in the range of $0 \leq |\theta| \leq \pi/6$, zigzag and armchair nanotubes correspond to $\theta = 0$ and $\theta = \pi/6$, respectively. One CNT contains $N_{\rm c}$ pair atoms in the unit cell in terms of $N_{\rm c} = (n^2+nm+m^2)/d$. All the rolled-up CNTs are translationally periodic along the axis of tube, with the period equal to the length of the lattice vector $\boldsymbol{T} = N_1\boldsymbol{a}_1 + N_2\boldsymbol{a}_2$, where $N_1 = (n+2m)/d$, $N_2 = -(2n+m)/d$. Here $d$ is equal to the highest common divisor of $(2m+n)$ and $(2n+m)$. However, even for relatively small-diameter CNT, the number of atom-pair in a translational unit cell can be large. Taking the tube (10, 9) for example, the number of carbon atoms is 1084 in one unit cell. When $n, m$ become even larger, $N_{\rm c}$ increases rapidly, which makes it a huge task to study the band structure comprehensively.

The SATB model raised by Popov[15,16] can overcome this difficulty by defining the nanotube helical and rotational symmetries. Using an atomic pair and two different screw operators,[20] we can produce all the other atoms of a tube. The screw symmetry of the nanotubes allows for the construction of a TB model by using a two-atom unit cell instead of the translational unit cell with $N_c$ two-atom unit cells. Such SATB model has advantages in respect of computational time and resources. For all valence TB model, the calculation for each wave vecter $k$ needs time scaling as $8N_{\rm c}$ eigenvalue problem in the symmetry-adapted TB scheme and as $(8N_{\rm c})^3$ in the nonsymmetry-adapted TB scheme. With the SA-NTB, Popov *et al.* have calculated the SWCNTs' band structure[15,16] and the resonant Raman intensity of the radial breathing models (RBMs).[21] In this paper, the narrow energy gaps in the small diameter SWCNTs are studied by using the SATB model.

## 3. Results and discussion

Both the hybridization of the $\sigma$–$\pi$ states and the overlap of the different atomic orbitals are considered in the SA-NTB model. The Hamiltonian matrix elements and the overlap matrix elements are calculated for all atomic pairs in the range between 1 and 7 bohrs. The corresponding $(l_1, l_2)$ pairs of two-atomic model are listed in Table 2.[22] As the comparison, the $\pi$-TB method is also included. The transfer integral between nearest-neighbouring carbon sites is set to 2.75 eV in the $\pi$-TB method.

### 3.1. Energy band for zigzag and armchair nanotubes

Figure 1 shows the calculated band structure of the tubes (6, 0) and (3, 3). The solid line and the dashed line represent the results from SA-NTB model and $\pi$-TB model, respectively. The SA-NTB band structure of these tubes deviates from the $\pi$-TB results. For the (6, 0) tube, the conducting band and the valence band from the $\pi$-TB model show significantly symmetric properties with regard to the Fermi level. The top of the valance band touches the bottom of the conduction band at $\Gamma$ point. However, the

SA-NTB model results show that the symmetric character of the energy band structure is changed greatly. The band structure has a narrow gap at the same point, which makes the "metal" tube actually a semiconducting one. The second lowest conduction-band state is pulled down and the second valance band state is pushed up. For comparison, the calculated energy-band structure of (3, 3) tube is also shown in Fig. 1. The band states of the (3, 3) tube calculated from $\pi$-TB method (shown by dashed line) also present a good symmetry with respect to the Fermi level. Although the results from SA-NTB model lower the symmetry of the band states, the (3, 3) tube has not energy gap at the Fermi level, and the curvature effect makes the crossing of the bands closer to the $\Gamma$ point. For the nanotubes with the similar diameter, the curvature effect of the zigzag tube is more significant than that of the armchair tube. Because of the different $\sigma$–$\pi$ states hybridization induced by the curvature on different C–C bond, the symmetry of the band states of the system is significantly lowered.

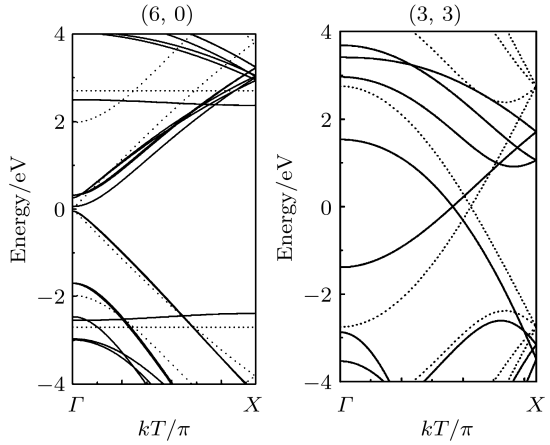



**Fig. 1.** The energy band structure of CNTs (6, 0) and (3, 3) in the energy range (–4, 4) eV. Solid lines represent the results from SA-NTB model and dashed lines represent the $\pi$-TB model results with transfer integral $\gamma_0 = 2.75$ eV. The Fermi level is at 0 eV.

Figure 2 shows the energy band structures of three zigzag nanotubes (6, 0), (9, 0) and (12, 0) from the SA-NTB model. The insets show the results in larger scale near the Fermi level. For the tubes (6, 0), (9, 0) and (12, 0), the energy gaps are 0.107 eV, 0.073 eV and 0.033 eV, respectively. Other calculated gaps of the zigzag SWCNTs (15, 0), (18, 0), (21, 0), (24, 0), (27, 0) and (30, 0) have the energy gaps of 0.021 eV, 0.013 eV, 0.011 eV, 0.009 eV, 0.007 eV and 0.004 eV, respectively, which are not presented in Fig. 2. For comparison, figure 3(a) shows the energy gaps of some ($n$, 0) zigzag tubes from our SA-NTB model and other methods.[8,11−13] Experimental results of Ref. [15] are also presented in Fig. 3(a). The most significant difference exists in the tube (6, 0), which was predicted to be metallic by the LDA method,[12,13] but is here semiconducting within SA-NTB model. This discrepancy between the two methods has been explained by Blase *et al.*,[9] who attributed the difference to a singly degenerate state which is lower in LDA method than in the TB calculations, and to the fact that the large hybridization effect of the $\sigma^*$–$\pi^*$ states in such small tubes could dramatically change the electron band structure. For the tubes (9, 0), (12, 0) and (15, 0), the energy gaps calculated here are in agreement with the results from LDA method, TB models and the experimental values. The discrepancy between LDA method and SA-NTB model decreases as the diameter of the nanotube increases. The band structures of some armchair nanotubes $(n, n)$ are also calculated with $n$ ranging from 3 to 10, while there is no splitting at the Fermi level. In Fig. 3(a), the energy gaps at the Fermi level decrease with the increase of diameter of the tubes. For the SWCNTs with the diameters bigger than that of the tube (24, 0), the curvature effect on the electronic energy band states is neglectable, and one can take into account only the $\pi$ electrons to describe the electronic energy band states of the SWCNTs. This agrees with the $\pi$-TB method calculation in large tubes, which presents very small curvatures.

All the energy band structures calculated in the paper utilize the optimized diameters from Ref. [16], which are shown in the first row of Table 1. The second row of Table 1 gives out the diameters calculated from the formula $d_{\rm t}^{\dagger} = \sqrt{3}a_{\rm c-c}n/\pi$, with $a_{\rm c-c} = 1.421$ Å. The differences between the optimized and non-optimized structure decrease as the diameter increases and the differences can be ignored when the diameter is larger than about 16 Å. The diameters of the tubes shown in the last three rows in Table 1 are from Refs. [11]–[13], which are also different from the optimized and nonoptimized results, especially for the very narrow SWCNT. The relation between the energy gap and the diameter for some zigzag tubes is shown in Fig. 3(b). The line with solid squares represents the newly calculated results, which is in agreement with the results from the formulas $E_{\rm gap} = 1.99/d_t^2 + 140.9/d_t^4$ by Zólyomi *et al.*[13] and $E_{\rm gap} = 0.043/d_{\rm t}^{1.73}$ from paper of Miyake.[14] In Fig. 3(b), the energy gap decreases with the increasing diameter at the vicinity of the Fermi level and the gap does not depend inversely on the square of the SWCNT diameter.

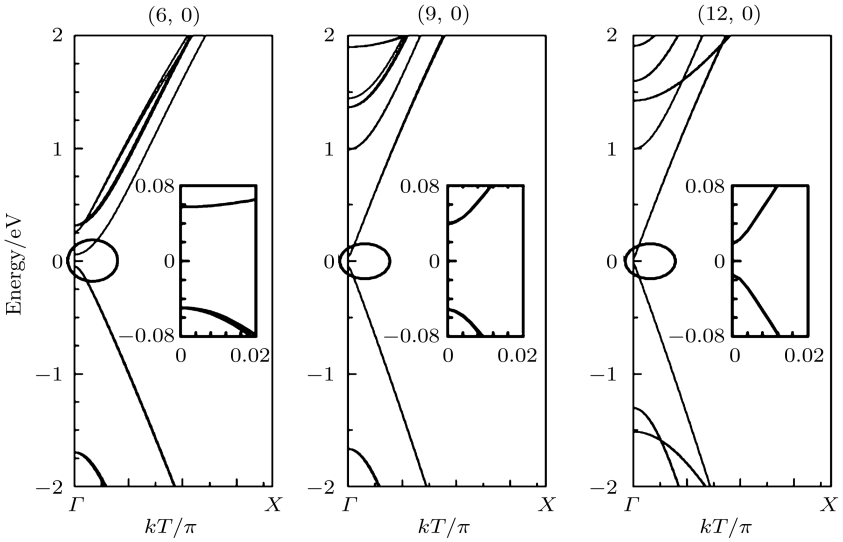



**Fig. 2.** The energy band structure of CNTs (6, 0), (9, 0) and (12, 0) in the energy range (–2, 2) eV. Solid lines represent the results from SA-NTB model and the Dirac point is indicated by a small ellipse. The insets (vertical scale ±0.08 eV) show in larger scale near the Fermi level. The Fermi level is at 0 eV.

**Table 1.** The diameter $d_t$ of $(n, 0)$ zigzag nanotubes. The optimized-diameters within the SA-NTB model are presented in the first row. The results ($d_t^\dagger$) in the second row are from the formula $d_t^\dagger = \sqrt{3}a_{c-c}n/\pi$, with $a_{c-c} = 1.421$ Å. The last three rows show the data from Refs. [12]–[14], respectively.

| $(n, 0)$ | (6, 0) | (9, 0) | (12, 0) | (15, 0) | (18, 0) | (21, 0) | (24, 0) | (27, 0) | (30, 0) |
|---|---|---|---|---|---|---|---|---|---|
| $d_t$/Å | 4.84 | 7.12 | 9.45 | 11.79 | 14.13 | 16.47 | 18.82 | 21.16 | 23.50 |
| $d_t^\dagger$/Å | 4.70 | 7.05 | 9.40 | 11.75 | 14.11 | 16.45 | 18.81 | 21.15 | 23.50 |
| Chen *et al.* | – | 7.04 | 9.40 | 11.73 | 14.10 | 16.44 | 18.80 | – | – |
| Gülseren *et al.* | 4.78 | 7.04 | 9.38 | 11.86 | – | – | – | – | – |
| Zólyomi *et al.* | 4.79 | 7.08 | 9.40 | 11.73 | 14.05 | – | – | – | – |

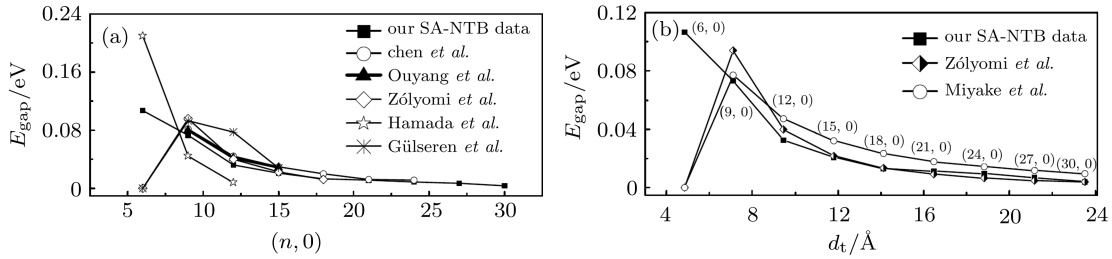



**Fig. 3.** (a) The energy gap of the zigzag tubes as a function of the $(n, 0)$ near the Fermi level. (b) The relation between the energy gap and the diameter for some zigzag tubes. The energy gap can be calculated from the Zólyomi's formula $E_{gap} = 1.99/d_t^2 + 140.9/d_t^4$ and the Miyake's formula $E_{gap} = 0.043/d_t^{1.73}$. The values of $d_t$ are presented in the first row of Table 1.

## 3.2. Energy band for chiral nanotubes

The energy band structures of CNTs (8, 2) and (11, 2) in the energy range (–1.5, 1.5) eV are shown in Fig. 4, with $\theta = 10.9°$ and $\theta = 8.2°$,[16] the chiral angles for the two tubes, respectively. The Dirac point of the band structure calculated from the SA-NTB model is indicated by a small ellipse. The insets (vertical scale ±0.08 eV) show the results in larger scale near the Fermi level. Figure 4 shows that the energy gap of the tubes (8, 2) is 0.043 eV, which is significantly smaller than that of the (9, 0) tube 0.073 eV. Both of the two tubes have similar diameter ∼ 7 Å, but different chiral angle ($\theta = 10.9°$ for the (8, 2) tube and $\theta = 0°$ for the (9, 0) tube). Comparing with the energy gaps 0.031 eV and 0.033 eV of (11, 2) and (12, 0) tubes with similar diameter but different chiral angle ($\theta = 8.2°$ for the (11, 2) tube and $\theta = 0°$ for the (12, 0) tube), we find that the energy gap decreases with the increase of chiral angle. In addition, the difference of energy gaps between the tubes (11, 2) and

(12, 0) is also smaller than that between the tubes (8, 2) and (9, 0). From both the ideal $\pi$-TB method and the SA-NTB model, there is no energy gap for the armchair nanotubes. The chiral angle of the armchair tube is $\theta = 30°$, which is the largest one among all the nanotubes. Compared with the similar diameter chiral tubes, the influence of the hybridization of $\pi$–$\sigma$ states decreases as the chiral angle increases.

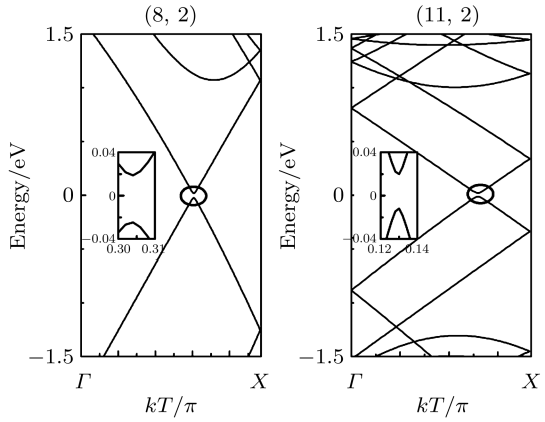



**Fig. 4.** The energy band structure of CNTs (8, 2) and (11, 2) in the energy range (–1.5, 1.5) eV. Solid lines represent the results from SA-NTB model and the Dirac point is indicated by a small ellipse. The insets (vertical scale ±0.08 eV) show in larger scale near the Fermi level. The Fermi level is at 0 eV.

## 3.3. The influence on the energy band from the overlaps of the atomic orbitals

In graphene, the $sp^2$ hybridized orbitals are symmetrical and the p orbital is perpendicular to the surface. There is no mixing between the evolving $\sigma$ and $\pi$ graphene bands. For the SWCNTs rolled up by a sheet of graphene, these bands become hybridized as a result of the curvature effect, especially for the small diameter tubes. In the orthogonal TB models, the overlap matrix elements can be defined from a unit matrix, because the overlap of the atomic orbitals on different atoms is neglectable, especially in the $\pi$-TB model. However, it cannot be omitted in studying the fine energy band structure of the tubes when the hybridization of $\sigma$–$\pi$ states is considered. The calculated band structure of the tubes (6, 0) and (3, 3) with SA-NTB model and $\pi$-TB method are shown in Fig. 1, in which the SA-NTB model takes into account the overlap of the atomic orbitals on different atoms, while the $\pi$-TB does not.

In the SATB model, the structures of the SWCNTs are also influenced by the overlap of the atomic orbitals. Table 2 shows the energy gaps of six SWCNTs from the two methods for the tubes (6, 0), (9, 0), (12, 0), (15, 0), (8, 2) and (11, 2). In Table 2, the energy gap difference of the two models for the three tubes (6, 0), (9, 0) and (12, 0) are 0.004 eV, 0.003 eV and 0.001 eV, respectively. The influence of the overlap of the atomic orbitals decreases when the diameter of the nanotube becomes larger. Comparing the energy gap for the (9, 0) tube with that for the (8, 2) tube, both tubes having the similar diameter but different chiral angles, we can make a conclusion that the difference of the energy gap increases with the decrease of chiral angle. The changes of the energy band structure are due to the switching on of an additional mechanism for rehybridization through the overlap of the atomic orbitals. The wrapping of the graphene sheet into a nanotube introduces nonorthogonality between the $sp^2$ hybridized orbitals and the p orbitals, oriented perpendicularly to the graphene sheet, which results in nonzero overlap. Therefore, this rehybridization mechanism is caused by the curvature effect and will disappear in the limit of large tube diameter and large chiral angle.

**Table 2.** The energy band gaps of six SWCNTs. $E_{\rm gap}^{\ddagger}$ and $E_{\rm gap}^{\S}$ are from the SA-NTB model and the SA-OTB model, respectively. The $\triangle E_{\rm gap}$ denotes the energy-gap difference between the SA-NTB model ($E_{\rm gap}^{\ddagger}$) and the SA-OTB model ($E_{\rm gap}^{\S}$).

| $(n, m)$ | (6, 0) | (9, 0) | (12, 0) | (15, 0) | (8, 2) | (11, 2) |
|---|---|---|---|---|---|---|
| $E_{\rm gap}^{\ddagger}$/eV | 0.107 | 0.073 | 0.033 | 0.021 | 0.043 | 0.032 |
| $E_{\rm gap}^{\S}$/eV | 0.111 | 0.076 | 0.034 | 0.022 | 0.045 | 0.033 |
| $\triangle E_{\rm gap}$/eV | 0.004 | 0.003 | 0.001 | 0.001 | 0.002 | 0.001 |

## 4. Summary

The electronic properties of CNTs are significantly affected by the $\sigma$–$\pi$ states hybridization induced by the curvature on different C–C bonds, especially for the narrow SWCNTs. Using the SA-NTB method, we find that some "metallic" SWCNTs predicted by $\pi$-TB model have energy gaps near the Fermi level, except for the armchair nanotubes. When the diameter or the chiral angle increases, the energy gaps decrease obviously for the small CNTs. The difference between the SA-NTB model and SA-OTB model is perceptible for the small tubes, indicating that the overlap of the atomic orbitals on different atoms is important in calculating the band structure of SWCNTs. The present results agree well with other theoretical and experimental results. These results should be helpful in understanding the electronic properties of the complex systems formed by the SWCNTs and more important in designing CNT devices in the future.

## References


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

[2] Ouyang Y, Peng J C, Wang H and Peng Z H 2008 *Chin. Phys.* B **17** 3123

[3] Miao L, Liu H J, Hu Y, Zhou X, Hu C Z and Shi J 2010 *Chin. Phys.* B **19** 016301

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

[5] Kudin K N and Scuseria G E 2000 *Phys. Rev.* B **61** 16440

[6] Saito R, Fujita M, Dresselhaus G and Dresselhaus M S 1992 *Phys. Rev.* B **46** 1804

[7] Kataura H, Kumazawa Y, Maniwa Y, Umezu I, Suzuki S, Ohtsuka Y and Achiba Y 1999 *Synthetic Metals* **103** 2555

[8] Hamada N, Sawada S J and Oshiyama A 1992 *Phys. Rev. Lett.* **68** 1579

[9] Blase X, Benedict L X, Shirley E L and Louie S G *Phys. Rev. Lett.* **72** 1878

[10] Cao J X, Yan X H, Ding J W and Wang D L 2001 *J. Phys.: Condens. Matter* **13** L271

[11] Chen J W, Yang Z H and Gu J 2004 *Mod. Phys. Lett.* B **18** 769

[12] Gülseren O, Yildirim T and Ciraci S 2002 *Phys. Rev.* B **65** 153405

[13] Zólyomi V and Kürti J 2004 *Phys. Rev.* B **70** 085403

[14] Miyake T and Saito S 2005 *Phys. Rev.* B **72** 073404

[15] Ouyang M, Huang J L, Cheung C L and Lieber C M 2001 *Science* **292** 702

[16] Popov V N 2004 *New J. Phys.* **6** 17

[17] Popov V N and Henrard L 2004 *Phys. Rev.* B **70** 115407

[18] Mintmire J W and White C T 1995 *Carbon* **33** 893

[19] Dresselhaus M S, Dresselhaus G and Saito R 1995 *Carbon* **33** 883

[20] White C T, Robertson D H and Mintmire J W 1993 *Phys. Rev.* B **47** 5485

[21] Popov V N, Henrard L and Lambin P 2004 *Nano Lett.* **4** 1795

[22] Li Z M, Popov V N and Tang Z K 2004 *Solid State Commun.* **130** 657