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*J. Phys. Chem. C, 2009, 113 (12), 4792-4796* • DOI: 10.1021/jp807206m • Publication Date (Web): 02 March 2009

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Electronic Structure Modulations of Radially Deformed Single Wall Carbon Nanotubes under Transverse External Electric Fields

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Received: August 12, 2008; Revised Manuscript Received: January 14, 2009

The electronic structure of radially deformed single walled carbon nanotubes under transverse external electric fields is studied by self-consistent density functional theory methods. The energy band structure modifications are analyzed, revealing that the admixture of the different states and increased $\sigma-\pi$ hybridization are responsible for opening and/or closure of the energy band gap. We find that the nanotube energy gap modulations can be achieved for various combinations of the degree of deformation, electric field strengths, and orientations with respect to the radial nanotube cross section, thus providing additional capabilities for experimental applications of carbon nanotubes.

1. Introduction

Carbon nanotubes (CNTs) are cylindrically rolled graphene sheets with many interesting properties and applications.1 The particular way of graphene rolling is described by a chirality index $(n, m)$ which determines the CNT characteristics. Much effort has been devoted to modulating their properties in various ways to achieve diverse functional devices with integrated nanotubes.2

The properties of nanotubes can be modified through mechanical deformations, and radial squashing is of particular interest. It has been shown that using an atomic force microscope, CNTs can be radially deformed, resulting in significant changes in their transport characteristics due to metal–semiconductor or semiconductor–metal transitions.3–5 Similar deformations and property changes can be achieved if CNTs are placed under sufficiently strong external hydrostatic pressure.6,7 Deformed nanotubes have also been studied theoretically to understand the relation between the radial deformations and electronic property changes.8,9 It was shown that factors such as the mirror symmetry breaking,10,11 the interaction between lower curvature sites of the deformed nanotube,12 and the $\sigma-\pi$ hybridization due to higher curvature regions13 can be responsible for metal–semiconductor or semiconductor–metal transitions in CNTs with different chiralities.

In addition to mechanical deformations, CNT properties can also be modified by applying a transverse to the nanotube radial direction external electric field (TEEF). Understanding the CNT electronic structure modifications due to TEEF is an important element in integrating nanotubes in devices such as field-effect transistors,14,15 rectifiers,16 $p-n$ junctions,17 or sensor.18 It was shown theoretically that strong enough TEEF can also couple different nanotube subbands, resulting in metal–semiconductor or semiconductor–metal transitions.19–23

Experimental modification of CNT properties can be challenging. For example, to transform a semiconducting $(10, 0)$ single wall carbon nanotube with an energy band gap $E_g = 0.92$ eV to a metallic one, the nanotube has to be radially squeezed applying a force $\sim 7.4$ N/m per unit length. This is equivalent to pressures $\sim 7$ GPa.24,25 Forces of similar values inducing semiconductor–metal transitions were calculated for other CNT.5 In addition, strong TEEFs are needed for semiconducting CNT band gap modulations. In particular, for a $(10, 0)$ CNT, a field with strength $\sim 0.65$ V/Å is needed to achieve closure of the gap.21 For metallic CNTs, screening effects cause the need for higher fields to modify the nanotube properties.22,26 The large electric field and deformation strength difficulties have led to the search for additional ways to modulate the CNT band gap.

Recently, researchers have investigated defective CNTs under TEEFs. It was found that for such nanotubes, the weaker TEEF can induce more dramatic changes in the nanotube resistance and gap as compared to the ones for perfect CNT.27,28 Similar effects were found for defective boron nitride nanotubes under TEEFs.29

In this work, we investigate for the first time how to modulate the CNT characteristics by considering a radially deformed single-walled CNT placed under a TEEF. We report first principle calculation studies of semiconducting and metallic CNTs with various degrees of radial deformation and strengths of the applied TEEF. Electric fields at three different radial directions perpendicular to the tube axis are also studied. Our calculations and electronic structure analysis show that the combined effect of radial deformation, TEEF strength, and direction can lead to various modulations of the CNT’s properties.

The rest of the paper is organized as follows. In Section 2, the method of calculation and the models are described. In Section 3, results for the electronic structure in terms of energy gap and band structure changes are discussed. The conclusions are given in Section 4.

2. Methods and Model

All calculations are obtained using self-consistent density functional theory (DFT) with the local density approximation for the exchange-correlation functional implemented in the Vienna Ab Initio Simulation Package (VASP).30 The code uses a plane wave basis and a periodic supercell method. It utilizes either ultrasoft Vanderbilt pseudopotentials or a projected augmented wave method to account for the core electrons.31 For all studied systems here, $(1 \times 1 \times 7)$ Monkhorst–Pack $k$-grid sampling of the Brillouin zone was taken for the self-consistent calculations with an energy cutoff of 420 eV. In
addition, all systems are allowed to relax with $10^{-5}$ eV total energy and 0.005 eV/Å force convergence criteria. No spin-polarization effects are included, since all systems have closed electron shell structure. Later on, we use 75 k-points for the (8, 0) nanotube and 63 k-points for the (9, 0) nanotube along the $\Gamma$–X direction for the energy band structure calculations.

To illustrate our results, we consider a single-walled (8, 0) and a single-walled (9, 0) CNTs. The (8, 0) nanotube is semiconducting with a gap 0.55 eV, and the (9, 0) nanotube has a small gap, 0.037 eV. The constructed unit cells contain one unit cell along each nanotube, and it has dimensions $(22.12 \times 22.12 \times 4.26) \AA^3$ for the (8, 0) CNT and $(22.08 \times 22.08 \times 4.25) \AA^3$ for the (9, 0) CNT after relaxation.

The radial deformation is obtained by squeezing the nanotube in the $y$ direction and elongating in the $x$ direction, and it is characterized by a dimensionless parameter $\eta = (R - R_y)/R$, where $R$ is the radius of the perfect CNT (Figure 1a) and $R_y$ is the semimajor axis connecting the CNTs’ lowest curvature regions (Figure 1b). For all $\eta$, the system is relaxed by freezing only the $y$ coordinate of the atoms on the top and bottom rows of the flattened regions while all others are left free.

To study the effect of TEEFs on the CNT electronic structure, the potential generated by the static electric field is modeled as a saw-tooth potential. The carbon nanotube is located at the center of the unit cell. Discontinuities at the cell boundary are avoided because the unit cell is large enough. Self-consistent calculations for the undeformed (8, 0) and (9, 0) CNTs with several values of the electric field strength in a larger cell, $(24.58 \times 24.58 \times 4.26) \AA^3$ for the (8, 0) CNT and $(24.53 \times 24.53 \times 4.25) \AA^3$ for the (9, 0) CNT, show a difference in the total energy on the order of 1 meV, as compared to the total energy obtained of perfect undeformed tubes. Figure 1a and b shows how the decrease in $E_g$ is much steeper for the (8, 0) CNT over a shorter field strength interval, as compared to the (9, 0) CNT. The gap for the (8, 0) CNT is $E_g = 0.4$ V/Å, whereas for the (9, 0) CNT, the closure occurs at $E = 0.8$ V/Å.

The geometry of the deformed CNTs indicates that the $x$ and $y$ directions of the transverse cross section are not equivalent. Therefore, the strength and the direction of the applied TEEF can affect the CNT electronic structure in different ways. In Figure 3c–j, we show how $E_g$ changes as a function of the TEEF strength for several values of $\eta$ when $\varepsilon$ along the $x$ and $y$ axes and along the 45° axis. Consider the (8, 0) CNT. For $\eta = 0.1$, the band gap is still relatively large: $E_g = 0.37$ eV. It decreases under the applied TEEF, and it is closed at $\varepsilon \sim 0.45$ V/Å for all three directions of TEEF (Figure 3e). However, for $\varepsilon < 0.4$ V/Å and TEEF along the $y$ axis, $E_g$ is first slightly increased until $E_g = 0.38$ eV, and after that, it decreases relatively sharply until closure. For TEEF along the $x$ axis, the gap continues to decrease until closure. $E_g$ for $\varepsilon = 0.2$ shows an intermediate behavior, and it decreases almost linearly as a function of the TEEF. For $\eta = 0.2$, the band gap is not affected significantly over a rather long range of TEEF strength for all directions until a sharp drop around $\varepsilon \sim 0.8$ V/Å (Figure 3g). For $\eta = 0.25$, the system is metallic and $E_g$ exhibits a maximum at $\varepsilon \sim 0.2$ V/Å for all directions. The maximum is largest for the field along the $y$ axis and smallest for the field along the $x$ axis. Additionally, the band gap closure occurs at different TEEF strengths, with $\varepsilon = 0.3$ V/Å being the smallest.

3. Results and Discussion

3.1. Deformation Energy and Band Gap Energy. The radially deformed (8, 0) and (9, 0) CNTs without TEEFs are calculated first. The energy needed to squash each perfect nanotube can be found from

$$E_{\eta}^{\varepsilon} = E_{\eta} - E$$

where $E$ is the total energy of the perfect nanotube, and $E_{\eta}$ is the total energy of the deformed nanotube for a specific value of $\eta$ after relaxation. In Figure 2, we show how the required energy to deform CNT$-E_{\eta}^{\varepsilon}$ varies as a function of $\eta$. It is seen that $E_{\eta}^{\varepsilon}$ increases nonlinearly, and the increase is larger for (8, 0) nanotubes. This is consistent with previous DFT studies, which showed that more energy is needed to deform smaller radius CNTs, as compared to larger radius ones.

Further, we show the evolution of the energy band gap $E_{\varepsilon}$ as a function of radial deformation $\eta$. The results are given in Figure 3. For the semiconducting (8, 0) nanotube, the band gap decreases from $E_g = 0.55$ eV at $\eta = 0$ to the closing point, $E_g = 0.0$ eV at $\eta = 0.25$, whereas for the semimetallic (9, 0) nanotube, the gap has a maximum value $E_g = 0.08$ eV at $\eta = 0.1$, and it closes at $\eta = 0.25$ (Figure 3a, b). Band gap modifications can also be achieved if TEEF is applied to the perfect undeformed tubes. Figure 3c and d indicates that the decrease in $E_g$ is much steeper for the (8, 0) CNT over a shorter field strength interval, as compared to the (9, 0) CNT. The gap for the (8, 0) CNT is $E_g = 0.4$ V/Å, whereas for the (9, 0) CNT, the closure occurs at $E = 0.8$ V/Å.

The geometry of the deformed CNTs indicates that the $x$ and $y$ directions of the transverse cross section are not equivalent. Therefore, the strength and the direction of the applied TEEF can affect the CNT electronic structure in different ways. In Figure 3e–j, we show how $E_g$ changes as a function of the TEEF strength for several values of $\eta$ when $\varepsilon$ along the $x$ and $y$ axes and along the 45° axis.

Consider the (8, 0) CNT. For $\eta = 0.1$, the band gap is still relatively large: $E_g = 0.37$ eV. It decreases under the applied TEEF, and it is closed at $\varepsilon \sim 0.45$ V/Å for all three directions of TEEF (Figure 3e). However, for $\varepsilon < 0.4$ V/Å and TEEF along the $y$ axis, $E_g$ is first slightly increased until $E_g = 0.38$ eV, and after that, it decreases relatively sharply until closure. For TEEF along the $x$ axis, the gap continues to decrease until closure. $E_g$ for $\varepsilon = 0.2$ shows an intermediate behavior, and it decreases almost linearly as a function of the TEEF. For $\eta = 0.2$, the band gap is not affected significantly over a rather long range of TEEF strength for all directions until a sharp drop around $\varepsilon \sim 0.8$ V/Å (Figure 3g). For $\eta = 0.25$, the system is metallic and $E_g$ exhibits a maximum at $\varepsilon \sim 0.2$ V/Å for all directions. The maximum is largest for the field along the $y$ axis and smallest for the field along the $x$ axis. Additionally, the band gap closure occurs at different TEEF strengths, with $\varepsilon = 0.3$ V/Å being the smallest.

Consider the (9, 0) CNT. For $\eta = 0.1$, $E_g$ shows similar functionality for all three directions (Figure 3f). The band gap is slightly increased until $\varepsilon \sim 0.6$–0.7 V/Å, where a rather sharp decrease and closure of $E_g$ occurs. One notes the similarity with the band gap dependence as a function of electric field strength.
for the (8, 0) CNT under deformation, \( \eta = 0.2 \). The \( E_g \) decrease is steeper for \( \epsilon_x \). For \( \eta = 0.2 \), the original band gap is increased \( \sim 4 \) times until \( \epsilon_x = 0.7 \) V/Å, followed by a sharp closure at \( \epsilon_x = 0.9 \) V/Å, whereas relatively weak \( \epsilon_y \) and \( \epsilon_{g5} \) cause \( E_g \) to be 0 eV. Similar behavior is found for \( \eta = 0.25 \) and TEEF along the \( y \) axis (Figure 3), for which \( E_g \) exhibits a pronounced maximum at \( \epsilon_y = 0.8 \) V/Å. However, the band gap is not affected at all for any strength of \( \epsilon_y \).

**3.2. Electronic Structure Changes.** To elucidate further the effect of radial deformation and electric field and understand the origin of the energy band gap evolution, we present results for the energy band structure for the (8, 0) and (9, 0) CNTs. In Figure 4, the energy band structure for the (8, 0) CNT with \( \eta = 0.1 \) for several TEEF values and orientations is shown. For a perfect CNT, the angular momentum, \( J \), is a good quantum number. \( J \) can be associated with a specific energy valence band and a specific energy conduction band. When only radial deformation is applied, electronic states can mix according to the selection rule \( \Delta J = \pm 1 \). In addition, \( \sigma-\pi \) hybridization occurs due to the higher curvature region. As a result, the single degenerate conduction band is brought closer to the Fermi level, \( E_F \), and for sufficiently strong deformation, closure of the band gap occurs. When TEEF is applied only, however, the electronic states mix according to the selection rule \( \Delta J = \pm 1 \), which also brings the conduction energy band closer to \( E_F \). For sufficiently strong \( \epsilon \), this band crosses the Fermi level; thus, \( E_g = 0.0 \) eV. When both \( \eta \) and TEEF are present, the closure of the energy gap is due to the motion of the conduction band closer to the Fermi level due the mixing of the electronic states according to \( \Delta J = 0, \pm 1, \pm 2 \) and the \( \sigma-\pi \) hybridization from the higher curvature regions.

The radial cross section of the deformed CNT implies that the direction of the applied TEEF can be important. As seen from Figure 4, the location of the lowest unoccupied single degenerate conduction band depends on the direction and a particular value of the applied electric field. Our calculations show that when TEEF passes through the highest curvature regions (along the \( x \) axis), the effect of the \( \sigma-\pi \) hybridization is stronger. Depending on the TEEF strength for a particular \( \eta \), the conduction band can move closer to \( E_F \), as compared to the other electric field orientations, (Figure 4, Figure 3e) or can have a relatively smaller effect if the gap is small (Figure 3g, 3i).

We also show the energy band structure of (9, 0) CNT with \( \eta = 0.25 \) for the same TEEF strengths and orientations as for (8, 0) CNT (Figure 5). For metallic tubes without \( \epsilon \), small \( \eta \)
Modulations of Radially Deformed SWCNTs

The results from our calculations show that the application of radial squashing and TEEF at the same time can provide a variety of CNT property modulations. If semiconducting or metallic tubes are slightly deformed, great variations in the electronic structure can be induced by external electric fields at different radial directions. For example, we showed that by changing the direction of the field from εx to εy for the slightly deformed (8, 0) CNT, the energy gap can be reduced ~2 times for the same field strength (Figure 3e). At the same time, for metallic (9, 0) CNT, smaller fields along the y axis can increase Eg significantly, but fields along the x axis affect very little or not at all their band structure (Figure 3i, h, j). In addition, for some CNTs with relatively small Egs, smaller electric fields tend to not affect the energy gap much, regardless of the TEEF orientation (Figure 3f), but for other CNTs, this is not the case (Figure 3g).

Thus, our calculations show that it is possible to obtain various carbon nanotube responses — metallic, semiconducting, and no significant change — for a specific radial deformation and transverse electric field strength simply by changing the direction of the electric field. The combination of deformation, electric field strength, and direction may provide additional flexibility in accommodating greater capabilities and reduce the need for very large deformations or very large TEEF for CNT property modulations. We suggest that such electric property modulations may be of interest to experimentalists working in the carbon nanotube field.

4. Conclusions

In conclusion, we have presented for the first time results from self-consistent DFT calculations for the electronic structure changes of radially deformed single-walled carbon nanotubes when a transverse external electric field is applied. These changes are analyzed in terms of energy band gap, energy band structure, and charge density plot dependences in terms of degree of radial deformation, strength, and direction of the electric field for metallic and semiconducting nanotube. We suggest that our results can have important implications to CNT performance in extreme conditions as well as CNT integrations in electronic devices.

Acknowledgement. Acknowledgement is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research. L.M.W. was also supported by the Center for Integrated Materials (CIFM) through Grant no. USAMRMC-07355004 during part of this work. We would like to acknowledge the use of the services provided by Research Computing, University of South Florida, and TeraGrid Advanced Support Program.

References and Notes
