Ab-initio Investigation to Understand the Electronic Properties of Hetero Graphene-Boron Nitride Nanotubes and Enhance their Properties

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Abstract

Using density functional theory (DFT) combined with a Green's function scattering approach (GFSA), we examine the electronic properties, the density of states (DOS), the transmission coefficient (T(E)) and the current-voltage features (I(V)), of the bare hetero nanotubes and the electronic properties of doped hetero nanotube by electron acceptor tetracyanoethylene molecule (TCNE) and electron donor tetrathiafulvalene molecule (TTF). Four different hetero nanotubes used in this investigation which are formed from alternating number of graphene rings in between the boron nitride rings as we shall show these hetero nanotubes in figure 3.1. Our results show that altering the number of graphene rings along the hetero nanotube has a huge effect on the energy gap (E_g) around Fermi energy (E_F). This methodology could be a good method to design a semiconductor with desirable band gap. Also, the results show that by doping the hetero nanotubes by electron acceptor tetracyanoethylene molecule (TCNE) and electron donor tetrathiafulvalene molecule (TTF) lead to enhance the conductance of the hetero nanotubes.

Keywords: carbon nanotubes, electronic properties, hetero nanotubes, energy gap.

دراسة نظرية باستخدام الطريقة التامة لفهم الخصائص الالكترونية للأنابيب النانوية المغايرة التركيب وتحسين تلك المواصفات

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الخلاصة

باستخدام نظرية الكثافة "DFT" جنبا إلى جنب مع تقريب دالة كرين لمنطقة التشتت 'GFSA'، تم دراسة الخصائص الإلكترونية للأنابيب النانوية المغايرة التركيب (المركبة من الكاربون والبرون نتراید) ، وهي كثافة الحالات "DOS" و معامل الانتقال T(E)ومميزات منحنى التيار I(V) ، للانابيب النانوية المغايرة التركيب المثالية النقية ونفس الانابيب النانوية المغايرة التركيب بعد تحفيزها بواسطة الجزيئة المتقبلة للالكترون (TCNE) tetracyanoethylene والجزيئة المانحة للالكترون (TTF) tetrathiafulvalene. اربعة انابيب نانوية مغايرة التركيب استخدمت في هذه الدراسة وهذه الانابيب المغايرة التركيب تم تشكيلها من خلال تغير عدد حلقات الكرافين المحصورة بين حلقات البورون نتراید والتي سيتم عرضها في الشكل 3.1 . نتائجنا اظهرت بانه عند تغير عدد حلقات الكرافين على طول الانبوب النانوي المغاير التركيب ادى الى تاثير ملحوظ وواضح على فجوة الطاقة (E_g) حول طاقة فيرمي (E_F). ومن الممكن ان تكون هذه الطريقة جيدة لتصميم مادة شبه موصلة مع فجوة طاقة مرغوبة. كذلك نتائجنا اظهرت ان تحفيز الانابيب الناونية باستخدام كل من الجزيئة المستلمة للالكترون tetracyanoethylene (TCNE) والجزيئة المانحة للالكترون tetrathiafulvalene (TTF) ادت الى تحسين المواصفات الالكترونية لهذه الانابيب الناوية المغايرة التركيب.

الكلمات المفتاحية: انابيب الكاربون النانوية، مواصفات الكترونية، الانابيب المغايرة التركيب النانوي وفجوة الطاقة.

1. Introduction

The discovery of carbon nanotubes (CNTs) by S. Iijima in 1991 [1] has attracted a lot of attention for their unique electronic and mechanical properties [2-5]. Nano mechanical systems based on CNTs have been extensively studied [6-8] and some examples of the many proposed applications for CNTs as structural mechanical elements include data storage [9], relays [10], switches [11], molecular sensors [12], and oscillators [13, 14]. Electronically, they can be metallic, insulating, or semi-conducting depending on the chirallity, which is often difficult to control in synthesis [15-19]. One solution to this problem is the sculpturene method [20], which consists of cutting nanoribbon strips out of bi-layer graphene or hetero material in vacuo. The resulting reconstruction leads to the formation of nanotube-like structures or in general, nanostructures known as sculpturenes. Critically, this means that nanotube-like structures can be manufactured deterministically from graphene nanoribbons (GNRs), which can themselves be produced more deterministically using lithographic, chemical, or sonochemical techniques, or

by assembling GNRs from chemical precursors [20]. The Sculpturene method also gives us the opportunity to create composite nanostructures [21, 22] and exotic topologies [23] and could be used to construct tapered nanotubes [24, 25], nanopipettes [26], nanohorns [27], and nanocones [28]. In this paper, we used sculpturene method to form the hetero nanotubes (figure 3.1) by cutting bi-layered hetero nanoribbons and relax them to form the hetero nanotube that we used in this study.

Recently, a heterostructures of graphene and hexagonal boron nitride has been synthesised [29, 30], they reported a pilot study on epitaxy of graphene boron nitride heterostructure, and they found that GNRs grow preferentially from the atomic steps of hexagonal boron nitride, forming in-plane heterostructures. in other words, these recent publications confirmed that the graphene boron nitride hetero structure could be synthesized.

Also, Hetero nanotubes received a huge interest from many scientific research groups to understand their electronic properties and their possible applications [21, 31-33]. These studies reported that boron nitride has a remarkable effect on the energy gap of ideal carbon nanotube. The importance of the interface between graphene and boron nitride has been investigated [21, 34, 35], the boron nitride impurities led to characteristic peak close to the Fermi energy is found, with the peak associated with boron below the Fermi energy and the peak associated with nitrogen above the Fermi energy[36].

2. Theoretical Method

We used the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [37] implementation of density functional theory (DFT) to optimise the structures using the local density approximation (LDA) with the Ceperley-Alder (CA) exchange correlation functional and double zeta polarized (DZP) basis set. The initial supercells are relaxed until the forces on the atoms are minimised to below 0.01 eV/Å with a real-space grid defined with a plane-wave cutoff energy of 300 Ry. The density of states (DOS) was calculated with 1× 1× 200 k-points. The obtained Mean-Field Hamiltonian (MFH) from SIESTA was used as an input data to feed the non-equilibrium Green's function (NEGF) code which called GOLLUM [38] to calculate transmission coefficient T(E). To investigate the I(V) curve, we used:

$$I(V) = \frac{2e}{h} \int_{E_F - \frac{eV}{2}}^{E_F + \frac{eV}{2}} T(E,V)dE \qquad (1)$$

Within a Landauer description of electron transport, since the investigated hetero nanotubes are periodic, the transmission coefficient T(E) for electrons of energy E travelling from left to right

is identical to the number of open channels (NOC) and therefore the maximum current I(V) carried by the hetero nanotube shown in figure 3.1 at a finite voltage V, is given by [21]:

$$I(V) = \frac{2e}{h} \int_{E_F - \frac{eV}{2}}^{E_F + \frac{eV}{2}} T(E)dE \qquad (2)$$

3. Electronic Properties of Bare Hetero Nanotubes

In this section, we investigate electronic properties of four bare hetero nanotubes by varying the number of graphene rings, from one ring to four rings of graphene in between the transverse boron nitride rings as shown in figure 3.1. The figure 3.1 shows the optimised hetero nanotubes obtained using the sculpturene method by cutting a hetero bi-layered nanoribbon which consists of graphene and boron nitride and allow them to reconstruct to form the hetero nanotubes, this method explained in reference [20]. The Mean-Field Hamiltonian (MFH) has been obtained by employing the SIESTA code and by using the obtained the MFH, we investigate the density of states (DOS). Also, The Mean-Field Hamiltonian (MFH) used to feed the GOLLUM code to obtain the transmission coefficient T(E). The calculations carried out with 1×1×200 k-points to make sure that the hetero nanotubes shown in figures (3.1a-3.1d) are perfectly periodic in Z direction.

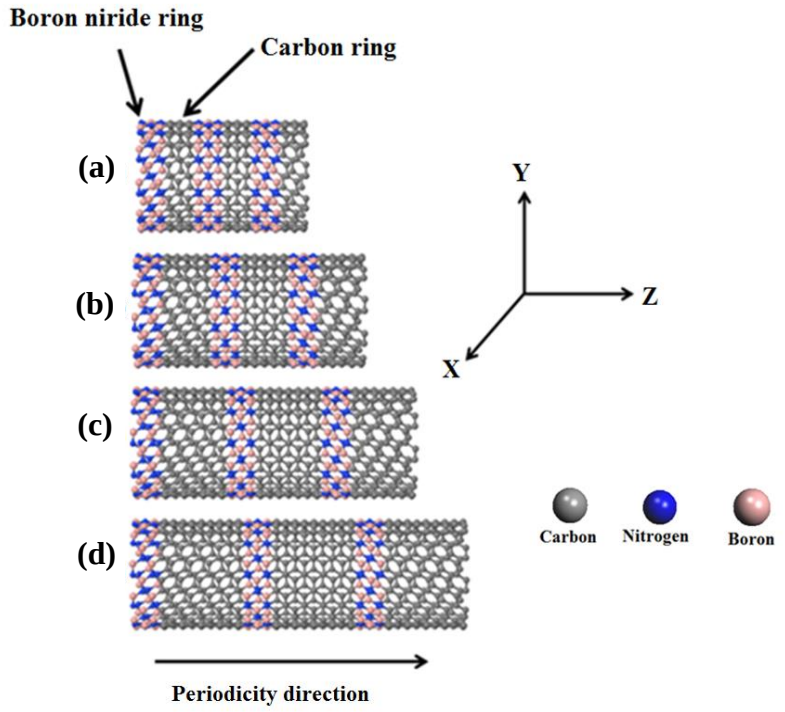

Figure 3.1: The relaxed hetero nanotubes, **(a)** with one boron nitride ring and one graphene ring, the structure contains 360 carbon, boron and nitrogen atoms, **(b)** with one boron nitride ring and two graphene rings (480 carbon, boron and nitrogen atoms), **(c)** with one boron nitride ring and

three graphene rings (600 carbon, boron and nitrogen atoms), and **(d)** with one boron nitride ring and four graphene rings, the structure consist of 720 carbon, boron and nitrogen atoms. All structures are periodic in Z direction.

The resulting density of states (DOS) and the T(E) of hetero nanotubes shown in figure 3.1 are shown in figure 3.2.

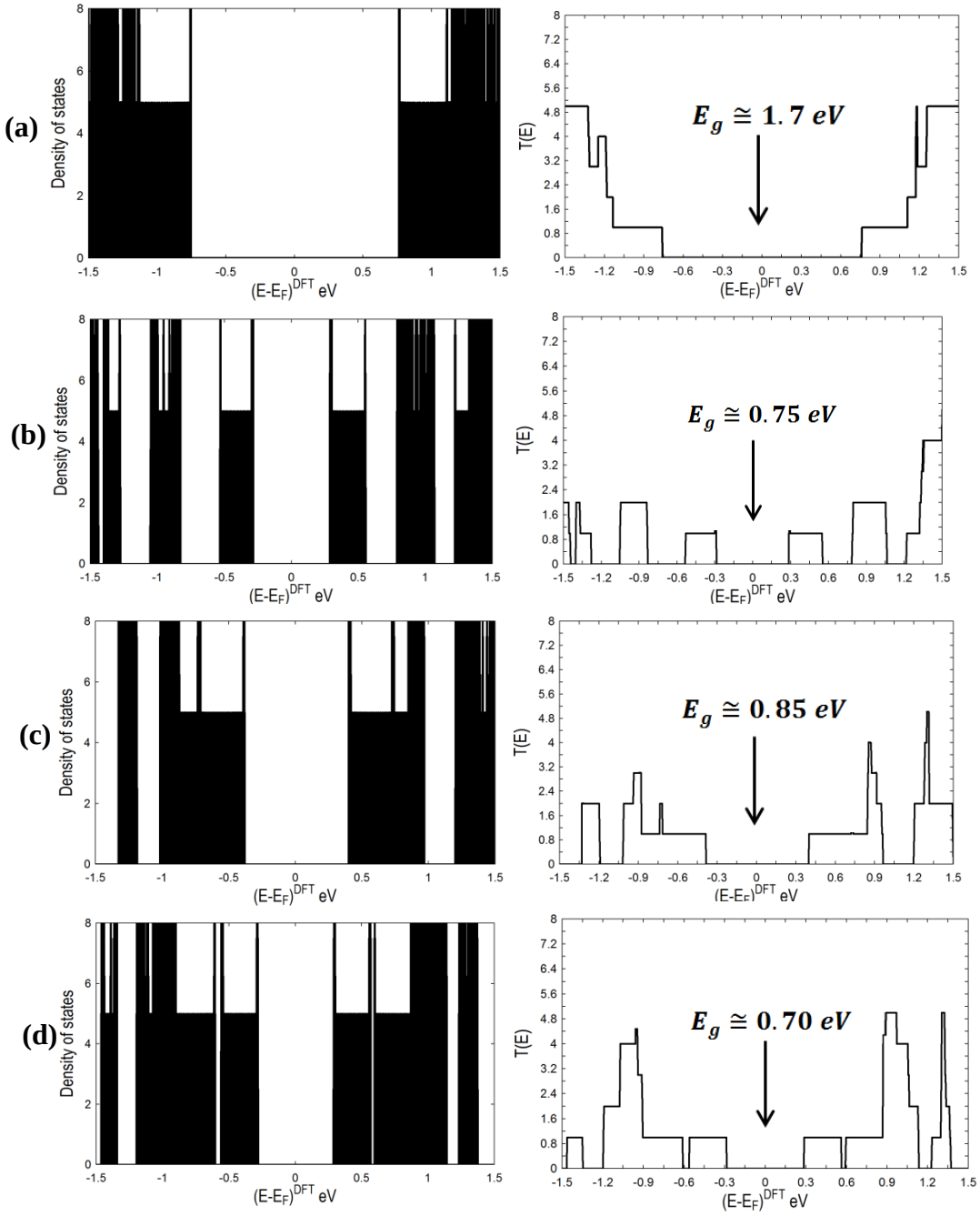

Figure 3.2: Shows the resulting electronic properties, the density of states (DOS) and the transmission coefficient T(E) for **(a)** the hetero nanotube shown in figure 3.1a, **(b)** the hetero

nanotube shown in figure 3.1b. **(c)** the hetero nanotube shown in figure 3.1c. **(d)** the hetero nanotube shown in figure 3.1d. In all figures, the left column shows the density of states (DOS) and the right column represents the transmission coefficient T(E).

From figure 3.2, it is easy to see that the energy gap changed dramatically. For example, the energy gap shown in figure 3.1a is about 1.7 eV which is belong to the hetero nanotube shown in figure 3.1a, this means there is a huge increasing in the energy gap comparing with the ideal carbon nanotube which is always behave as a conductor [39, 40] and also there is an enormous reduction in the energy gap comparing with the ideal boron nitride nanotube which behaves as a perfect insulator with a wide band-gap of approximately 5 eV [41-43]. Overall, the energy gap around Fermi energy for all hetero nanotubes shown in figure 3.1 are varying from approximately 0.7 eV to 1.7 eV.

To clarify the results shown in figure 3.2 and using equation 2, we calculate the current (I) of the travelling electron through the hetero nanotubes from the left to the right. The resulting current plots are shown in figure 3.3.

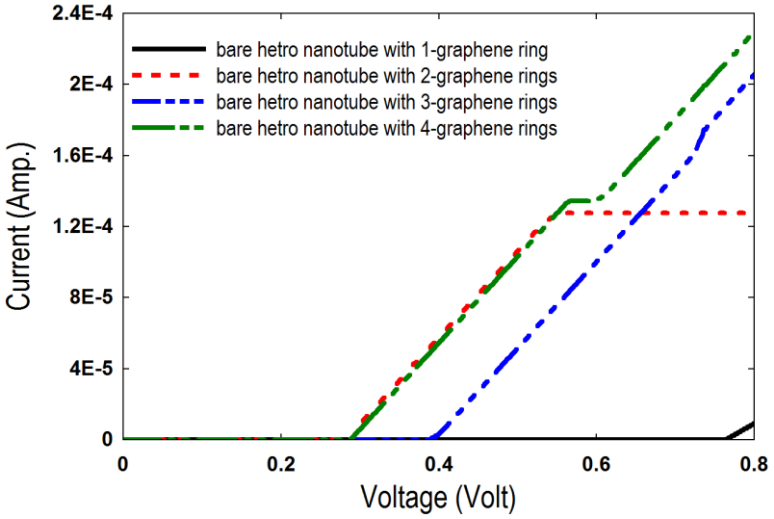

Figure 3.3: Shows the calculated I(V) curve for **(a)** the hetero nanotube shown in figure 3.1a, **(b)** the hetero nanotube shown in figure 3.1b, **(c)** the hetero nanotube shown in figure 3.1c, and **(d)** the hetero nanotube presented in figure 3.1d.

Figure 3.3 shows clearly that at specific voltage value, for example at 0.8 volt the hetero structure with one graphene ring (shown in figure 3.1a) has the lowest current and the hetero nanotube with four graphene rings (shown in figure 3.1d) has the highest current. This result is due to the available states at and around the Fermi energy (E_F) which means increasing the graphene rings layer lead to enhance the conductance of the hetero nanotubes.

4. **Doping the Hetero Nanotube**

We avoid introducing unnecessary scattering, rather than introducing substituents, we shall consider doping the hetero nanotubes using adsorbates of the electron acceptor tetracyanoethylene (TCNE) [44-46] and the electron donor tetrathiafulvalene (TTF) [46, 47]. Here and to benchmark our study, we present the resulting current-voltage plots for the two doped hetero nanotubes shown in figures 4.2, 4.3 and figure 4.4 by the TCNE, TTF-1 and TTF-2. These two doped hetero nanotubes are infinitely periodic in the longitudinal Z direction and contain narrow transverse rings of boron nitride, separated by rings of graphene of length three and four rings. Figure 4.1 shows the TCNE and TTF molecules.

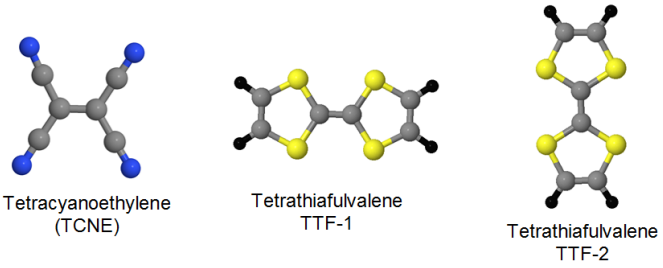

Figure 4.1: the far left shows the electron acceptor tetracyanoethylene (TCNE), the middle and far right figures shows the electron donor tetrathiafulvalene (TTF) in different configuration, we refer to the middle one as TTF-1 and the far right one as TTF-2.

We repeat the same producer to calculate the electronic properties of the doping hetero nanotubes by TCNE, TTF-1 and TTF-2 which are shown in figure 4.2, figure 4.3 and figure 4.4.

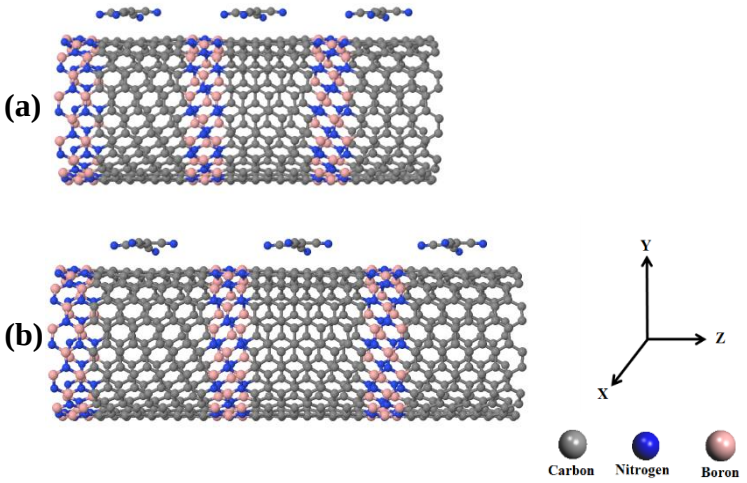

Figure 4.2: The TCNE-doped hetero nanotubes **(a)** with three graphene rings, and **(b)** with four graphene rings.

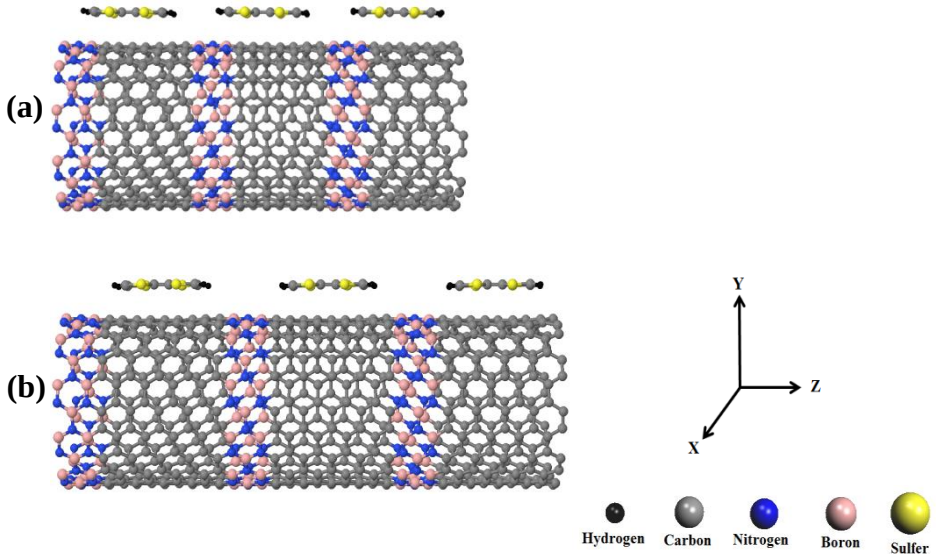

Figure 4.3: The doped hetero nanotubes by TTF-1 for **(a)** with three graphene rings and (b) with four graphene rings.

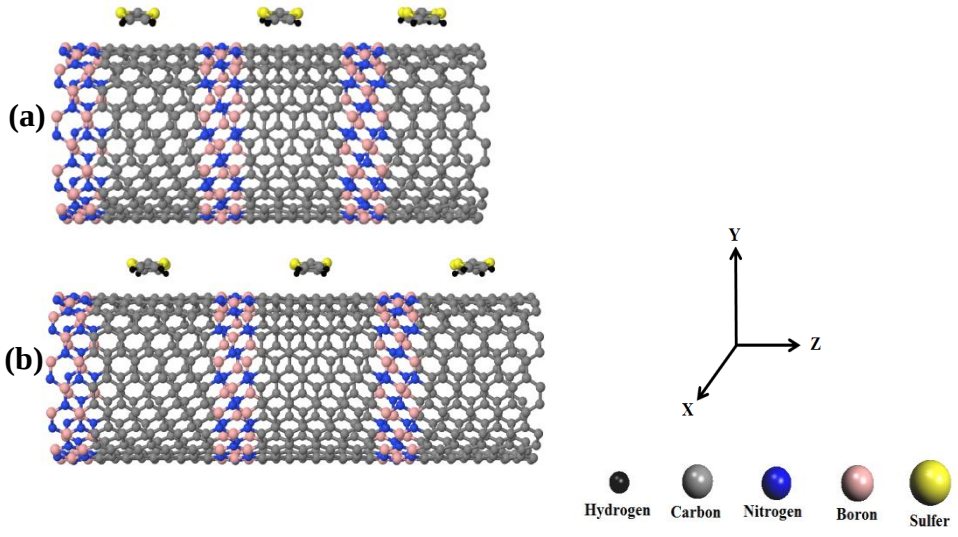

Figure 4.4: The doped hetero nanotubes by TTF-2 for **(a)** with three graphene rings and (b) with four graphene rings.

Once again, by using the obtained T(E) and equation 2, we calculate the current (I) of the travelling electron through the doped hetero nanotubes (figures 4.2, 4.3 and 4.4) from the left to the right. The resulting I(V) shown in figure 4.5.

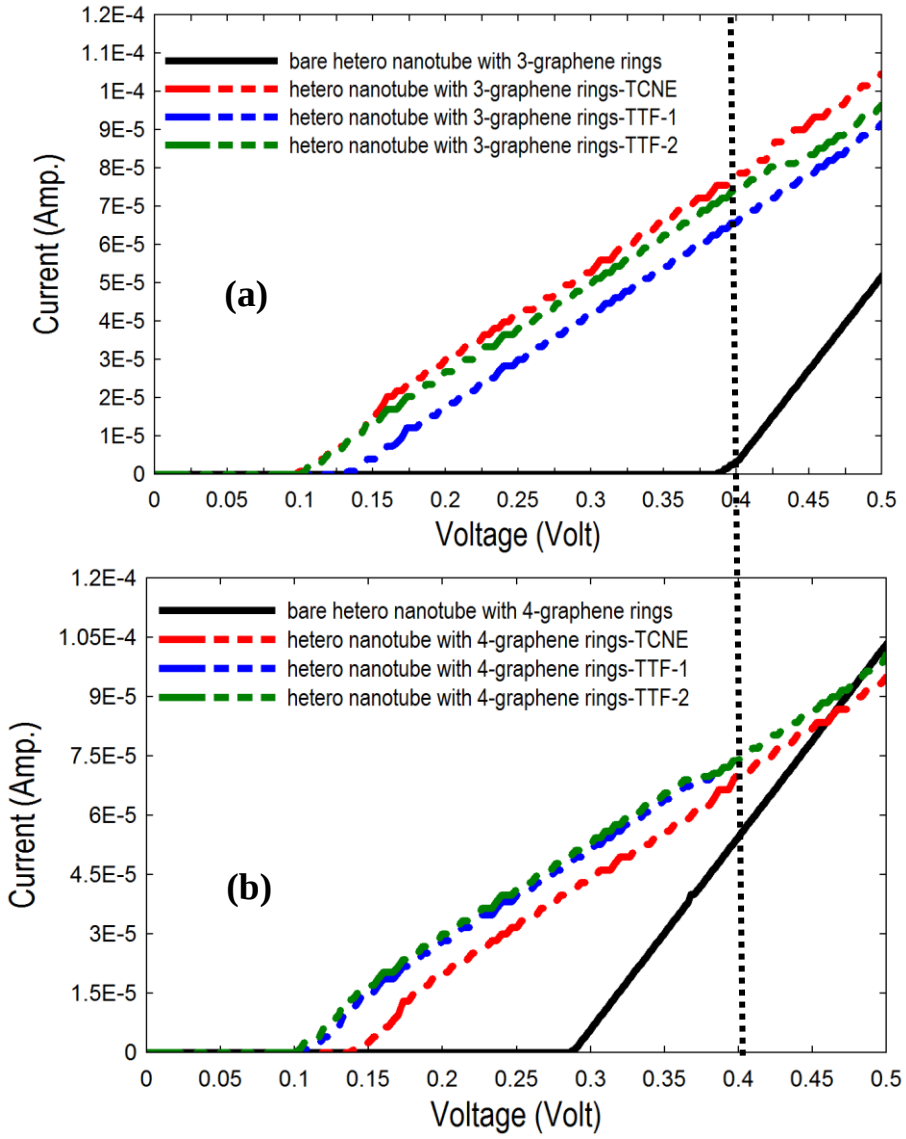

Figure 4.5: The I(V) plot for (a) the hetero nanotubes with three graphene rings which are doped by the TCNE, TTF-1 and TTF-2 (figures 4.2a, 4.3a and 4.4a) (b) the hetero nanotubes with four graphene rings which are the TCNE, TTF-1 and TTF-2 (figures 4.2b, 4.3b and 4.4b).

Having look at the figure 4.5a which shows the resulting I(V) of the doped hetero nanotube with three graphene rings by the TCNE and TTF. As a comparison with the bare hetero nanotubes, we can see at for example 0.4 volt that there is an enhancement in the current which means the

electronic properties of the hetero nanotube with three graphene ring has been improved after the doping. Also, looking at the figure 4.5b and again at 0.4 volt, we can see the same outcome for the doped hetero nanotube with four graphene rings. For selected voltage window, we can see a remarkable enhancement in the conductance, for example from 0.2 volt to 0.4 volt of voltage window.

5. Results and Discussion

We demonstrated that the electronic properties of hetero nanotubes (figure 3.1) and by altering the number of graphene rings along the nanotube tuned the size of the energy gap (E_g) around the Fermi energy (E_F). For example, we could manipulate the energy gap around the Fermi energy as shown in figures 3.1a, 3.1b, 3.1c and 3.1d. For these hetero nanotubes the energy gap size changed from 1.7 eV to 0.7 eV. Our procedure could be a good methodology to design a semiconductor material with desirable energy gap. Also, we proved that by doping the bare hetero nanotubes (figure 3.1) by both electron acceptor TCNE molecule and electron donor TTF molecule lead to enhance the conductance of the hetero nanotubes. For example, in figures 4.5a and 4.5b and at 0.4 volt, we can see that the I(V) enhanced comparing with the bare hetero nanotubes. The overall results for finite voltage window, for example from 0.2 volt to 0.4 volt of voltage window, we can clearly see that the conductance of the doped hetero nanotubes has been improved. Our results could be useful to open a new research idea to examine these hetero nanotubes as a nano-sensor device with other interesting molecules, such as drugs molecules.

Acknowledge

I would like to thank Lancaster University/UK for allowing me to access the Central Computer (HEC, High End Computing) at the University through the Visiting Researcher I awarded from Physics Department/Lancaster University, Also I would like to take this opportunity to express my gratitude to Prof. Colin J. Lambert and his group for their support to finish this work.

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