Electronic and Transport Properties of Radially Deformed Double-walled Carbon Nanotube Intramolecular Junction

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Abstract

The electronic and transport property of a radially deformed double-walled carbon nanotube (DWNT) intramolecular junction (IMJ) has been studied by the tight-binding (TB) model combined with the first-principle calculations. The geometrical structures of the DWNT IMJ have been first optimized in energy by the universal force field (UFF) method. It is found that when heavily squashed, the DWNT will become an insulator-coated metallic wire, and the conductance near the Fermi level has been significantly changed by the radial squash. Specially, several resonance conductance peaks appear at some energies in the conduction band of the squashed DWNT IMJ. Finally, we have also investigated the conductance variation due to change of the length of the central semiconductor in the squashed DWNT IMJ. Furthermore, a promising pure carbon nanoscale electronic device is proposed based on the DWNT IMJ.

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I. INTRODUCTION

In the past decade carbon nanotubes (CNTs) [1-3], both single-walled (SWNT) and multi-walled (MWNT) had been extensively investigated due to their special electrical and mechanical properties, as well as their potential applications in future nanostructured materials, such as nanoscale quantum wires, single electron and field-effect transistors and sensors.

The SWNT is composed of a rolled-up 2D-graphite sheet, and discovered first by Iijima’s group in 1991. The carbon atoms on a SWNT are arranged on a helical line around its axis. The geometrical structure of a SWNT can be defined by a pair of integers \((n,m)\), which determines its radius and chirality, and so entirely its electronic structure, and optical property. It is known that the SWNTs with \(n - m\) being a multiple of 3 are metallic, and all others are semiconducting [4]. The DWNT is the simplest type of MWNT, which has been made experimentally by many different methods. The nucleation of its inner tube should occur after the growth of the outer tube according to the ‘yarmulke mechanism’ [5], which means that the inner tube diameter is determined by that of the outer tube. A DWNT can be composed of a pair of inner and outer constituent layers with any chiralities, leading to different kinds of DWNT, such as metal–metal, metal–semiconducting, or semiconducting–semiconducting nanotubes. Early studies on DWNT focused mainly on their electronic structure, and stability, etc. [6–9]. It was shown that the band structure of a DWNT depends on the combined configurations of the inner and outer tubes [7], but their stability depends only on their interlayer spacing [6].

It is well known that a mechanical deformation of a SWNT affects heavily its electronic properties [10–14]. For example, Lu et al. [15,16] indicated that a metal-to-semiconductor transition (MST) can be achieved by a radial deformation of the armchair SWNT. Furthermore, they studied the transport properties of effectual metal–semiconducting–metal (MSM) heterojunction in the metallic armchair tube, and the effect of deformed radially finite length. In addition, a natural MST is found theoretically in the DWNT \((7,0)@(16,0)\) and \((7,0)@(17,0)\) due to the differences of the downward shifts of the \(\pi\) and \(\pi^*\) electron states between the inner and outer nanotubes [17], which reminds us of the possible existence of the DWNT junction. Recently, a new metal–semiconducting MWNT IMJ has been made [18], which shows reproducible rectifying diode behavior. So, it is interesting to study the electronic structure and transport property of the DWNT IMJ, produced by squashing radially a DWNT, which is just the main goal of this paper.

The paper is organized as follows: In Sec. II, we introduce the model Hamiltonian, and the employed method. Then, the calculated results and discussions are given in Sec. III. The conclusions are shown in Sec. IV.

II. MODELS AND METHOD

A finite DWNT \((10,0)@(19,0)\) with a central segment of inner tube uncovered is shown schematically in Figs. 1(a) and 1(b), viewed from \(x\)-axis and \(z\)-axis direction, respectively. Two identical lithium tips (with definite width of \(d_x\) and length of \(d_z\)) are applied from \(\pm y\) directions on the system with a separation distance \(d_y\). With the two tips moving towards the DWNT, the cross sections of the inner and outer tube are deformed from circle to ellipse, and finally to stadium-shaped shown in Figs. 1(c) and 1(d). Then the geometrical structure of the DWNT for various tip distances \(d_y\) are optimized by the universal force field (UFF)
method [19,20]. When the deformation becomes bigger enough, the inner (10,0) tubes in
the left DWNT and the right one will be able to exhibit a transition from semiconducting
to metal. In this case, the original system will become a MSM DWNT IMJ, which has no
any topological defects in the M-S and S-M junction region.

After the geometrical structure of the DWNT IMJ is optimized, we will employ a TB
Hamiltonian including four orbitals per atom to study its electronic and transport properties,
in which the $\sigma - \pi$ electron hybridization can be included [21,22,23]. The model Hamiltonian
can be written as follows:

$$H = \epsilon_s^0 c_{is}^\dagger c_{is} + \sum_{jp} \epsilon_p^0 c_{jp}^\dagger c_{jp} + \sum_{ijmn} (t_{ij}^{mn} c_{im}^\dagger c_{jn} + H.c.),$$

where $\epsilon_s^0$ and $\epsilon_p^0$ are the on-site energies of the 2s and 2p orbitals, respectively. $c_{is}(c_{is}^\dagger)$ and
$c_{jp}(c_{jp}^\dagger)$ denote the annihilation (creation) operators of an electron on Carbon 2s orbitals at
site $i$ and Carbon 2p orbitals at site $j$, respectively. $m$ and $n$ are the orbital indices. $t_{ij}^{mn}$
are the hopping integrals between the $m$ orbital on the site $i$ and the $n$ orbital on the first
or second-nearest neighbor site $j$, which are expressed in terms of Slater-Koster parameters
$V_{ss\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$ and $V_{pp\pi}$ [24]. Since the inter-wall interaction strength is about eighth of the
intralayer hopping integrals, which has minor effect on the band structure of a DWNT [25],
so we do not take it into account in this paper.

The parameter values in Eq. (1) are taken to be close to those used for graphite in
Ref. [26], which was also successfully used to study the physical properties of the SWNT
with small-radius [23], the SWNT with polygonized cross sections [21]. Among the four
orbitals per atom, its $s$ level is located at $\epsilon_s^0 = -7.3$ eV below the triply-degenerated $p$
level taken as the zero of energy ($\epsilon_p^0 = 0.0$ eV). The Slater-Koster hopping parameters for
the nearest-neighbor pairs are taken as $V_{ss\sigma} = -4.30$ eV, $V_{sp\sigma} = 4.98$ eV, $V_{pp\pi}^\sigma = 6.38$ eV
and $V_{pp\pi} = -2.66$ eV. The second-nearest interactions are taken into account by using
$V_{ss\sigma} = -0.18Y$ eV, $V_{sp\sigma} = 0.21Y$ eV, $V_{pp\pi} = 0.27Y$ eV and $V_{pp\pi} = -0.11Y$ eV, where
$Y = (3.335/r_{ij})^2$ is a scaling factor, depending on the interatomic distance $r_{ij}$ (in unit of
Å).

First, we study the band structures of the radially deformed DWNT IMJ, and then, its
transport properties. In the conductance calculation, the whole system is considered to be
composed of two leads (left and right ones) plus a central DWNT IMJ (L-C-R), where the
two leads are taken as the same type of the deformed metal inner tube (10,0) as those in
the left and right deformed DWNT of the system. This problem can be most conveniently
-treated by the Green’s function matching method [27], in which the conductance is expressed
by the Landauer formula:

$$G = (2e^2/h) Tr[\Gamma_LG_C^r\Gamma_RG_C^a],$$

where,

$$G_C^r = (\epsilon + \gamma - H_C + h_{LC}^\dagger g_L h_{LC} - h_{RC}^\dagger g_R h_{RC})^{-1},$$
\( G_C^a = (\epsilon - i\gamma - H_C - h_{LC}^H g_L h_{LC} - h_{RC}^H g_R h_{RC})^{-1}, \) (4)

and

\[ \Gamma_{L,R} = ih_{L,R}^H (g_{L,R}^a - g_{L,R}^a) h_{L,R}. \] (5)

Here, \( H_C \) is the Hamiltonian of the central DWNT IMJ, and \( h_{L,C} (h_{R,C}) \) is the coupling matrix between the central DWNT IMJ and the left (right) lead. \( g_L \) and \( g_R \) are the Green’s functions of the semi-infinite left and right leads, which are calculated by using an iterative procedure [28]. Also, we can calculate the local density of states (LDOS) by using \( \text{LDOS}(j, \epsilon) = -(1/\pi) \text{Im}(G_{C}^r(j,j,\epsilon)) \), where \( j \) is the ordinal number of carbon atoms in the DWNT IMJ.

III. RESULTS AND DISCUSSIONS

Based on the computational scheme, we optimized the geometrical structure of a finite DWNT (10,0)@ (19,0) IMJ under the different tip distance \( d_y \). The obtained results show that small radial deformations generally cause elliptical cross sections for the DWNT. A further squashed deformation will lead the tubes to be flattened, producing a stadium-shaped cross section (\( d_y = 13.67 \text{Å}, \) Fig. 1(c) and 1(d)), and meanwhile causing a semiconductor-to-metal transition (SMT) for the inner (10,0) tube of the DWNT. So, by using this model and the optimization procedure, we can get any of the MSM or semi-conducting–metal–semi-conducting (SMS) DWNT IMJ.

First, we study the electronic structure of the DWNT (10,0)@ (19,0) IMJ. It is found that the outer tube (19,0) always remain in the semiconducting state when squashed (see Fig. 2(g)). But the band gap of the inner tube (10,0) decreases significantly from 0.69 eV to zero. Thus the squashed DWNT becomes an insulator-coated metallic wire. The obtained band structures for the perfect (10,0) tube and a series of deformed inner (10,0) tubes are shown in Figs. 2(a)-2(e). It can be seen from a comparison between Figs. 2(a) and 2(c) that when the tip distance \( d_y \) decreases from 16.07 Å to 15.27 Å, the conduction band of the deformed (10,0) tube shifts down to the Fermi level and tends to split off, but the valence band is still similar to that of the perfect tube, accompanied by a very small energy split, which leads the energy gap to be reduced. Of special interest is that the non-degenerate state labeled by \( s \) in Fig. 2 moves down under radial deformation, which is caused by the enhanced \( \sigma^* - \pi^* \) hybridization, since the tube curvature is increased in the curved tube regions [20,21,22]. When the \( d_y \) decreases to 14.47 Å, the gap is closed due to the lowest split conduction band touching the highest valence band, indicating a phase transition from semiconductor to metal (see Fig. 2(d)). Further squashing the DWNT (\( d_y = 13.67 \text{Å}, \) Figs. 1(c) and 1(d)) will make the lowest split conduction band shift down deeper, leading to intercross of the original conduction and valence bands (see Fig. 2(e)), and meanwhile, all the bands near the Fermi level to be non-degenerate. In order to check the validity of the TB calculations, we have also carried out the first-principles calculation [29] on the deformed inner (10,0) tube with \( d_y = 13.67 \text{Å}. \) The obtained results (shown in Fig. 2(f)) indicate that, our TB calculations can correctly reproduce the first-principles results.
Next, we investigate the transport properties of the MSM DWNT IMJ by the above said method. Since the outer tube actually acts as an insulator coat of the inner metal wire, we do not take into account it in our transport calculation.

As is well known, the ballistic conductance at an energy level is proportional to the number of conduction channels at the same energy [30], from which the change of band structure may be clearly found by the conductance measurement. We have calculated the conductance and the total density of states (DOS) of the MSM DWNT IMJ with the central semiconductor length of \( L = 14 \) unit cell, and obtained results are given in Figs. 3(a) and 3(b). The calculated conductances of the perfect semiconducting (10,0) tube and the squashed metal (10,0) tubes \( (d_y = 13.67 \text{ Å}) \) are also shown in Fig. 3(a).

It is seen from Fig. 3(a) that radical squash induces the significant changes of the conductance near the Fermi level. And the conductances of the MSM DWNT IMJ below the Fermi level and above 1.37 eV are similar to those of deformed metal (10,0) tube. The biggest changes of the conductance appear in the energy window from 0 to 1.37 eV. Firstly, at 0.52 eV there is a conductance jump, which arises from the conductance jump of the squashed metal (10,0) tube at the 0.52 eV. Secondly, in the region of 0 \( \sim \) 0.69 eV (the band gap of the ideal (10,0) tube), there exists nonzero conductance, which comes from quantum tunnelling. Third, the resonance electron transmissions occur in the energy area of 0.69 \( \sim \) 1.37 eV, giving three conductance oscillation peaks at 0.69, 0.88 and 1.07 eV, respectively. Using a 1D square potential barrier with finite height, which is used to model the central semiconducting segment of the DWNT IMJ, we can simply get three oscillation peaks in their positions to be the same as those of the above three conductance peaks.

These interesting phenomena related to the conductance can be explained by the DOS shown in Fig. 3(b). From Fig. 3(b), we can see that there are four DOS peaks in the energy area of 0 \( \sim \) 1.37 eV, coinciding well with the four conductance peaks in the same energy window of Fig. 3(a). The LDOS along the tube axis at these four energy levels of 0.52, 0.69, 0.88 and 1.07 eV are shown in Fig. 4(a), it is clearly seen that all of the four states are extended along the tube axis. Also, the LDOS on the up surface of the MSM DWNT IMJ, shown in the left panel of Fig. 4(a), is much lower than that on the side surface, shown in the right panel, indicating that the conductances at these energy levels are contributed mostly by the atoms on the side surface [31]. In Fig. 4(b), we show the LDOS at four energy levels of -0.05, -0.09, -0.27 and -0.46 eV in valence band, respectively. The large contribution to conductance, coming from the atoms on the side surface of the MSM DWNT IMJ, can also be seen from Fig. 4(b). But we found that at energy levels of -0.05 and -0.09 eV exist the quasibound states with their largest LDOS at positions of \( \pm 34.43 \text{ Å} \) (represented by the broken vertical lines) lying in the transition region between the deformed inner metal tube and the semiconductor tube. However, LDOSs at the energy levels of -0.27 and -0.46 eV show the characteristics of extended states.

In order to know effect of the length of central semiconducting part in the MSM DWNT IMJ, we have also calculated conductance of the IMJ with \( L = 8 \) unit cell and shown the obtained result in Fig. 3(a). For the transmission electrons, the middle semiconductor act as an energy barrier. And it is well known that the tunnelling probability decays exponentially with the increasing width of the energy barrier, which is well consistent with what shown in Fig. 3(a). Comparing with the conductance of the IMJ with \( L = 14 \) unit cell, we find the lower edge of the energy gap shifts to a higher energy, and a bigger conductance jump to \( G_0 \) (where \( G_0 = 2e^2/h \) is the conductance quantum) appears at 0.52 eV due to the stronger quantum tunnelling. And in the region of 0.69 \( \sim \) 1.37 eV, the resonance electron
transmission peaks move to the higher energies.

Based on the MSM DWNT IMJ, we can easily make a pure carbon nanoscale transistor by applying a gate voltage $V_g$ to the DWNT junction with a inner semiconductor (10,0) tube. When $V_g = 0$, the conductance is zero and the transistor is OFF. With change of $V_g$, the transistor can jump to an ON state.

IV. CONCLUSION

In summary, based on Slater-Koster tight-binding and the first-principle calculations, we found that the different radically squashed DWMT IMJs have very different $\sigma - \pi$ and $\sigma^* - \pi^*$ hybridizations, inducing big changes of their electronic structures. It has been shown that the big enough radial squash can induce an insulator-metal transition for the inner semiconducting (10,0) tube, but the outer (19,0) tube remains to be semiconducting. The LDOSs of the MSM DWNT IMJ at different energies indicate the emergence of two quasibound states at -0.05 and -0.09 eV near the Fermi level, and large contributions to the conductance, coming from the atoms on the side surfaces of the IMJ. In addition, There exist several resonance conductance peaks at some energies in the conduction band of the MSM DWNT IMJ, which can be explained by electron resonance transmission effect. Also, the conductance variation due to length change of the central semiconducting part in the MSM DWNT IMJ has been found. Finally, a promising pure carbon nanoscale transistor is proposed based on the DWNT IMJ.

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FIG. 1: Schematic view of a finite (10,0)@(19,0)DWNT with a central segment of uncovered inner tube along (a) $x$-axis direction, and (b) $z$-axis direction, respectively. (c) and (d) Relaxed atomic structures of the deformed (10,0)@(19, 0) DWNT by the Li tip with separation distance $d_y$ of 13.67 Å. $L$ is the length of the uncovered semiconducting inner (10,0) tube in the DWNT IMJ.
FIG. 3: (a) Conductance of the perfect semiconductor (10,0) tube, the radially deformed metal (10,0) tube with $d_y$ of 13.67 Å (represented by the dash and solid line, respectively), and that of the MSM DWNT IMJ with two different semiconductor lengths of $L = 8$ unit cell (the Circle), and $L = 14$ unit cell (the star). (b) The total DOS of the IMJ with $L = 14$ unit cell. The Fermi level is set at zero.
FIG. 4: The LDOSs of the MSM DWNT IMJ at different energy levels with its middle point set at zero. (a) At four energy levels of 0.52, 0.69, 0.88 and 1.07 eV in the conduction band. (b) At four energy levels of -0.05, -0.09, -0.27 and -0.46 eV in the valence band. In (a) and (b), the left and right panels correspond, respectively, to a scanning parallel to the tube axis along the atom-line on the up surface ($y > 0.0 \text{ Å, } |x| < 0.6 \text{ Å}$), and on the side surface ($x > 0.0 \text{ Å, } |y| < 0.6 \text{ Å}$). The insets in the left panels show the corresponding enlarged LDOSs.