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In search of molecular scale devices: Theoretical study of linearly fused straight single-walled carbon nanotube junctions based on the pentagon/heptagon pair defects

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ABSTRACT

The structural and electronic properties of topological defect of straight intramolecular junctions between two zigzag single-walled carbon nanotubes (SWCNT-IMJ) were studied theoretically. The interfacial junctions can be constructed by fusing two zigzag tubes that differ in helicities and diameters. In the present study, one segment is kept constant by using the (5,0) nanotube, while varying another segment from (6,0) to (10,0). Practically, these (5,0)//(*m*,0) structures are composed of one or more pentagon/heptagon pairs as "defect" functioning to fuse other perfect hexagonal lattices. It was found that, at the interfacial junctions the 5/7 pair defects induce modified rehybridization of the carbon–carbon networks, which directly affect the geometric and electronic properties. Consequently, the electronic structures are dependent on the variation of diameter and length of carbon nanotubes. Analyses of the electronic structures reveal that the HOMO and LUMO levels exhibit the even–odd "quantum size" oscillation versus varying nanotube chiralities, even with increasing length of nanotubes. The energy gap that indicates metallic or semi-conducting behavior depends on correlation between the tubes indices and tubule length. The NBO analysis has revealed that topological pair defects variation could be an important role for altering the electronic characteristics on these intramolecular junctions. By screening all structures based on their electronic structure diagrams and orbital visualization, we have found that the straight (5,0)//(7,0) junction should be suitable as a molecular rectifying diode. However, other junction structures can also be useful with appropriate tuning of the bias voltage. The outcome of this study would be of help as a knowledge base in the field of carbon nanomaterials molecular electronics.

1. Introduction

Carbon nanotubes (CNTs) are still one of the most fascinating nanoscaled materials [1]. An unimaginably large number of carbon nanotube structures can be formed in several kinds such as single-walled [2–4], double-walled [5,6] and multi-walled CNTs [7–9], X/Y/T [10–14], bended junctions [15,16], carbon nanocones [17], nanopods [18], 3D-hybrid CNTs-graphene as nanopillar [19] and multi-terminals of CNT junctions [20,21]. Such richly available derivative nanostructures are experimentally possible through deformations of CNT structure from a perfect hexagonal network [22].

Although the defect-free CNTs are most favorably desirable in use for a building block of any nanoscaled applications [23], the defects, however, can still not deny on the CNT's wall. In general, these defects can be classified into three groups: *i.e.* topological, rehybridization, and incomplete bonding defects. In the case of the topological defects, two nanotubes can be fused to form a tubular junction with different electronic properties from their parents [24].

Such defect onto nanotube structures can be useful for designing and constructing of all-nanotube or composited nanotube in the molecular electronic circuits [25–28] and Photovoltaic cells [29,30], Theoretically, two carbon nanotubes with different diameters and helicities can be connected by insertion of pentagon and heptagon rings onto the hexagonal lattice of carbon nanotubes [31,32]. Since a single-walled carbon nanotube (SWCNT) can be either metallic or semi-conducting depending on its chirality and

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diameter [33], a combination of two SWCNTs having different diameters and helicities using such a pair defects [34,35] will lead to unique electronic properties of that nanotube junction. Nanotube junctions that composed of single, double, or more such defects have been theoretically and experimentally examined [36–38].

It has been reported that joining a semiconducting nanotube with a metallic one, using a pentagon–heptagon (5/7) pair defects can thus be proposed as the basis of a nanodiode (or molecular diode), an essentially building block for nanoelectronics [15,34,39,40]. Such joint CNTs are usually called the straight intramolecular junction and have recently become promising molecular architecture for nanocircuitry. Frontera et al. have investigated the distributions of 5/7 pair defects in two zigzag SWCNTs [41] and found that the energetic of those junctions are quite favorable. Recently, theoretical calculations of straight asymmetric metallic–metallic armchair SWCNT junctions have also been reported [42] in which the favorable junction structures can be formed by insertion of pentagon–heptagon pair defects between hexagonal rings. Experimentally, although the existence of these junctions can be observed by HR-TEM [43], structural details on the defects and their distributions are difficult to be evidently verified.

In the present study, the molecular straight zigzag//zigzag intramolecular junctions of single-walled carbon nanotubes (SWCNT-IMJs) were constructed by fusing two nanotube segments having different diameters through a distribution of associated numbers of topological 5/7 pair defects radially around the junctions (denoted zigzag (5,0)//(*m*,0)). Different junction geometries were modeled to investigate geometric parameters, electronic structures, and their molecular rectifications upon the variation of tubes' diameter and their length using semi-empirical and first principles density functional calculations.

2. Theoretical model and methodologies

Two carbon nanotubes with different chiralities (*i.e.* intrinsically change in diameters) can be fused by incorporating an appropriate number of 5/7 pair defects. Thus, different combination of 5/7 pair defects result in different kinds of junctions. As a result, in this work, the straight intramolecular junctions of single-walled carbon nanotubes (SWCNT-IMJs) are constructed by joining a zigzag (5,0) with another (*m*,0) nanotube segments; where *m* is an integer and varies from 6 to 10 (see Fig. 1). In this case, the ultra-small diameter (5,0) segment is kept constant. Creation of different junction structures can be done by inserting suitable numbers of 5/7 pair defects into a perfect cylindrical hexagonal lattice around the circumference of SWCNTs. The finite-length effect was also investigated. The hydrogen atoms are used to saturate the dangling bond at the tube ends in order to stabilize the nanotubes and mimic the CNTs under the ambient conditions.

Since this is theoretical work, the optimistic geometries of all structures were initialized via the lowest level of theory which has followed the molecular mechanics (MM3) method. This force field was using interatomic potential functions which composite in terms of the bond stretching ($\varphi_{bond\text{-}str}$), bond dipole ($\varphi_{bond\text{-}dipole}$), bond-angle bending ($\varphi_{angle\text{-}bend}$) which also used to entirely modify the out of plane bending ($\varphi_{out\text{-}of\text{-}plane}$) term. It was also incorporated the crossing between bond stretching and angle bending ($\varphi_{cross\text{-}term}$), torsion or dihedrals ($\varphi_{torsion}$), and van der Waals (φ_{vdW}) potential terms. All interatomic potential terms (E_{pot}^{MM3}) can be expressed as

$$
\begin{aligned}
E_{pot}^{MM3} &= 143.88\sum_{bonds}\frac{1}{2}k_r(r-r_0)^2[1+\gamma(r-r_0)] \\
&\quad + 14.39418\varepsilon\sum_{ij\,\in\,polarbonds}\mu_i\mu_j\left[\frac{cos\chi-3cos\alpha_i cos\alpha_j}{R_{ij}^3}\right] \\
&\quad + 0.04383\sum_{angles}\frac{1}{2}k_\theta(\theta-\theta_0)^2[1+\beta(\theta-\theta_0)^4] \\
&\quad + 2.51118\sum_{angles}k_\delta(\theta-\theta_0)_{ijk}[(r-r_0)_{ik}+(r-r_0)_{jk}] \\
&\quad + \sum_{torsion}\left\{\frac{V_1}{2}[1+cos\varnothing]+\frac{V_2}{2}[1+cos2\varnothing]+\frac{V_3}{2}[1+cos3\varnothing]\right\} \\
&\quad + \sum_{ij\,\in\,vdW}\varepsilon_{ij}\left[2.9\times10^5(e^{-12.5\rho_{ij}})-2.25\rho_{ij}^{-6}\right] \qquad (1)
\end{aligned}
$$

A first term is the bond stretching ($\varphi_{bond\text{-}str}$), which γ is, in this case, a cubic stretch factor with −0.2. The term $r - r_0$ is quadratic stretch and k_r is the stretch force constant. Second is bond dipoles ($\varphi_{bond\text{-}dipole}$) term, which was used instead of an electrostatic interaction of atomic charge on each atom. In such term the bond dipole moments were associated with bond polarities in which two dipoles μ_i and μ_j are separated by R_{ij}. The parameter ε is the dielectric constant factor with 1.5. A factor χ is the angle of two dipole vectors, and α_i and α_j are the angles between the two dipole vectors make with the R_{ij}. The angle bending ($\varphi_{angle\text{-}bend}$) term is the third term which was includes factor 1/2 in a harmonic function. This quadratic bending term is particularly incorporated to a harmonic function with a scale factor β is equal 7.0×10^{-8}. The forth term is cross-term ($\varphi_{cross\text{-}term}$) of coupling between bond stretching and angle bending. The angle defined by including atom *i*, *j*, and *k*, where *k* is the central atom. The coupled stretching was worked through *ik* and *jk* bonds. However, if atom *i* (or *j*) is hydrogen, stretch-bend interaction can be eliminated. The factor k_δ was defined the values of the stretch-bend force constants on different atomic species. The latter is an incorporation of torsion angles ($\varphi_{torsion}$) which have certain *n*-fold symmetry. It was set to have minimum energy for the *cis*-, *gauche* or *trans*-conformation, etc. The V_n is energy barrier of curving situation between minimum energy for the *trans*-conformation to the highest energy of *cis*-conformation. This term was reduced to a phase angle ϕ_0, which defined for curve shift between available conformational situations by choose only parameter *n* is 1, 2, and 3, respectively. And last term is a non-bond van der Waals interaction (φ_{vdW}). The term was combination of an exponential repulsion with an attractive $1/R^6$ dispersion interaction. The van der Waals radius, r_i^*, on each atom type was used to define the interactions for each non-bond *ij* paired in which the parameters of a pair are follows $\rho_{ij} = R_{ij}/r_{ij}^*$ parameters, where $r_{ij}^* = r_i^* + r_j^*$.

The geometries of all structures were initially optimized by molecular mechanics (MM3) method. These structures were used a basis geometry for further optimization by higher-level techniques. The optimized SWCNT-IMJ geometries, which incorporate energetics of the entire structural variables, were obtained by the semi-empirical AM1-RHF calculations [44]. The charge density optimization was followed by SCF scheme which converging criteria *ca.* 10^{-5} eV/atom. The quadratic approximation was used as optimization algorithm. This method was used to evaluate the formation energy, H_n, obtained from the expression:

$$H_n = \frac{-E_{SWCNT-IMJ} + E_{(m,0)} + E_{(5,0)} + E_{junc}}{N}, \qquad (2)$$

where $E_{SWCNT\text{-}IMJ}$ is the total energy of a whole system, $E_{(m,0)}$, $E_{(5,0)}$, and E_{junc} are a total energy of the nanotube (*m*,0) segment, a fixed-(5,0) segment, and junction segment, respectively. *N* is numbers of all atoms in system. The electronic structure of all optimized SWCNT-IMJs were then calculated by hybrid GGA functional formalism B3LYP [45,46] and Gaussian wave basis functions 6-31G(d). The charge density in this method was set to converge by 2×10^{-6} eV/atom. All computations were performed using the GAMESS package [47].