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FIRST PRINCIPLE STUDIES OF CU-CARBON NANOTUBE HYBRID STRUCTURES
WITH EMPHASIS ON THE ELECTRONIC STRUCTURES AND THE TRANSPORT
PROPERTIES

by

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ABSTRACT

Carbon nanotubes have been regarded as ideal building blocks for nanoelectronics and multifunctional nanocomposites due to their exceptional strength, stiffness, flexibility, as well as their excellent electrical properties. However, carbon nanotube itself has limitations to fulfill the practical application needs: 1) an individual carbon nanotube has a low density of states at the Fermi level, and thus its conductivity is only comparable to moderate metals but lower than that of copper. 2) Metallic and semiconducting nanotubes are inherently mixed together from the synthesis, and the selection/separation is very difficult with very low efficiency. 3) Carbon nanotubes alone cannot be used in practical application and a bonding material is normally needed as the join material for actual devices.

In this work, we fundamentally explored the possibility that metals (Cu, Al) could tailor carbon nanotube’s electronic structure and even transit it from semiconducting to metallic, thus skipping the selection between the metallic and the semiconducting CNTs. We also found out a novel way to enhance a semiconducting CNT system’s conductance even better than that of a metallic CNT system. All these researches are done under density functional theory (DFT) frame in conjunction with non-equilibrium Green functions (NEGF).

At first we studied the adsorbed copper’s influence on the electronic properties of CNT (10, 0) and CNT (5, 5). Results indicate that both the Density of States (DOS) and the transmission coefficients of CNT (5,5) /Cu have been increased. For CNT (10,0)/Cu, the band gap has been shrank, which means the improved conducting properties by the incorporation of copper.
As a further case, semiconductor SWCNT (10, 0) with more adsorbed copper chains outside has been studied. 1, 4, 5 and 6 Cu chains have been added onto the carbon nanotube (10,0), and the adsorption of 6 Cu chains finally lead to the transform of the system from semiconducting to metallic.

Considering the confining effect, the case that Cu filled into CNT (10, 0) is also studied. It is found that the filled copper chains could modify the system to be metallic more efficiently than the adsorbed Cu chain.

Similarly, Al adsorbed on CNT (10, 0) is also studied, and it is found that Al has a better efficiency than copper in tuning the semiconducting CNT to metallic. The existing chemical bonds between the CNT and Al atoms may account for this higher efficiency. In addition, the resultant conductivity of the Al/CNT system is better than that of Cu/CNT system.

The Cu/CNT (5,5)+Cu/Cu junction, as another realistic device setup, has been studied in terms of the conductance. The results show that the incorporation of Cu would enhance the conductance of the Cu/CNT/Cu system due to the interaction between Cu and the CNT.
To, my dearest family
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# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... xiii  

LIST OF TABLES ............................................................................................................. xviii  

CHAPTER ONE: INTRODUCTION .................................................................................. 1  

1.1 Carbon Nanotube’s Properties .............................................................................. 1  

1.1.1 Introduction to Carbon Nanotubes ................................................................. 1  

1.1.2 The Structure of Carbon Nanotubes ............................................................... 3  

1.1.3 The Landauer Approach for Describing Quasi-One Dimensional Transport ........ 9  

1.2 Carbon Nanotube/Cu Interconnect Modeling ..................................................... 13  

1.2.1 Background ..................................................................................................... 13  

1.2.2 Fabrication of CNT/Copper Composites ....................................................... 14  

1.2.3 Conductivity of Cu/CNT Nanocomposite ..................................................... 15  

1.2.4 Conduction Mechanism of Cu/CNT Nanocomposites .................................... 18  

CHAPTER TWO: QUANTUMWISE AND ITS RELATED FUNCTIONAL THEORY ........ 20  

2.1 Introduction ......................................................................................................... 20  

2.2 Many-body Problem ............................................................................................ 20  

2.2.1 Schrödinger Equation .................................................................................. 20  

2.2.2 Variational Principle ..................................................................................... 22  

2.2.3 Born-Oppenheimer Approximation ............................................................. 23  

viii
2.2.4 Mean Field Approach ................................................................. 24
2.2.5  Hatree-Fock Approximation ....................................................... 25
2.2.6 Thomas-Fermi Approach ............................................................. 26
2.3 Density Functional Theory ............................................................. 27
   2.3.1 The First Hohenberg-Kohn Theorem ......................................... 27
   2.3.2 The Second Hohenberg-Kohn Theorem ..................................... 28
   2.3.3 Kohn-Sham Equation ............................................................... 28
2.4 The Non-equilibrium Green's Function Method .................................. 30
2.5 QuantumWise .............................................................................. 32

CHAPTER THREE: TRANSPORT AND ELECTRONIC PROPERTIES OF HYBRID
   NANOWIRES CONSISTS OF COPPER AND CARBON NANOTUBES .......... 34
   3.1 Introduction ............................................................................... 34
   3.2 The Calculation Method and The Simulation Model ..................... 35
   3.3 Results and Discussions ............................................................. 36
      3.3.1 Electronic Structures ............................................................ 36
      3.3.2 Transmission Spectrum ....................................................... 41
      3.3.3 Transmission Eigenchannel .................................................. 42
   3.4 Conclusion ............................................................................... 43
CHAPTER FOUR: TUNING SEMICONDUCTING CARBON NANOTUBES TOWARDS METALLIC WITH THE ADSORBED COPPER CHAINS

4.1 Introduction .................................................................................................................................................. 45

4.2 Procedure of the Calculation ....................................................................................................................... 46

4.3 Results and Discussion ................................................................................................................................. 48

4.3.1 The Transmission Spectrum .................................................................................................................... 48

4.3.2 The Band Structure .................................................................................................................................. 49

4.3.3 Transmission Eigenstates ......................................................................................................................... 54

4.3.4 The Mulliken Population ......................................................................................................................... 54

4.4 Comparison among Different Semiconducting CNTS ............................................................................... 56

4.5 Conclusion ................................................................................................................................................... 57

CHAPTER FIVE: THE INFLUENCE OF THE INTERACTION BETWEEN CNT AND CLAMPED CU CHAIN ON THE ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES OF CU-CLAMPED-CNT SYSTEMS ............................................................................. 59

5.1 Introduction ................................................................................................................................................... 59

5.2 Electronic Structure .................................................................................................................................... 63

5.2.1 Band structure ........................................................................................................................................ 63

5.2.2. DOS ...................................................................................................................................................... 66

5.2.3. Charge Density ..................................................................................................................................... 67
5.2.4 LDOS ................................................................................................................. 69
5.3 Transmission Spectrum ......................................................................................... 70
5.4 Conclusion ............................................................................................................... 72

CHAPTER SIX: ELECTRIC RESISTANCE AND TRANSPORT STUDY OF CARBON NANOTUBE WITH A CU CHAIN: A FIRST PRINCIPLE CALCULATION ............... 74
6.1 Introduction .............................................................................................................. 74
6.2 Calculation and Simulation Model .......................................................................... 75
6.3 Results and Discussion ......................................................................................... 77
  6.3.1 Transport Properties at Equilibrium ................................................................. 77
  6.3.2 Transport Properties at Non-equilibrium ......................................................... 79
  6.3.3 Transmission Eigenstates at the Fermi Level .................................................. 82
6.4 Conclusion ............................................................................................................. 84

CHAPTER SEVEN: THE EFFECT OF END GEOMETRY ON THE ELECTRICAL CONTACT RESISTANCE OF THE CARBON NANOTUBE (10, 0)/CU INTERFACES ...... 85
7.1 Introduction .............................................................................................................. 85
7.2 Geometry Configuration ......................................................................................... 87
7.3 Results and Discussion ......................................................................................... 89
  7.3.1 LDOS ................................................................................................................ 89
  7.3.2 Transmission Spectrum ................................................................................. 90
7.3.3 I-V Curve ........................................................................................................... 94

7.3.4 MOP/ Transmission Eigenvalues .................................................................. 97

7.4 Conclusion ............................................................................................................ 101

CHAPTER EIGHT: ELECTRONIC STRUCTURES AND THE TRANSPORT PROPERTIES
OF CARBON NANOTUBES ADSORBED WITH AL CHAINS .................................... 102

8.1 Introduction ............................................................................................................ 102

8.2 Electronic Structure ............................................................................................ 104

8.3 Transmission Spectrum ....................................................................................... 105

8.4 Conductivity of Al/CNT Compared with Cu/CNT at Fermi Level ....................... 107

8.5 Transmission Eigenstates ..................................................................................... 108

8.6 Charge Density .................................................................................................... 109

8.7 Mulliken Overlap Population ............................................................................... 110

8.8 Conclusion ............................................................................................................ 111

CHAPTER NINE: CONCLUSION .................................................................................. 113

REFERENCE ............................................................................................................... 117
LIST OF FIGURES

Figure 1 Left: Graphene lattice with every unit cell shaded. $a_1$ and $a_2$ are the primitive vectors of graphene. $a$ is the length of C-C bond. $C_h$ is a circumferential vector, and $T$ is a primitive vector. Right: atomic structures of (a) zig-zag tube (12,0), (b) armchair tube (6,6) and (c) chiral (6,4) tube. [1, 3]........................................................................................................................................... 3

Figure 2 Graphene lattice and its Brillouin zone. Left: lattice structure of graphene, in which $a_1$ and $a_2$ are its lattice unit vectors, and $\delta_1$, $\delta_2$, $\delta_3$ are the three nearest-neighbor vectors. Right: corresponding Brillouin zone. [11]............................................................................................................................................... 6

Figure 3: Electron band structure of graphene from ab-initio calculations and nearest tight binding model[4]. The two agree well on the K point........................................................................................................ 7

Figure 4 Nanotube (2,0). Left: corresponding real space graphene lattice. Right: reciprocal lattice of graphene and the allowed carbon nanotube’s states(indicated in red lines).[3]......................... 8

Figure 5: Energy bands for left: armchair (5,5), middle: zig-zag (9,0) and right: zig-zag (10,0) tube, obtained by the zone folding [3].................................................................................................................................................. 9

Figure 6 A conductor stretched between two large contact pads.[3]................................. 9

Figure 7 Quantized conductance of a ballistic waveguide. (a) A device using negative voltage on a pair of metallic gates. to constrict the conducting area progressively. (b) Measured conductance vs. gate voltage[15]................................................................................................................................. 11

Figure 8 Temperature dependence of electrical resistivity for the as-deposited SWNT-Cu (in red line). electrical resistivity data of OFHC Cu are also included (in black line) for comparison.... 17

Figure 9 A typical device system in QuantumWise[25]............................................................................................................................. 30
Figure 10  Flowchart for DFT calculations, self-consistent loop[34]................................. 33

Figure 11 Geometric structure of adsorbed Cu chains on (10,0) (left) and (5,5) (right) carbon nanotubes. .................................................................................................................. 36

Figure 12 The band structure of (a) CNT(10,0)/Cu hybrid system. (b) distorted carbon nanotube(10,0). (c) Free standing Cu chain............................................................. 38

Figure 13 The band structure of (a) CNT (5, 5) with a Cu chain. (b) distorted carbon nanotube (5, 5). (c) Freestanding Cu chain............................................ 39

Figure 14 Density of States for CNT (10, 0)/Cu system (left); CNT (5, 5)/Cu system (right)..... 40

Figure 15 Transmission Spectrum for CNT (10, 0)/Cu system (left); CNT (5, 5)/Cu system (right). Left: (a) Cu atomic chain, (b) distorted CNT (10, 0), and (c) CNT (10, 0) with a Cu chain. ............................................................................................................. 41

Figure 16 Transmission eigenstates at 0.32eV below (a) and higher (b) than the Fermi level for CNT (10, 0) with a Cu chain, and at the Fermi level for CNT (5, 5) with a Cu chain(c)-(e). 42

Figure 17 The optimized unit cells of the semiconducting (zigzag) CNT(10,0) adsorbed with different number of copper chains. The two probe models are constructed by the optimized unit cell.(a)(c)(e)(g) are the optimized unit cells of CNT(10,0) with 1,4,5,6 Cu chain(s) when viewed in the z axial direction, and (b)(d)(f)(h) are the two probe models constructed using the corresponding unit cells, viewed in the sidewise direction......................................................... 47

Figure 18 Transmission spectrum of (a) the pristine CNT (10,0); (b) the CNT(10,0) adsorbed with 1 Cu-chain; (c) the CNT(10,0) adsorbed with 4 Cu-chains; (d) the CNT(10,0) adsorbed with 5 Cu-chains; and (e) the CNT(10,0) adsorbed with 6 Cu chains. ................................................................. 49
Figure 19 Band structures of (a) pristine CNT (10,0); (b) CNT-1Cu; (c) CNT-4Cu; (d) CNT-5Cu; (e) CNT-6Cu. ................................................................. 51

Figure 20 The transmission gap and the Conduction Band Energy Ec versus the number of adsorbed Cu chains. The red arrow indicates the suddenly change from the pristine CNT(10,0) to the CNT (10,0) adsorbed with one Cu chain. ......................................................... 53

Figure 21 a) Transmission eignenstates at the Fermi level for the CNT-4Cu system. .......... 54

Figure 22 Contours of charge densities of CNT(10,0)/Cu-chain structures (a - d) and the loss of Mulliken population associated (e). ................................................................. 56

Figure 23 The optimized unit cells of the semiconduting (zigzag) CNT(8,0) adsorbed with 8 copper chains. The two probe models are constructed by the optimized unit cell. (a) is the optimized unit cells of CNT(8,0) with 8 Cu chains when viewed in the z axial direction, and (b) is the two probe models constructed using the corresponding unit cells, viewed in the sidewise direction. ......................................................................................................................... 57

Figure 24 Transmission spectrum of the CNT (8, 0) adsorbed with 8 Cu-chains. .............. 57

Figure 25 Sketch of a copper wrapped CNT in the form of a hybrid Cu-CNT nanowire or Cu-CNT composite in which no matter the CNT is metallic or semiconductor the CNT will be metallic in nature......................................................................................................................... 58

Figure 26 The optimized unit cells of the zigzag CNT(10,0) clamped with different number of copper chains, and the two probe models constructed by the optimized unit cell. (a)(c)(e)(g) are the optimized unit cells of CNT(10,0) clamped with 1, 4, 6, 8 Cu chain(s), (b)(d)(f)(h) are the two probe models constructed by corresponding unit cell................................................................. 62

Figure 27 The bandstructures for (a) CNT-1Cu; (b) CNT-4Cu; (c) CNT-6Cu; (d) CNT-8Cu. ....... 63
Figure 28 The density of states for (a) Pristine CNT; (b) CNT-1Cu; (c) CNT-4Cu; (d) CNT-6Cu; (e) CNT-8Cu.

Figure 29 The charge density for (a) CNT-1Cu; (b) CNT-4Cu; (c) CNT-6Cu; (d) CNT-8Cu.

Figure 30 The isosurface plot of LDOS of the zigzag CNT(10,0) clamped with different number of copper chains. (a)(c)(e)(g) are the LDOS isosurface of CNT(10,0) clamped with 1, 4, 6, 8 Cu chain(s), (b)(d)(f)(h) are the side view of LDOS for corresponding systems.

Figure 31 Transmission spectrum of (a) pristine CNT (10,0); (b) CNT-1Cu; (c) CNT-4Cu; (d) CNT-6Cu; (e) CNT-8Cu.

Figure 32 (a) The geometry of the Cu/CNT(5,5)/Cu two probe system. (b) The geometry of the Cu/CNT(5,5)+Cu/Cu two probe system.

Figure 33 Transmission spectrum of Cu/CNT/Cu junction and Cu/CNT + Cu/Cu junction.

Figure 34 Current-voltage (I-V) curve of the two-probe systems. (a) I-V curve. (b) Slope of I-V curve as a function of bias voltage.

Figure 35 Transmission spectrum at different bias voltage for two-probe systems. (a) Cu/CNT/Cu system. (b) Cu/CNT+Cu/Cu system.

Figure 36 Transmission eigenstates at Fermi level: (a) isosurface for Cu/CNT/Cu junction. (b) isosurface for Cu/CNT+Cu/Cu junction. (c) contour for Cu/CNT/Cu junction. (d) contour for Cu/CNT+Cu/Cu junction.

Figure 37 Typical structure of two-probe device with different CNT and Cu chain sandwiched between two Cu electrodes.

Figure 38 isosurface plot of LDOS of different CNT open/close ends with Cu chain.

Figure 39 Transmission Spectrum at zero voltage bias.
Figure 40  Transmission Spectrum at different voltage bias ......................................................... 93
Figure 41 Current-voltage (I-V) curves of the two probe systems ................................................. 95
Figure 42 Mulliken overlap population of Cu/CNT+Cu/Cu two-probe systems[80]......................... 98
Figure 43 Transmission eigenstates of Cu/CNT+Cu/Cu two-probe systems .............................. 100
Figure 44 The optimized unit cells of the zigzag CNT(10,0) adsorbed with different number of aluminum chains, and the two probe models constructed by the optimized unit cell. (a)(c)(e) are the optimized unit cells of CNT(10,0) with 2,4,6 Al chain(s), (b)(d)(f) are the two probe models constructed by corresponding unit cell. .............................................................................................................. 104
Figure 45 Band structures of (a)pristine CNT (10,0); (b)CNT(10,0) adsorbed with 2 Al-chains; (c) CNT(10,0) adsorbed with 4 Al-chains; (d) CNT(10,0) adsorbed with 6 Al-chains. . 105
Figure 46 Transmission spectrum of (a)pristine CNT (10,0); (b)CNT(10,0) adsorbed with 2 Al-chains; (c) CNT(10,0) adsorbed with 4 Al-chains; (d) CNT(10,0) adsorbed with 6 Al-chains. . 106
Figure 47 Transmission eigenstates of (a)(b)(c)CNT(10,0) adsorbed with 4 Al-chain; (d)-(j)CNT(10,0) adsorbed with 6 Al-chains. ......................................................................................................................... 109
Figure 48 Electron density distribution of CNT/Al systems. (a)CNT(10,0) adsorbed with 2 Al-chain; (b) CNT(10,0) adsorbed with 4 Al-chains; (c) CNT(10,0) adsorbed with 6 Al-chains; (d)pristine CNT (10,0). .......................................................................................................................... 110
Figure 49 Mulliken Overlap population of CNT/Cu and CNT/Al systems. (a)(b)(c) are CNT/Al system, and (d)-(g) are CNT/Cu system. (h) is the pristine CNT as a reference. ......................... 111
LIST OF TABLES

Table 1 Comparison of electrical resistivities of different thin films [7] .................................. 16
Table 2 Measured electrical resistivity, $\rho$, at 0K and 293 K, and temperature coefficient of resistivity, $\alpha$, at 293K. Data of oxygen-free high-conductivity(OFHC) Cu are included for comparison. [17] ......................................................................................................................................................................................... 17
Table 3 The band gap of CNT clamped with different number of Cu chains. ......................... 64
Table 4 Transmission Coefficient T (Ef) Value for each component part ............................... 71
Table 5 The conductance of the two probe systems ...................................................................... 80
Table 6 The conductance of the two probe systems ...................................................................... 96
Table 7 The resistivity for CNT-4Al, CNT-6Al, CNT-6Cu systems .............................................. 107
CHAPTER ONE: INTRODUCTION

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1.1 Carbon Nanotube’s Properties

1.1.1 Introduction to Carbon Nanotubes

Carbon nanotube (CNT) was regarded as one of the most exciting new materials during the last 30 years and has attracted intense interest since the discovery observation of multi-walled CNT made by Japanese electron microscopist Iijima in 1991[1, 2], although similar claims were made earlier by others. Structurally, carbon nanotube can be imagined as a graphene sheet rolls into a tubule, or can be seen as hollow structure of carbon fibers[2, 3]. A carbon nanotube can have high aspect ratios of 1000 or more[2], with nanometric diameter and length in micrometer range[3]. A single-wall carbon nanotube can have a diameter of 0.4 nm to 3 nm[3].

Due the fact that the sp² bonding in graphene is even stronger than the sp³ bonding in diamond[4], plus the CNT’s high symmetric, defect-free structure, carbon nanotube has very high mechanical strength and stiffness. Its Young’s modulus is estimated of the order of 1 TPa[1], while the typical Young’s modulus for carbon fibers and glass fibers are about 800 GPa, and 70 GPa respectively. Reported carbon nanotube strengths are 10-100 times higher than the strongest steel with a fraction of the weight[5]. On the other hand, carbon nanotube is not brittle but has extraordinary flexibility: they can deform extremely and return to origin without fracturing[1, 6].
Besides excellent mechanical properties, carbon nanotube also presented excellent electrical and thermal properties. Depending on diameter and structure, carbon nanotubes can be either semi-conducting or metallic. Metallic carbon nanotubes are excellent electrical conductors: carbon nanotube has a resistivity in the order of \( 10^{-1} - 10^{-2} \mu \Omega \cdot \text{cm} \) [7], which is several orders lower than the copper resistivity of \( 1.67 \mu \Omega \cdot \text{cm} \) [8], and they could carry current densities up to \(10^{11} \text{A} \cdot \text{m}^{-2} \) [1], which is about 1,000 times higher than copper wires. They are also good thermal conductors with thermal conductivity about twice of the diamond, and is thermally stable up to 2800°C[5].

The superior electrical and thermal properties may be given rise to by carbon nanotube’s unique quasi-one dimensional structure. In one dimensional structure, the electrons can only move in one direction, and the scattering is very limited, while in the three dimensional conventional material, a series of small angle backscattering could happen to the electrons, and the mean free path is sharply reduced. For example, the mean free path (MFP) of carbon nanotube, is around \(1 \mu m - 30 \mu m \) [9], in micron range, while in three dimensional metallic wire, the MFP is usually in the range of a few tens of nanometers[4]. Cu, for example, has a mean free path of 40 \( \text{nm} \) for electrons in bulk at the room temperature [9].

There are three main methods for the production of CNTs, which are arc discharge, laser ablation and chemical vapor deposition (CVD)[3]. In this thesis we will mainly focus on single wall carbon nanotubes (SWCNT). The following carbon nanotubes are all indicating SWCNT if not specially indicated.
1.1.2 The Structure of Carbon Nanotubes

Carbon nanotube can be seen as a graphene sheet rolled into a hollow cylinder, and thus its structure is closely related to the hexagonal structure of graphene[5], which is described as a Bravais lattice with a basis[3]. As shown in Figure 1 left, graphene’s primitive vectors are presented as $a_1 = (3/2a, \sqrt{3}/2a)$ and $a_2 = (3/2a, -\sqrt{3}/2a)$, where $a$ is the length of the carbon-carbon bond. The direction the graphene sheet rolling along with is very important and can be described using a vector $C_h$, known as the circumferential vector of carbon nanotubes (Figure 1), which can be expressed in terms of the primitive vectors of the graphene sheet [2]:

$$C_h = na_1 + ma_2$$ [10].

![Graphene lattice with every unit cell shaded. $a_1$ and $a_2$ are the primitive vectors of graphene, $a$ is the length of C-C bond. $C_h$ is a circumferential vector, and T is a primitive vector. Right: atomic structures of (a) zig-zag tube (12,0), (b) armchair tube (6,6) and (c) chiral (6,4) tube. [1, 3]](image)

Figure 1 Left: Graphene lattice with every unit cell shaded. $a_1$ and $a_2$ are the primitive vectors of graphene, $a$ is the length of C-C bond. $C_h$ is a circumferential vector, and T is a primitive vector. Right: atomic structures of (a) zig-zag tube (12,0), (b) armchair tube (6,6) and (c) chiral (6,4) tube. [1, 3]
The way of rolling is important to the carbon nanotube properties, and a slight change of the translation indices \((n,m)\) will change the electronic conductivity\(^5\).

Specifically, carbon nanotubes are classified into the three groups according to values of \(n\) and \(m\),

- armchair tubes - \((n,n)\);
- zig-zag tubes - \((n,0)\);
- chiral tubes - \((n,m \neq n)\).

The terms ‘zigzag’, ’armchair’ refer to the arrangement of hexagons around the circumference. The three classes are illustrated in Figure 1 right. As we can see from Figure 1, in the ‘armchair’ class, C-C bonds are parallel to the tube axis, while in the ‘zigzag’ class, the C-C bonds are perpendicular to the tube axis. For the third class, ‘chiral’, the hexagons are arranged helically around the tube axis\(^1,3\).

From zone-folding theory one can conclude the standard to determine the metallic/semiconducting characters of carbon nanotube\(^3\):

- Metallic: \(n - m = 3l\)

- Semiconducting: \(n - m = 3l \pm 1\)

\(n, m, l\) are all integers here. Besides the conducting character, the chiral vector can also be used to know the diameter of the tube, and also the unit cell and its number of carbon atoms.

\[
\text{d}_i = \left| C_h \right| / \pi = \frac{a_1}{\pi} \sqrt{n^2 + nm + m^2}
\]  

(1.1)
Where \( a_1 \) is the primitive vector for graphene.

The *primitive vector* of carbon nanotube’s lattice is defined as the shortest vector of the graphene lattice perpendicular to \( C_h \). It can be seen from Figure 1, the lattice vector \( T \) can also be expressed using primitive vectors of graphene lattice: \( T = t_1 a_1 + t_2 a_2 \). Using the geometry relation: \( C_h \cdot T = 0 \), we can get the expressions for \( t_1 \) and \( t_2 \):

\[
t_1 = \frac{2m + n}{N_R}, \quad t_2 = -\frac{2n + m}{N_R}
\]

(1.2)

here \( N_R \) is the greatest common divisor of \((2m+n)\) and \((2n+m)\).

The length of the translational vector \( t \) is

\[ t = |T| = \sqrt{3}a \sqrt{(n^2 + nm + m^2) / N_R} \]

Thus we get the nanotube unit cell, which is a cylindrical surface with height \( t \) and diameter \( d_t \). We could also get the number of carbon atoms per unit cell \( N_C \):

\[ N_C = 4(n^2 + nm + m^2) / N_R [3,10]. \]

(1.3)

1.1.2.1 Elementary Electronic Properties of Graphene: Tight Binding Model

Graphene’s honeycomb structure can be seen as a triangular lattice with a basis of two atoms in each unit cell. The lattice vectors are \( a_1 = \frac{a}{2} (3, \sqrt{3}), a_2 = \frac{a}{2} (3,-\sqrt{3}) \), where \( a \) is the carbon-carbon bond as above mentioned. The reciprocal lattice parameters can be calculated accordingly as \( b_1 = \frac{2\pi}{3a} (1, \sqrt{3}), b_2 = \frac{2\pi}{3a} (1,-\sqrt{3}) \). The two points at the corners of the graphene Brillouin Zone(BZ) are of great physics importance and are named as Dirac points. Their positions are
given as $K = \left( \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right), K' = \left( \frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right)$. The three nearest-neighbor vectors in graphene are given by $\delta_1 = a \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right), \delta_2 = a \left( \frac{1}{2}, -\frac{\sqrt{3}}{2} \right), \delta_3 = -a(1,0)$ [11].

![Graphene lattice and its Brillouin zone.](image)

Figure 2  Graphene lattice and its Brillouin zone. Left: lattice structure of graphene, in which $a_1$ and $a_2$ are its lattice unit vectors, and $\delta_1, \delta_2, \delta_3$ are the three nearest-neighbor vectors. Right: corresponding Brillouin zone. [11].

Carbon atom has four valence orbitals: $2s, 2p_x, 2p_y, 2p_z$. In graphene, the $2s, 2p_x, 2p_y$ orbitals combine to form three planar hybridized $\sigma$ orbitals, while the $p_z$ orbitals are out of the plane and cannot couple with $\sigma$ orbitals. The neighboring interaction between $p_z$ orbitals created delocalized $\pi$ orbitals. The occupied $\sigma$ and unoccupied $\sigma^*$ bands are known to be far away from the Fermi level, and don’t play a role in graphene’s electronic properties, while the $\pi$ bands and $\pi^*$ bands cross at the high symmetry $K$ points in graphene’s Brillouin zone, so we will just focus on $\pi$ bands[3, 10].
Considering only the nearest neighbors, the dispersion relations can be obtained using the tight binding method approximation:

\[ E(k) = \pm \gamma_0 \sqrt{3 + 2 \cos(k a_1) + 2 \cos(k a_2) + 2 \cos(k(a_2-a_1))}, \]

where \( \gamma_0 \) is the transfer integral between first neighbor interactions, with a value of about 3 eV (Figure 3)[3, 10].

![Electron band structure of graphene from ab-initio calculations and nearest tight binding model[4]. The two agree well on the K point.](image)

Figure 3: Electron band structure of graphene from ab-initio calculations and nearest tight binding model[4]. The two agree well on the K point.

1.1.2.2 From Graphene to carbon nanotube: zone folding approximation.

Zone folding approximation is used to calculate carbon nanotube’s electronic structure. The idea is to take graphene’s electronic states, and to apply the periodic boundary condition in the circumferential direction.
The periodic boundary condition for carbon nanotube’s wavefunction is:

\[ \varphi_m(r) = \varphi_m(r + C_h) \]  

(1.4)

Since \( C_h \) is a lattice vector for graphene, by the Bloch theorem, we could get:

\[ \varphi_g(r + C_h) = e^{ik \cdot C_h} \varphi_g(r) \]  

(1.5)

Combine these two equations, and ignore the curvature effects, we could get that carbon nanotube’s states are those graphene states who satisfy the equation:

\[ k \cdot C_h = 2\pi q, q \in Z \]  

(1.6)

Allowed states belong to a series of parallel lines and have distinct values of \( k \) (see Figure 4)

Figure 4 Nanotube (2,0). Left: corresponding real space graphene lattice. Right: reciprocal lattice of graphene and the allowed carbon nanotube’s states(indicated in red lines).[3]

For each allowed line we get two energy bands. Degeneration usually happens and the number of bands gets smaller. Resulting energy bands for different carbon nanotubes are presented in Figure 5[3, 10].
1.1.3 The Landauer Approach for Describing Quasi-One Dimensional Transport

1.1.3.1 Theory of Ballistic Conductors

1.1.3.1.1 Resistance of a Ballistic Conductor

A conductor is considered as ballistic when its mean free path is larger than the length of the conductor[12]. Carbon nanotube is proved to be possible ballistic conductors if using high-quality SWNTs, and produced by a chemical vapour deposition(CVD) method[12]. Nanotubes are usually regarded as quasi-one-dimensional systems with interesting properties that cannot be found in normal three-dimensional world[3].
Consider a conductor is sandwiched between two large contact pads as shown in Figure 6. Normally we know the conductor’s conductance would be given by an ohmic scaling law: \( G = \sigma W / L \), where \( \sigma \) is the material’s conductivity independent of the sample dimensions. When \( L \) is reduced, and if the Ohmic scale still holds, then the conductance will go infinitely. However, experimentally found that there is a limiting value \( G_c \) for the conductance when \( L \) becomes much shorter than the mean free path \( (L/\langle L_m \rangle) \). For a ballistic conductor with no scattering, the resistance is not zero, as expected. This resistance comes from the interface between the conductor and the contact pads which are very dissimilar materials having different number of modes. This resistance \( (G_c^{-1}) \) can be referred as the contact resistance, and can be given by[13]:

\[
G_c^{-1} = \frac{h}{2e^2 M} \approx \frac{12.9 k\Omega}{M} \tag{1.7}
\]

\[
G_c = \frac{2e^2}{h} M \tag{1.8}
\]

\( M \) is the number of transverse modes in the conductor. For wide conductors with thousands of modes, the contact resistance is very small and usually get unnoticed, however, for a single-moded conductor the contact resistance is 12.9k\( \Omega \) and cannot be ignored. In a ballistic conducting single-walled carbon nanotube \( M = 2 \) [12]. Individual carbon nanotube has an intrinsic ballistic resistance of approximately 6.5 \( k\Omega \) that is not dependent on the length of the nanotube [14].
1.1.3.1.2 Experimental results

Figure 7 Quantized conductance of a ballistic waveguide. (a) A device using negative voltage on a pair of metallic gates to constrict the conducting area progressively. (b) Measured conductance vs. gate voltage[15]

The first experiment on ballistic semiconductors was reported in 1988 and quantized conductances were observed. In semiconductors, the number of propagating modes is small, and the contact resistance can thus be measured. As shown in Figure 7, a pair of metallic gates is used to create a constriction (much shorter than a mean free path) progressively in the conductor.
As the width $W$ of the constriction was reduced, the conductance decreased in discrete steps of height $\frac{2e^2}{h}$. Only in narrow conductors with small number of transverse modes in the conductor can such a small fractional change in width cause a big change in the conductance. These striking results not only proved the existence of a contact resistance of a ballistic conductor, but also emphasize the importance of transverse modes for narrow conductors[13].

1.1.3.1.3 Landauer Formula

From above discussions, we get two corrections to the Ohmic scaling law: $G = \sigma W/L$ when entering smaller dimensions.

Firstly, there’s an interface resistance independent of the length of the sample.

Secondly, the conductance doesn’t decrease linearly with the width $W$. It has a relation with the number of transverse modes $M$ and goes down in discrete steps[13].

The Landauer formula is derived and incorporated these two features:

$$G = \frac{2e^2}{h} MT$$

(1.9)

The factor $T$ here represents the average probability that an electron injected at one end of the conductor will transmit to the other end.

For a ballistic conductor, which has a transmission probability of unity, the expression directly goes to the contact resistance of a ballistic conductor, as illustrated in $G_c$ (Equation1.5)[13].
For a non-ballistic conductor, since there are scatterings in the conductor, and the probability that an electron can pass through it (transmission probability $T$) is no longer equals to one as in ballistic conductor, we could rewrite our Landauer formula like this\cite{16}:

$$G^{-1} = \frac{h}{2e^2M} \frac{1}{T} = \frac{h}{2e^2M} + \frac{h}{2e^2M} \frac{1-T}{T} \Rightarrow G_c^{-1} + \text{Actual resistance.}$$  

(1.10)

The first part still keeps the form of contact resistance, while the second part comes from the conductor, and is thought as actual resistance. We could apply this formula to calculate the resistance of carbon nanotube, and carbon nanotube related devices\cite{16}.

1.2 Carbon Nanotube/Cu Interconnect Modeling

1.2.1 Background

Cu has been widely used as interconnects in the electronics since the 1998 because of its low resistance and low cost of production \cite{7, 17, 18}. However the copper interconnect has been facing a series of problems since the continuing reduction of the feature size (line width) in semiconductors. As the interconnect feature size shrinks by 30%, the current density through the interconnect will increase as a square of the scaling factor. And the electromigration(EM) , which refers to the current-induced displacement of atoms that occurs in a conductive material\cite{19}, will become more and more serious due to the high current density($10^6 \text{A/cm}^2$) \cite{7}. Thus the copper interconnect will become more and more vulnerable as the line width reduces further. The scaling feature size also cause the increased electrical resistivity due to increased carrier scatterings at surface and grain boundary\cite{7, 9}. 

13
On the other hand, copper’s intrinsic softness\cite{18} usually caused the failure of electronic components, while normal strengthening method like solid solution alloying, cold working, and grain refinement would usually decrease the conductivity pronouncedly\cite{9}.

Some also proposed that the huge coefficient of thermal expansion\( (CTE) \) mismatch with silicon leads to thermal mechanical stress which is also a issue for copper interconnect\cite{17}.

The appearance of CNT is a possible solution of replacing copper interconnects due to their high aspect ratio, large current carrying capacity and large electron mean free path, extremely high EM resistance, as well as excellent mechanical properties\cite{7, 9, 17}. However, carbon nanotube has its own engineering problem to overcome and it still needs time to mature from laboratory \cite{7, 17}. Instead, carbon nanotubes as filler materials in copper have been investigated and carbon nanotube-Cu composites have been fabricated in many ways. By doing this, people are aimed to create a new material with improved EM resistance, enhanced mechanical properties, without compromising with copper’s conductivity. The carbon nanotube-Cu composite should also have the potential to reduce the thermal mismatch in CMOS due to CNT’s rather lower coefficient of thermal expansion\( (CTE) \) than copper\cite{9, 17}.

1.2.2 Fabrication of CNT/Copper Composites

CNT/Copper composites have been prepared through a variety of processing techniques. Reported techniques including powder metallurgy technique, which consists of mixing CNTs with metal powders followed by compaction or sintering\cite{20}, Spark plasma sintering of Cu-CNT composite, electrochemical deposition, and novel method like molecular level mixing\cite{20}. 

14
1.2.3 Conductivity of Cu/CNT Nanocomposite

CNTs have become a promising candidate to improve copper’s electrical conductivity due to their ballistic transport property. It has an electron mean free path of $1\mu m$, considerable larger compared to that of bulk copper ($\sim 40nm$) [9]. It also has a current-carrying capacity of $20-25\mu A$ [21], which is 1000 times higher than copper wires [5]. Besides, individual carbon nanotube has a resistivity in the order of $10^{-1} \sim 10^{-2} \mu \Omega \cdot cm$ [7, 22], which is several orders lower than the copper resistivity $1.67\mu \Omega \cdot cm$ [8]. This implies that a system based on ballistic CNT imbedded in metal might work as material with a much lower room temperature resistivity than conventional metal conductors like Cu, Al, Ag [12]. With its improved EM resistance, enhanced mechanical properties, Cu-CNT composite can certainly be a promising replacement to the current copper interconnects.

A lot of reports on Cu-CNT systems deal with improvement in electrical properties [23]. Yang Chai et al. fabricated a CNT-reinforced copper matrix composite using the bottom-up growth of CNT and electrochemical plating (ECP) of copper. This composite exhibits electrical resistivity comparable to pure copper, as presented in Table 1 [7]. The larger resistivity than copper has been attributed to the scattering at the interface.
Table 1 Comparison of electrical resistivities of different thin films [7]

<table>
<thead>
<tr>
<th>Metal thin film</th>
<th>$\rho$ ((\mu\Omega\cdot\text{cm})) at 20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2.6 [8]</td>
</tr>
<tr>
<td>Sputtered Cu</td>
<td>1.9 [8]</td>
</tr>
<tr>
<td>Al (0.5 wt% Cu)</td>
<td>3.0 [8]</td>
</tr>
<tr>
<td>Cu (0.5 wt% Sn)</td>
<td>2.4 [8]</td>
</tr>
<tr>
<td>Cu (graphite)</td>
<td>4.0 [7]</td>
</tr>
<tr>
<td>Cu/CNT</td>
<td>2.2 this study</td>
</tr>
<tr>
<td>Al/CNT</td>
<td>4.9 [28]</td>
</tr>
<tr>
<td>CNT</td>
<td>$10^{-1}$-$10^{-2}$ [29, 30]</td>
</tr>
</tbody>
</table>

Y.L. Yang et al. used the electrochemical deposition technique under ultrasonic field to prepare SWNT-reinforced Cu composite coatings (SWNT-Cu). The ultrasonic field is used to improve the interfacial adhesion between the SWNTs and the Cu matrix. As presented in Figure 8, the conductivity of SWNT-Cu is nearly the same as that of OFHC Cu throughout the temperature range.
By fitting the data in the resistivity-temperature curve, they get that at room temperature, the electrical resistivity of SWNT-Cu is slightly lower than that of OFHC Cu [18], while at zero temperature, the SWNT-Cu has a higher resistivity than that of OFHC Cu. Values are presented in Table 2.

Table 2 Measured electrical resistivity, $\rho$, at 0K and 293 K, and temperature coefficient of resistivity, $\alpha$, at 293K. Data of oxygen-free high-conductivity (OFHC) Cu are included for comparison. [18]
N. Ferrer-Anglada et al also prepared SWNT-Cu composites electrochemically, and get an electrical conductivity of the composite the same as for Cu metal at room temperature.

A electro co-deposition approach was given by patent filed from University of Central Florida by Dr. Chen[24]. The SWCNT with the copper was deposited with an external magnetic field to orient the nanotubes as they deposit. There is at least a 40% decrease in the electrical resistivity of the composite (1.22×10^{-6} \Omega \cdot cm) when compared with pure copper (1.72×10^{-6} \Omega \cdot cm)[17].

Ying’s Ph.D. thesis reported the decreased resistivity as a function of the concentration of MWNT in the electrolyte. She found that when the MWNT concentration increased to 50mg/150ml, the resistivity would decreases to 0.8×10^{-6} \text{ohm} \cdot \text{cm}, which is a very low value. The measured resistivity on Cu/SWCNT was 1.0 ∼ 1.2×10^{-6} \text{ohm} \cdot \text{cm}, which is about 40% less than pure copper [25].

1.2.4 Conduction Mechanism of Cu/CNT Nanocomposites

Hjortstan et al have reported a concept for creating an ultra-low-resistivity material based on carbon nanotube-metal composite. An effective-medium model shows that a room-temperature resistivity 50% lower than Cu can be achieved with a SWNT filling factor in the range of 30%-40%[7, 12].

However, this theoretical model deviates from the experimental results because it ignores the interfacial bonding between the CNT and the copper matrix. The interface phase increases the scattering of the charge carrier and thus the electrical resistivity[7].
Up to now the resistivity results from Cu/CNT composites are scattered and cannot be explained in a uniform way. Although the copper/CNT composite exhibits mostly larger resistivity than pure copper, large improvements could be achieved from the following aspects: (1) introducing an intermediate layer to improve the interface bonding between CNT and metal matrix; (2) synthesizing the high-quality single-walled CNTs. (3) Remove the semiconducting CNT in as grown CNTs product. By modeling the conductance of CNT/metal systems, we could also get more clear directions of lower the total resistivity experimentally in the near future.
CHAPTER TWO: QUANTUMWISE AND ITS RELATED FUNCTIONAL THEORY

2.1 Introduction
Atomistix ToolKit (ATK) is a commercial software package that can simulate nanostructures and calculate the properties of nano systems on the atomic scale. QuantumWise is its new version[26]. This software is a powerful combination of DFT, semi-empirical tight-binding, classical potentials, and can conduct NEGF simulations to study transport properties like I-V characteristics of nanoelectronic devices. It’s scripted in Python, while its advanced graphical user interface enables one to build complicated structures conveniently[27].

The software is used by over 150 research groups in universities, government labs, and companies around the world. More than 600 scientific articles using ATK have been published since 2006. ATK is an ideal tool for both researching and teaching the basic concepts in nanotechnology and solid state physics[27].

In our research, we mainly use Density functional theory (DFT) in conjunction with Non-equilibrium Green’s function (NEGF) method to calculate the properties of our device and nanostructures. These theory and method will be introduced below.

2.2 Many-body Problem

2.2.1 Schrödinger Equation

\[
\frac{-\hbar^2}{2m} \nabla^2 \Psi(r,t) + V(r,t) \Psi(r,t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t}
\]  (2.1)
Equation 2.1 is the time dependent Schrödinger Equation, everything that has to do with time development follows from this fundamental equation[28]. When the potential is assumed to be time independent \( V = V(r) \), the equation becomes Equation 2.2:

\[
-\frac{\hbar^2}{2m} \nabla^2 \Psi(r,t) + V(r) \Psi(r,t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t}
\]  

(2.2)

One can solve this equation by using the method of separation of variables as following. Assume

\[
\Psi(r,t) = \varphi(r)f(t)
\]  

(2.3)

And insert it into Equation 2.2, then separate the sides with different variables, both sides must be equal to a constant \( E \), and we yield:

\[
i\hbar \frac{d}{dt} f(t) = Ef(t) \Rightarrow f(t) = \exp\left(-i\frac{E}{\hbar}t\right)
\]  

(2.4)

\[
\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right]\varphi(r) = Ef(r)
\]  

(2.5)

Equation 2.5 is the time independent Schrödinger Equation, which describe stationary states. It has a final form as:

\[
\hat{H}\varphi(x) = E\varphi(x)
\]  

(2.6)

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(x)
\]  

(2.7)

Where 2.7 is the Hamiltonian.

A state is called stationary if it is represented by the following wave function form:
\[ \Psi(x,t) = \varphi(x) f(t) = \varphi(x) \exp(-i \frac{E}{\hbar} t) \] (2.8)

For a stationary state, \( \|\Psi(x,t)\|^2 \) is the probability of finding an electron in \( x \) and \( t \).

\[ \|\Psi(x,t)\|^2 = \|\varphi(x) \exp(-i \frac{E}{\hbar} t)\|^2 = \|\varphi(x)\|^2 \] (2.9)

As one can interpret from 2.9, the probability density to find such a stationary state is time independent.

2.2.2 Variational Principle

For an arbitrary atom or molecular system, if we want to solve the Schrödinger Equation, then the first thing is to set up the specific Hamilton operator for the system, and then find the eigenfunctions \( \Psi_i \) and corresponding eigenvalues \( E_i \) of \( \hat{H} \). Once \( \Psi_i \) is determined, all the properties can be obtained by applying the appropriate operators to the wave function[29]. However, this simple program is not practical and no strategy to solve the Schrödinger Equation exactly is known for atomic and molecular systems.

Nevertheless, a hope is raised by a recipe to systematically approach the ground state wave function \( \Psi_0 \) : the variational principle. It holds a very important role in all quantum-chemical applications[29].

\[ E[\phi] = \frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} \] (2.10)

\[ E[\phi] \geq E_0 \] (2.11)
The variational principle states that for any trial wave function $\phi$, the expectation value of the Hamilton operator from it would be no less than the true energy of the ground state. If $E[\phi] = E_0$, then $\phi$ is the ground state wave function, and vice versa.

2.2.3 Born-Oppenheimer Approximation

Here we begin with writing the Hamiltonian for the many body system.

For a collection of atoms:

$$\hat{H} = \hat{T}_e + \hat{T}_N + \hat{V}_{e-N} + \hat{V}_{N-e-N}$$

$$\hat{T}_e = -\frac{1}{2} \sum_i \nabla_i^2 \quad \hat{V}_{e-N} = \sum_i \left[ \sum_l V(R_i - r_l) \right] \quad \hat{V}_{e-N} = \sum_i \sum_{j>i} \frac{1}{r_i - r_j}$$

$$\hat{H} \Psi(r_1, \ldots, r_n, R_1, \ldots, R_N) = E_{rot} \Psi(r_1, \ldots, r_n, R_1, \ldots, R_N)$$

We treat only the electrons as quantum particles, in the field of the fixed (or slowly varying nuclei). This is generically called the Born-Oppenheimer approximation. It takes advantage of the masses differences between the nuclei and electrons. The nuclei, which is at least 1800 times heavier than an electron (the proton $^1H$), moves much slower than the electrons. This fact allows a good approximation that the electrons are moving in a field of fixed nuclei from an extreme point of view.

If it doesn’t move, then the kinetic energy is zero and the nucleus-nucleus repulsion is merely a constant. Thus the complete Hamiltonian could be reduced to a so-called electronic Hamiltonian[29]:

```
```

23
\[ \hat{H} = \hat{T}_e + \hat{V}_{e-e} + \hat{V}_{e-N} \]  

(2.15)

And the Schrodinger Equation is further simplified as

\[ \hat{H}_{\text{elec}} \Psi_{\text{elec}} = E_{\text{elec}} \Psi_{\text{elec}} \]  

(2.16)

2.2.4 Mean Field Approach

The many-body problem is still very complex, and it needs huge number of tabulates to get a single wavefunction. In face of such a complicated calculation, the mean field approach has been advanced.

The Independent particle model (Hartree): each electron moves in an effective potential, representing the attraction of the nuclei and the average effect of the repulsive interactions of the other electrons\([30]\).

\[
\Psi(r_1, ..., r_n) = \varphi_1(r_1)\varphi_2(r_2) \cdots \varphi_n(r_n)
\]  

(2.17)

\[
\begin{bmatrix}
-\frac{1}{2} \nabla_i^2 + \sum_j V(R_j - r_i) + \sum_{j \neq i} \int \left| \varphi_j(r_j) \right|^2 \frac{1}{r_j} d r_j \\
\end{bmatrix} \varphi_i(r_i) = \varepsilon \varphi_i(r_i)
\]  

(2.18)

This average repulsion is the electrostatic repulsion of the average charge density of all other electrons. Instead of considering how electrons are exactly interacting with each other (like in equation 2.13), it only considers all other electrons’ effect as a whole, which makes the calculation more simplified.
2.2.5 Hatree-Fock Approximation

The Hatree approximation treated electrons as distinguishable particles[31]. However, electrons are indistinguishable fermions. According to spin statistics, a set of identical fermions has a wave function that is antisymmetric by exchange[30]:

$$\Psi(r_1, r_2, \ldots, r_j, \ldots, r_n) = -\Psi(r_1, r_2, \ldots, r_k, \ldots, r_j, \ldots, r_n)$$  \hspace{1cm} (2.19)

As stated by equation 2.19, the wave function must change sign when two electrons are exchanged. The Hartree approximation doesn’t contain this feature. As an improvement, an antisymmetric wave function is constructed via a Slater determinant of the individual orbitals (instead of just a product, as in the Hartree approach 2.17)[30, 32]

$$\Psi(r_1, r_2, \ldots, r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_{\alpha}(r_1) & \varphi_{\beta}(r_1) & \ldots & \varphi_{\nu}(r_1) \\ \varphi_{\alpha}(r_1) & \varphi_{\beta}(r_1) & \ldots & \varphi_{\nu}(r_1) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{\alpha}(r_1) & \varphi_{\beta}(r_1) & \ldots & \varphi_{\nu}(r_1) \end{vmatrix}$$ \hspace{1cm} (2.20)

$$\left[ -\frac{1}{2} \nabla_i^2 + \sum_i V(\vec{r}_j - \vec{r}_i) \right] \varphi_\lambda(\vec{r}_j) + \sum_\mu \left[ \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\mu(\vec{r}_j) d\vec{r}_i \right] \varphi_\lambda(\vec{r}_j)$$

$$- \left[ \sum_\mu \int \varphi_\mu^*(\vec{r}_j) \frac{1}{|\vec{r}_j - \vec{r}_i|} \varphi_\lambda(\vec{r}_j) d\vec{r}_j \right] \varphi_\mu(\vec{r}_j) = \lambda \varphi_\lambda(\vec{r}_j)$$ \hspace{1cm} (2.21)

This equation is self-consistent and received the name of self-consistent field (SCF)[31]. Because in deriving the Hartree equation, it depends on itself on the orbitals that are the solution
of all other Hartree equations. We have \( n \) simultaneous integro-differential equations for the \( n \) orbitals. Solution is achieved iteratively\([30]\), and self-consistency is required.

2.2.6 Thomas-Fermi Approach

The Hartree-Fock approximation uses the wave function \( \Psi \) as the central quantity, and then get all system information from it. There’s a severe problem, however. The wave function is a very complicated quantity that depends on \( 4N \) variables, 3 spatial variables and 1 spin variable for each of the \( N \) electrons. While the actual system we are dealing with usually contains many atoms and many more electrons. Thus, the wave function based calculation would reach an unmanageable size\([29]\). Due to its own limitations, Hartree-Fock approximation only works well for atoms.

As early as 1927, almost at the same time as quantum mechanics emerged, the first attempts to use the electron density rather than the wave function to obtain information about atoms and molecular systems have been made by Thomas and Fermi\([29]\).

They use a local density approximation to get the kinetic energy term:

\[
T(r) = A \rho^5(r)
\]  

(2.22)

This expression is achieved based on the homogenous electron gas, and can be applied on systems whose electron density changes slowly. Combined with the classical expression for the nuclear-electron potential, and the electron-electron potential, we get the famous Thomas-Fermi expression for the energy of an atom:
\[ E_{Th-Fe}[\rho] = A \int \rho^3(r) \, d\vec{r} + \int \rho(r) \nu_{ex}(r) \, d\vec{r} + \frac{1}{2} \iint \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} \, d\vec{r}_1 \, d\vec{r}_2 \]  

(2.23)

Since it does not include exchange effects, Dirac proposed to add the LDA exchange energy:

\[-C \int \rho(r)^4 \, d\vec{r} \]. Thus we get an approach which describes energy only in terms of electron density \( \rho(r) \). It is a function of only 3 coordinates, and scales linearly. This approach works poor for non-homogeneous system since \( T(\vec{r}) \) is very coarse in approximating the true kinetic energy, however, it’s still very important because it’s the grandfather of our genuine accurate density functional theory[29, 30].

### 2.3 Density Functional Theory

#### 2.3.1 The First Hobenberg-Kohn Theorem

The augment that the energy as a function of \( \rho(\vec{r}) \) in Thomas-Fermi approach is not physically justified, and only put onto a firm physical foundation in 1964 by Hobenberg and Kohn after about 40 years[29]. They proved the density as the basic variable: the external potential determines uniquely the charge density, and the charge density determines uniquely the external potential[30]. Ground state density, just like the ground state wave function, is also a basic variable and can be used to obtain all the information.
2.3.2 The Second Hohenberg-Kohn Theorem

The Second Hohenberg-Kohn theorem is the Variational Principle, expressed in terms of the charge density only.

\[
E_v\left[ \vec{\rho}(\vec{r}) \right] = F\left[ \vec{\rho}(\vec{r}) \right] + \int V_{\text{ext}}(\vec{r}) \vec{\rho}(\vec{r}) d\vec{r} \geq E_0
\]  
(2.24)

\[
F[n(r)] = T_s[n(r)] + E_H[n(r)] + E_{xc}[n(r)]
\]  
(2.25)

\[
E_H[n(r)] = \frac{1}{2} \iiint \frac{n(r_1)n(r_2)}{|r_1 - r_2|} dr_1 dr_2
\]  
(2.26)

As equation 2.24 presented, the second Second Hohenberg-Kohn theorem states that \( E_v\left[ \vec{\rho}(\vec{r}) \right] \) delivers the lowest energy if and only if the input density is the true ground state density \( \rho_0 \). In other words, for any trial density \( \vec{\rho}(\vec{r}) \), \( E_0 \) results if and only if the exact ground state density is inserted into the equation[29].

2.3.3 Kohn-Sham Equation

Kohn and Sham introduced a non-interacting reference system which is called the Kohn-Sham system. In this system the electrons (the Kohn-Sham electrons) do not interact, and live in an external potential (the Kohn-Sham potential) such that their ground-state charge density is identical to the charge density of the interacting system[30].

For a system with non interacting electrons, the Slater determinant is the exact wave function, and the kinetic energy can be exactly determined by:
\[ T_S = -\frac{1}{2} \sum_i \langle \varphi_i | \nabla^2 | \varphi_i \rangle \]  

(2.27)

For the non-interacting reference system, the electrons are moving in an effective potential \( \vec{V}_S(r_i) \), and the Hamiltonian can be written as:

\[ \hat{H}_S = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \vec{V}_S(r_i) \]  

(2.28)

Since this Hamilton operator does not contain any electron-electron interactions it indeed describes a non-interacting system[29]. For each specific orbital in the determinant, we have

\[ \hat{f}^{KS} \varphi_i = \varepsilon_i \varphi_i \]  

(2.29)

With the one-electron Kohn-Sham operator \( \hat{f}^{KS} \) defined as

\[ \hat{f}^{KS} = -\frac{1}{2} \nabla^2 + \vec{V}_S(r) \]  

(2.30)

In our real system, for any specific orbital, we could have:

\[
\left[ -\frac{1}{2} \nabla^2 + \nu_H(r) + \nu_{xc}(r) + \nu_{eu}(r) \right] \varphi_i(r) = \hat{H}_{KS} \varphi_i(r) = \varepsilon_i \varphi_i(r) 
\]  

(2.31)

\[ \nu_{KS}(r) \equiv \int \frac{n(r')}{|r-r'|} dr' + \nu_{xc}(r) + \nu_{eu}(r) \]  

(2.32)

\[ \nu_{H}(r) = \int \frac{n(r')}{|r-r'|} dr' \quad \nu_{xc}(r) = \frac{\delta E_{xc}}{\delta n(r)} \quad n(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2 \]  

(2.33)

\( \nu_{KS}(r) \) is the Kohn-Sham potential. Here we use the exact kinetic energy of the non-interacting reference system as that of the real, interacting one. The non-interacting kinetic energy is not
equal to the true kinetic energy of the interacting system, and the residual part has been added to the exchange-correlation energy $E_{xc}$. $E_{xc}$ in fact contains everything that is unknown. The exchange-correlation potential $\nu_{xc}(r)$ is simply defined as the derivative of $E_{xc}$ with respect to $n(r)$.

Thus, the Kohn-Sham approach is in principle an exact theory. The approximation only enters when we decide the form of the exchange-correlation energy. $E_{xc}$ has a good approximation and is easier to be calculated than the Hartree-Fock approach.

### 2.4 The Non-equilibrium Green's Function Method

Non-equilibrium Green's function method is usually used to calculate current and charge densities in nanoscale conductors under bias. This method is mainly used for ballistic conduction[33].

Instead of using the scattering states, Quantum Wise uses the Non-equilibrium Green's function(NEGF) method to calculate the non-equilibrium electron density [26].

![Figure 9 A typical device system in QuantumWise](image)

30
A typical device system is illustrated in Figure 9. It can be divided simply into three parts: the left contacts, the right contacts, and the central part. The left and right regions are equilibrium systems with periodic boundary conditions, for which a conventional electronic structure calculation can get all the properties. For the central part, the electrons are in non-equilibrium distribution, and Non-equilibrium Green’s function is applicable[26].

\[ G = [EI - H - \Sigma_L - \Sigma_R]^{-1} \]  (2.34)

Eq.2.34 is the definition for the Green’s function[13] for such a device of a conductor coupled with two electrodes. \( \Sigma_L \) and \( \Sigma_R \) are the so called self-energies of the left and right electrode.

In NEGF, the electron density is given in terms of the charge density matrix.

The left density matrix contribution is given by

\[ \rho^L = \frac{1}{2\pi} \int_{E=-\infty}^{\infty} dE f(E, \mu_i) G_d \Gamma_L G_d^\dagger \]  (2.35)

Where \( \Gamma_L = \tau_L^a \alpha_L \tau_L = i(\Sigma_L - \Sigma_L^+) \) is the broadening function of the left electrode. A similar equation for the right density matrix contribution can be written, and the total charge density becomes a sum over all contacts[33].

\[ \rho = \frac{2(\text{for spin})}{2\pi} \int_{E=-\infty}^{\infty} dE \sum_i f(E, \mu_i) G_d \Gamma_i G_d^\dagger \]  (2.36)

\( G_d \) is the retarded Green’s function for the device.

If we define the transmission as the trace of the matrix quantity, then the current is still given by the Landauer formula [34]:

\[ I = e T \int dE \sum_i f(E, \mu_i) G_d \Gamma_i G_d^\dagger \]
QuantumWise can model the electronic properties of closed and open quantum systems based on density-functional theory (DFT)[26]. Density-functional theory (DFT) transforms the many-body Schrödinger equation into an effective one-electron equation. The electrons are non-interacting particles moving in an effective potential. This effective potential needs to be determined self-consistently[35].

The key parameter in the self-consistent loop is the density matrix. For open systems, the density matrix is obtained using non-equilibrium Green’s functions, while for closed or periodic systems it is calculated by diagonalizing the Kohn-Sham Hamiltonian[26].

The Density Matrix defines the electron density, and the electron density sets up an effective potential. From the effective potential, one can obtain the Kohn-Sham Hamiltonian[26]. From the Hamiltonian one can determine the one-electron eigenstates by solving the one-electron Schrödinger equation. By summing all occupied one-electron eigenstates, the electron density is determined. These steps can be described using the following equations[35]:

\[
\hat{H}_{1el} = -\frac{\hbar}{2m} \nabla^2 + V^{\text{eff}} [n](r)
\]

(2.39)

\[
\hat{H}_{1el} \Psi_{\alpha}(r) = \varepsilon_{\alpha} \Psi_{\alpha}(r)
\]

(2.40)
\[ n(r) = \sum_{\epsilon_{\mu}(r)} |\psi_{\mu}(r)|^2 \] (2.41)

The flow chart (Figure 10) below describes the self-consistent loop in DFT:

Figure 10  Flowchart for DFT calculations, self-consistent loop[35, 36]
CHAPTER THREE: TRANSPORT AND ELECTRONIC PROPERTIES OF HYBRID NANOWIRES CONSISTS OF COPPER AND CARBON NANOTUBES


3.1 Introduction

Carbon nanotubes [37] have been widely investigated due to their special properties, including the high symmetric arrangements, defect free-structure that leads to high strength and stiffness [38] and the high Young’s modulus[1] as well as the extraordinary flexibility makes it both strong and resilient. In addition, carbon nanotubes have shown special electric conduction capabilities. For example, the armchair type carbon nanotube ((n ,n) type) has been proved to be metallic with a resistivity as low as \( \sim 10^{-5} \ \Omega \cdot \text{cm} \) [16] and the large current carrying capacity[5], mainly due to the facts that the metallic carbon nanotube has large mean free path and its electronic transport properties is mostly considered ballistic[9]. All these make it a good candidate in nanoelectronic applications[38].

However, Carbon nanotubes alone cannot be used in some practical applications since it cannot satisfy many requirements of actual devices[39]. While metal could give carbon nanotube both as support and link with their environment, in which hybrid material like metal/CNT nanowire is an important form. Metal/Carbon nanotube system would be the most important system in nanotechnology[40]. If combined with metals like copper, the large mean free path of CNT and the large free electron density of copper may form a novel material with
ultra-low resistivity. Some theorist predicted that it is possible to achieve the ultra-low resistivity in carbon nanotube-based metal composites[8, 12], and some experimental efforts employing different methods have been made to synthesis such composites[7, 18], but no improved low resistivity has been reported up to now.

The authors have conducted an analytical study on this matter. The main work of this study was to investigate the electronic and transport properties of carbon nanotube/copper hybrid nanowire by density functional theory (DFT) and non-equilibrium Green functions (NEGF) approaches. The goal of this work was to understand the basics of conduction mechanism of Cu/CNT combined system and to guide further development in an efficient way.

3.2 The Calculation Method and The Simulation Model
The electronic/transport properties of the Cu/CNT hybrid nanowire and the optimization in geometry were performed by using the QuantumWise/ (ATK2008.10) package[41-43]. In the relaxation process, authors employed local density approximation (LDA) with the Perdew-Zunger (PZ) exchange-correlation functional[44]. 1×1×30 k points sampling and double-zeta polarized (DZP) basis set were used for both carbon and copper atoms during the relaxation process. Figure 11 shows the atomic structure of a hybrid nanowire consists of a CNT (10, 0) and a copper chain as well as that of a hybrid Cu/CNT nanowire consisting of a CNT (5, 5) and a copper chain. Both structures were fully relaxed until the maximum force was less than 0.05 eV/Å. The relaxed geometry can be seen in Figure 11.
CNT (10,0) is a zigzag SWCNT which is semiconducting and the CNT (5,5) is a armchair or a metallic one. For (10,0) zigzag SWCNT, there’s two Cu atoms in a unit cell. For (5,5) SWCNT, there’s only one Cu atom in a unit cell. The initial distance between the Cu atom and its nearest carbon atom neighbor in both cases are kept at around 1.5 Å, and the final distance varies due to the relaxation.

The electronic structure and the transport properties are calculated using the relaxed geometries. In this part, the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[45] and a Monkhorst-Pack grid of 1×1×100 were used. A tolerance of 1×10⁻⁵ of the total energy was used as the convergence criterion.

3.3. Results and Discussions
3.3.1 Electronic Structures

3.3.1.1 Band Structures

Figure 12 shows the bandstructure of the CNT(10,0) with a Cu chain. As a comparison, the bandstructure of the distorted carbon nanotube, as well as the freestanding Cu chain have also been calculated. The geometry of the distorted CNT has been obtained by removing the Cu chain from the relaxed hybrid system. While the geometry of freestanding Cu chain is achieved by removing the CNT from the relaxed hybrid system.
Bandgaps are observed in both the hybrid system and the distorted CNT. When a Cu chain is absorbed, the bandgap is only smaller than the distorted CNT. It implies that the addition of Cu chain doesn’t change the semiconducting nature of the CNT(10,0).

By comparing the bandstructures of the three components, we could see that two new bands around the Fermi level have been derived by the existing Cu chain, with one above and one below the Fermi level. In addition, the bandgap is narrowed due to the function of Cu chain as mentioned above.

The bandstructure of CNT(5,5) with a Cu chain has shown differences from that of the CNT(10,0)(see Figure 13), characterized with a cross at two-thirds of the distance between \( \Gamma \) and \( Z \) point [46], implying its metallic character.

Secondly, the bandstructure of CNT(5,5) has been modified by Cu in terms of that the Fermi level has shifted toward the conduction band of the carbon nanotube. Similar behavior was observed in the case that a single Cu chain wrapped in a carbon nanotube[47]. Besides the shift, more bands crossing the Fermi level are derived by the existing Cu chain, and the conductance of the system has been improved.
Figure 12 The band structure of (a) CNT(10,0)/Cu hybrid system. (b) distorted carbon nanotube(10,0). (c) free standing Cu chain.
Figure 13: The band structure of (a) CNT (5, 5) with a Cu chain. (b) distorted carbon nanotube (5, 5). (c) freestanding Cu chain.

3.3.1.2 DOS (density of states)

A better insight into the electronic interaction between CNT and the Cu chain is the density of states (DOS). The DOS for a CNT(10,0)/Cu system is presented in the Figure 14 (left), while the DOS for a CNT (5,5)/Cu system is shown in the bottom part.

In Figure 14 (left), the top part (a) shows the DOS for the distorted CNT(10,0), while the middle part (b) shows the DOS for the free-standing Cu chain and the bottom part (c) indicates
that of hybrid CNT(10,0)/Cu. The integration of Cu chain doesn’t change the DOS of the system around the Fermi level (c), but the gap of DOS gets shrank.

In Figure 14 (right), as a comparison, the top part (a) is for the DOS of CNT(5,5)/Cu, the middle part (b) shows the DOS for the distorted CNT(5,5), while the bottom part (c) shows the DOS for the free-standing Cu chain. The Cu chain creates some additional states around the Fermi level, which enhances the conductivity of CNT(5, 5). An increased value of DOS at the Fermi level is found in CNT (5, 5)/Cu system (Figure 14 right(a)). It is also indicated that the density of states of the CNT(5,5)/Cu is not a simple superposition of the CNT (5, 5) and the Cu chain. This means that there is interaction between the carbon nanotube and the copper chain and this interaction modifies each other’s electronic structure.

Figure 14 Density of States for CNT (10, 0)/Cu system (left); CNT (5, 5)/Cu system (right). Left: (a) distorted CNT (10, 0), (b) Cu atomic chain, and (c) CNT (10, 0) with a Cu chain. Right: (a) CNT (5, 5) with a Cu chain, (b) distorted CNT (5, 5), and (c) Cu atomic chain.
3.3.2 Transmission Spectrum

The calculated transmission spectra at the zero bias for the two systems are presented in Figure 15. The left part is the transmission spectrum for the CNT (10, 0)/Cu system, while the right part is the transmission spectrum for the CNT (5, 5)/Cu system.

![Figure 15](image)

Figure 15  Transmission Spectrum for CNT (10, 0)/Cu system (left); CNT (5, 5)/Cu system (right). Left: (a) Cu atomic chain, (b) distorted CNT (10, 0), and (c) CNT (10, 0) with a Cu chain. Right: (a) Cu atomic chain, (b) CNT (5, 5) with a Cu chain, and (c) distorted CNT (5, 5).

According to Figure 15 (Left), a transmission gap retains for the CNT (10, 0) after a Cu chain absorbing onto it. It means that the CNT (10, 0) remains semiconducting nature even after addition of the Cu chain. However, the transmission gap has been decreased. This result agrees with the DOS as well as the band structure of the CNT (10, 0)/Cu system.

In comparison to the transmission coefficient of CNT (10, 0) at Fermi level, the transmission of CNT (5, 5) has been significantly enhanced after the absorption of the Cu chain. According to Figure 15 (Right), the transmission coefficients around the Fermi level for the pure CNT (5, 5) is 2, in agreement with the well-known results. However, the transmission coefficient at the Fermi
level is 2.999992 for the CNT (5, 5)/Cu, and 0.9999622 for the Cu chain, respectively. The transmission coefficient for the CNT/Cu is not the exactly superposition of the Cu and the CNT, which indicates some interactions between the CNT and the Cu chain.

3.3.3 Transmission Eigenchannel

![Transmission eigenstates](image)

Figure16 Transmission eigenstates at 0.32eV below (a) and higher (b) than the Fermi level for CNT (10, 0) with a Cu chain, and at the Fermi level for CNT (5, 5) with a Cu chain(c)-(e).

Transmission eigenstates is also called eigenchannel; it indicates that the electronic states contribute to the conductance[48]. Since the CNT (10, 0) is semiconducting and it has a gap in its band structure, it’s reasonable to analysis the transmission eigenstates not at the Fermi level, but at 0.32eV above and below the Fermi level, which is almost the same value of its band gap
energy. By performing the eigenchannel analysis, we found that there’s only one eigenchannel at each case (+0.32eV, -0.32eV).

Figure 16(a) shows the transmission eigenstates at 0.32eV below the Fermi level of CNT(10,0). For this case, the eigenstates is not localized in the Cu atoms alone, but also include the electronic states of the carbon atoms. That means electrons can pass the system through both the carbon nanotube and the copper chain, or both the Cu and the C atoms are contributing to the conductance of the system. While for the case of 0.32eV higher above the Fermi level, the transmission eigenstates concentrate on the Cu atoms. Comparing the band structure of the CNT(10,0) with a Cu chain system, it is concluded that the highest valence band originates from the combined system of Cu and CNT, while the lowest conduction band originates from the Cu chain.

The CNT(5,5) with a Cu chain system is metallic and by performing the eigenchannel analysis at its Fermi level, it can be found that the number of eigenstates is 3, the same as its transmission coefficient at the Fermi level. The three transmission eigenstates at the Fermi energy are listed in Figure 16(c) – (e), and all the three transmission eigenstates are found to be contributed by the Cu/CNT(5,5) hybrid systems, which proves that it’s a typically metallic system.

3.4 Conclusion
In summary, authors employed the density functional theory (DFT) and the non-equilibrium Green function (NEGF) to investigate the electronic structures and the transport properties of the CNT/Cu system.
The results have proved that the incorporation of a Cu chain enhances the density of states (DOS), the transmission coefficient at Fermi level of the metallic CNT (5, 5), and thus the conductivity of the hybrid system.

The incorporation of a Cu chain reduces the band gap of a semiconducting (10, 0) zigzag carbon nanotube. The transmission eigenstates near the Fermi level has shown that not only the copper chain but also the carbon nanotube contribute to the resultant conductance of the system.

The integration of a copper chain would increase the conductivity of both the metallic and the semiconducting carbon nanotubes. Based on these results it is possible to include more copper chains to reduce the band gap further to even transform the carbon nanotube from the semiconducting to the metallic. For the metallic carbon nanotubes the integration of more copper chains will increase the conductance further. Therefore, hybrid CNT/Cu nanowires and nanocomposites with unprecedented electric conductivities can be developed.
CHAPTER FOUR: TUNING SEMICONDUCTING CARBON NANOTUBES TOWARDS METALLIC WITH THE ADSORBED COPPER CHAINS

4.1 Introduction
Carbon nanotubes (CNTs)[37] have exhibited exceptional mechanical properties like the ultra-high strength [43] and Young’s modulus [1] plus the extraordinary resilient properties. However, for the electric properties it varies between metallic and semiconducting. Metallic CNTs have shown excellent electrical properties with a resistivity as low as $\sim 10^{-5} \ \Omega\cdot\text{cm}$[16] plus a large current carrying capacity[5], mainly due to its ballistic electron transport nature with its large mean free path (MFP)[9]. Metallic CNTs have been regarded as ideal building blocks to develop conductive composites like interconnects in nanoelectronics[43].

However, it is difficult to produce pure metallic CNTs alone, and the synthesis of CNTs usually produces a mixture of metallic and semiconducting CNTs[48]. Although it is possible to separate metallic CNTs from the semiconducting ones, the separation efficiency is very low and the residual parts will be wasted if one cannot find suitable use of it. Therefore, it is important to explore if the semiconducting nature of CNT could be tailored to be metallic to skip any difficult separations. In this part the authors presented a work done by using first principle calculations to study the adjustable conduction ability of semiconducting SWCNT (10, 0) with different number of copper chains adsorbed onto its periphery. It is a model to mimic a hybrid metallic nano wire. Copper is selected here because copper does not form a compound with carbon and the interaction between copper and CNT will not involve any chemical reactions.
4.2 Procedure of the Calculation

The electronic structure, and the transport properties of the Cu/CNT (10, 0) hybrid structure were performed by using the QuantumWise 2012/(ATK12.2.0) package[27, 41-43].

Figure 17 shows the unit cells and the two probe models of the hybrid CNT (10, 0) with different number of adsorbed copper chains (1, 4, 5 and 6, respectively), which are denoted as CNT-1Cu, CNT-4Cu, CNT-5Cu, and CNT-6Cu in descriptions below. There’re two copper atoms in each unit cell, and the copper atoms in each unit cell are twice the number of the absorbed copper chains. The pristine CNT is also investigated for comparison.

In all cases, the initial distance between Cu atoms and their nearest carbon atoms were set as 1.5 Å and all unit cells were then fully relaxed until the maximum force was less than 0.05eV/Å. In the geometry optimization process, the local density approximation (LDA) with the Perdew-Zunger (PZ) exchange-correlation functional[44] were employed. Sampling of 1×1×30 k points and double-zeta polarized (DZP) basis set were used for both the carbon atoms and the copper atoms.

The two probe models (Figure 17 right) were then constructed using the correspondent relaxed unit cell geometries (Figure 17 left).

The electronic structure and the transport properties were then calculated using the two probe model. In this calculation the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function[45] and a Monkhorst-Pack grid of 1×1×100 were used. A tolerance of 1×10⁻⁵ of the total energy was applied as the criterion for convergence during all calculations.
Figure 17 The optimized unit cells of the semiconducting (zigzag) CNT(10,0) adsorbed with different number of copper chains. The two probe models are constructed by the optimized unit cell. (a)(c)(e)(g) are the optimized unit cells of CNT(10,0) with 1,4,5,6 Cu chain(s) when viewed in the z axial direction, and (b)(d)(f)(h) are the two probe models constructed using the corresponding unit cells, viewed in the sidewise direction.
4.3 Results and Discussion

4.3.1 The Transmission Spectrum

The calculated transmission spectrum at zero bias for the pristine CNT (10, 0), CNT-1Cu, CNT-4Cu, CNT-5Cu, and CNT-6Cu are presented in Figure 18. According to Figure 18, a large transmission gap exists for the pristine CNT (10,0) with the gap value of 0.88eV. When a single copper chain is adsorbed on the CNT (CNT-1Cu), there is still a gap but the gap is reduced to 0.56eV. When 4 copper chains are adsorbed the gap is narrowed further to 0.28eV. Similarly when 5 copper chains are adsorbed the transmission gap is reduced to 0.16eV. Even the gap for CNT-5Cu is very small but it remains its semiconducting nature. Significantly, when 6 copper chains were adsorbed onto the CNT (10,0), the transmission gap is completely closed. This implies the semiconducting CNT (10, 0) has become metallic when 6 copper chains are adsorbed.
Figure 18 Transmission spectrum of (a) the pristine CNT (10,0); (b) the CNT(10,0) adsorbed with 1 Cu-chain; (c) the CNT(10,0) adsorbed with 4 Cu-chains; (d) the CNT(10,0) adsorbed with 5 Cu-chains; and (e) the CNT(10,0) adsorbed with 6 Cu chains.

4.3.2 The Band Structure

Figure 19 presented the band structure of the pristine CNT (10, 0) and CNT/Cu systems which shows a similar trend as the transmission spectrum. A large band gap is clearly seen in the pristine CNT(10,0), as shown in Figure 19. When a copper chain is adsorbed (Figure 19b), there is still a band gap but this gap is getting smaller than that of the pristine CNT. When four and
five copper chains are adsorbed onto the CNT(10,0), the gap between the conduction bands and the valence bands is getting even smaller (Figure 19c and Figure 19d, respectively). However, when 6 copper chains are adsorbed, both the conduction bands and the valence bands touch the Fermi energy level and the band gap disappears (figure 3e). Figure 19 also indicates that the more Cu chains are incorporated the more bands are generated in the band structure. The degeneration of the bands in Figure 19d is due to the symmetric structure of CNT-5Cu as presented in Figure 17e.
Figure 19 Band structures of (a) pristine CNT (10, 0); (b) CNT-1Cu; (c) CNT-4Cu; (d) CNT-5Cu; (e) CNT-6Cu.

Figure 19 indicates that the band structures of CNT(10,0) have been modified by the adsorption of Cu chains also in terms that the Fermi level has been shifted toward to the
conduction bands of the carbon nanotube. Similar behavior was also observed in the case when a single Cu chain was trapped inside a carbon nanotube[47]. The fact that the Fermi level is getting closer to the conduction band can be explained by the semiconductor theory. When copper atoms are adsorbed onto the semiconducting CNT, to retain the overall system as charge-neutral the excess electrons from the copper must reside in the conduction bands. To have access to electrons in the conduction band, the Fermi level must lie near the conduction band. More Cu atomic chain brings more extra electrons, which causes the more shift of Fermi level towarded the conduction band. In another word, the conduction band energy ($E_c$) becomes lower and lower as more copper atoms are adsorbed onto the semiconducting CNT.
Figure 20 The transmission gap and the Conduction Band Energy $E_c$ versus the number of adsorbed Cu chains. The red arrow indicates the suddenly change from the pristine CNT (10,0) to the CNT (10,0) adsorbed with one Cu chain.

Figure 20 shows the transmission gap and the conduction band energy ($E_c$) versus the number of adsorbed Cu chains. The conduction band energy is denoted as zero when the conduction band crosses the Fermi level. Figure 20 shows that as more Cu chains are adsorbed on the semiconducting CNT (10,0), it shrinks both the transmission gap and the conduction band energy in a similar trend. When 6 copper chains are adsorbed, both the transmission gap and the conduction band energy get to zero, and the semiconducting CNT (10,0) is transformed to metallic. The decreasing trend of both the transmission gap and the conduction band energy versus the number of the adsorbed Cu chains is almost linear (Figure 20).
4.3.3 Transmission Eigenstates

CNT(10,0) is semiconducting and it is not conductive at zero bias. In order to make sure that the conductance of CNT-6Cu is not only from the copper chains, authors have performed calculation of transmission eigenstates which provides a direct picture of the electronic states contributing to the conductance[48]. Figure21a shows the calculated transmission eigenstates at the Fermi level of the CNT-4Cu system. It indicates that there is no transmission eigenstate at the Fermi level, similar as that of the pristine CNT (10,0). However, when 6 copper chains are adsorbed, there is one transmission eigenstate at the Fermi level, as Figure21b shows. By examining this transmission eigenstate of the CNT-6Cu system, we found that the eigenstate is not only localized at the Cu chain locations, but the electronic states of carbon atoms also contribute to the system’s conductance (Figure21b), evidenced by electrons not only run through the Cu chains but also through the carbon nanotube. All parts of the Cu/CNT systems are conductive now. Therefore the adsorption of 6 copper chains indeed transforms the semiconducting CNT(10,0)–Cu system to metallic.

![Figure 21](image)

(a) CNT-4Cu  
(b) CNT-6Cu

Figure21 a) Transmission eigenstates at the Fermi level for the CNT-4Cu system.  
b) Transmission eigenstates at the Fermi level for the CNT-6Cu system.

4.3.4 The Mulliken Population

The contour views of the charge densities of the CNT(10,0)-Cu hybrid systems are shown in
Figure 22. For quantitative analysis, the authors have also done the Mulliken population analysis, since the Mulliken population of electrons of atoms are important characteristics associated with the bonding nature. The calculated Mulliken population of the carbon atom shows an increment of 0.00875e when 1 copper chain is adsorbed to the CNT(10,0). The Mulliken population of carbon atom is increased further to 0.034225e for the case of CNT-4Cu, and 0.039725e for the case of CNT-6Cu. Meanwhile, the Mulliken population for copper atom are reduced. The more copper chains are adsorbed, the less loss of Mulliken population of the copper atom. Specifically, the Mulliken population of the copper atom is reduced by 0.181e when 1 copper chain is adsorbed onto the CNT (10,0), and it is reduced by 0.1705e for CNT-4Cu and 0.1325e for CNT-6Cu, respectively. The change in the Mulliken population of copper atom versus the number of adsorbed copper chain is indicated in Figure 6e. On average, when 6 Cu chains are adsorbed, and the CNT (10,0) is transformed from semiconducting to metallic, the Mulliken population change of the carbon atom (increase) and the copper atom (decrease) are both about 1%. This small change in Mulliken population indicates no formed chemical bonds, but this charge transfer may enable the carbon nanotube to become conductive.
4.4 Comparison among Different Semiconducting CNTS

As a verification, the case of carbon nanotube(8,0) is also investigated. Figure 23 presented the unit cell and the two probe model of the hybrid CNT (8, 0) with 8 copper chains. Geometry relaxation and transport properties calculation were conducted, using the same parameter settings from the beforehand calculations. The transmission spectrum for CNT(8,0)-8Cu chains (Figure 24) shows that, when 8 Cu chains have been adsorbed, the Cu/CNT(8,0) system is also successfully transformed from semiconducting to metallic, with a transmission coefficient of approximately 4 at Fermi level.
Figure 23 The optimized unit cells of the semiconducting (zigzag) CNT(8,0) adsorbed with 8 copper chains. The two probe models are constructed by the optimized unit cell. (a) is the optimized unit cells of CNT(8,0) with 8 Cu chains when viewed in the z axial direction, and (b) is the two probe models constructed using the corresponding unit cells, viewed in the sidewise direction.

Figure 24 Transmission spectrum of the CNT (8, 0) adsorbed with 8 Cu-chains.

4.5 Conclusion
In summary, the adsorption of Cu chains could be used to modulate the electronic properties of semiconducting CNTs, in terms of narrowing the transmission gap, pulling down the conduction band, and transforming the semiconducting CNTs to metallic. These research results have also suggested that there is no needs to separate metallic CNTs from semiconducting ones to develope hybrid CNT/Cu nanowires or nanocomposites (see Figure 25), since the system with semiconducting CNT will be transformed to metallic after sufficient Cu atoms are adsorbed. For
the fabrication of conductive materials such as one-dimensional hybrid Cu/CNT nanowires, or three-dimensional CNTs-copper nanocomposites, all types of CNTs will behave metallic regardless of their chirality or nature (semiconducting or metallic). This finding is important to develop hybrid conductive nanowires and nanocomposites to achieve good electric conductivities at room temperature as desired electric conducting materials.

Figure 25 Sketch of a copper wrapped CNT in the form of a hybrid Cu-CNT nanowire or Cu-CNT composite in which no matter the CNT is metallic or semiconductor the CNT will be metallic in nature.
CHAPTER FIVE: THE INFLUENCE OF THE INTERACTION BETWEEN CNT AND CLAMPED CU CHAIN ON THE ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES OF CU-CLAMPED-CNT SYSTEMS

5.1 Introduction
Ever since carbon nanotube has been discovered about two decades ago, its remarkable properties have been found to be superior to that of metal in many aspects, mainly due to its highly perfect graphenic lattice. Carbon nanotube has good electronic properties like ballistic conductance, due to the overlap between the π bonds that extend normal to the carbon layers. Carbon nanotube also has enormous mechanical strength based on the strong σ bond between carbon atoms[40].

On the other hand, metallic nanowires have been developed and showed novel properties relative to corresponding bulk materials[49, 50]. Nanocrystalline copper shows the superelasticity or elastoplasticity at room temperature, while ZnO nanowire has a higher size-dependent Young’s modulus than that of bulk ZnO[49].

CNT filled with metal, however, is a novel one dimensional [51]nano composite in combining the good aspects of both CNT and metallic nanowire. Several techniques were developed in fabricating the CNT filled with metal: capillary action[40], wet chemical technique, in situ filling, chemical vapor diffusion, and plasma irradiation[49, 51]. CNT filled with metal has exhibited notable properties: Their small size promises potential applications in data-storage nanotechnology or as one dimension nanocable[52]. They are also interesting for electrical applications, by using the inside metal wire as the electron conductor[40]. The carbon shell plays
as an effective barrier against oxidation of the metal core and ensures its long-term stability[51, 52].

In another term, the introduction of metal wire inside CNT could lead to essential changes of the electronic properties of both the carbon nanotube and the metals[50]. The electronic transmission properties of such nanocomposites like Ni-encapsulated, and Ge-encapsulated CNTs are very different from that of bulk materials[49].

CNT filled with Copper has been prepared in several ways[53, 54], however, few research has been done on the electronic structure and transport properties of CNT filled with Cu. Xiu-Juan Du [52] et al have researched on the binding energies and electronic structures of a square close-packed Cu$_8$? nanowire encapsulated in semiconducting (n,0) CNT (n=11,13,14), while our research placed an emphasis on studying the semiconducting CNT(10,0) clamped with several Cu chains.

Matter has been proposed to exhibit extraordinary and unusual properties within a confined nanospace, which is quite different from the behavior in its normal bulk form[55]. Our assumption is that, Cu, since it showed excellent ability in tuning the electronic structure of CNT when adsorbed peripherally on carbon nanotube in our previous research, now it would show much better ability in tuning the electronic properties of semiconducting carbon nanotube when clamped inside a CNT.

The electronic structure, and the transport properties of the Cu/CNT hybrid structure were performed by using the Quantum Wise 2012/(ATK12.2.0) package[27, 41-43].
Figure 26 shows the unit cells and the two probe models of hybrid CNT (10, 0) with clamped copper chain (1, 4, 6 and 8 chain(s) respectively). The left side of Figure 26 shows the relaxed structure of each unit cell. Cu atoms were placed at around 1.5 Å away from nearest carbon atoms in all the cases, and then the unit cell is relaxed until the maximum force was less than 0.05eV/Å. Local density approximation (LDA) with the Perdew-Zunger (PZ) exchange-correlation functional[44] was employed in the geometry optimization process, and 1×1×30 k points sampling and double-zeta polarized (DZP) basis set were used for both the carbon atoms and the copper atoms. We constructed two probe devices based on the relaxed unit cell, as presented on the right side of Figure 26. For convenience, we denote each case as CNT-1Cu, CNT-4Cu, CNT-6Cu, and CNT-8Cu.

The electronic structure and the transport properties were then calculated using the two probe model in Figure 26. In this part of work the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[45], and a Monkhorst-Pack grid of 1×1×100 were used. A tolerance of 1×10^{-5} of the total energy was used as the convergence criterion.
Figure 26 The optimized unit cells of the zigzag CNT(10,0) clamped with different number of copper chains, and the two probe models constructed by the optimized unit cell. (a)(c)(e)(g) are the optimized unit cells of CNT(10,0) clamped with 1, 4, 6, 8 Cu chain(s), (b)(d)(f)(h) are the two probe models constructed by corresponding unit cell.
5.2 Electronic Structure

5.2.1 Band structure

Figure 27: The band structures for (a) CNT-1Cu; (b) CNT-4Cu; (c) CNT-6Cu; (d) CNT-8Cu. The left: free-standing Cu chain; middle: Cu@CNT; The right: distorted CNT.
Shown in Figure 27 are the band structures for (a) CNT-1Cu; (b) CNT-4Cu; (c) CNT-6Cu; (d) CNT-8Cu. As a comparison, the bandstructure of the distorted carbon nanotube, as well as the freestanding Cu chain have also been calculated. All in the left side are the bandstructures for the freestanding Cu chain, in the middle are the bandstructures for Cu@CNT, and in the right side are the bandstructures for CNT in each case. The geometry of the distorted CNT has been obtained by removing the Cu chain from the relaxed hybrid system. While the geometry of freestanding Cu chain is achieved by removing the CNT from the relaxed hybrid system.

As can be observed in Figure 27, there are still band gaps in all the distorted carbon nanotubes, indicating that their semiconducting character. However, the band gaps are mostly in a decreasing trend as the number of Cu chains increasing, as presented in Table 3.

Table 3 The band gap of CNT clamped with different number of Cu chains.

<table>
<thead>
<tr>
<th>Case</th>
<th>Band gap /eV</th>
<th>Band gap value /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-1Cu</td>
<td>[-0.332, 0.318]</td>
<td>0.65</td>
</tr>
<tr>
<td>CNT-4Cu</td>
<td>[-0.255, 0.248]</td>
<td>0.503</td>
</tr>
<tr>
<td>CNT-6Cu</td>
<td>[-0.031, 0.031]</td>
<td>0.0614</td>
</tr>
<tr>
<td>CNT-8Cu</td>
<td>[-0.047, 0.027]</td>
<td>0.0742</td>
</tr>
</tbody>
</table>

The bandstructure in CNT-1Cu is almost the superposition of CNT and Cu chain. However, as the number of Cu chains increasing, the CNT-Cu’s band structure is not simply the superposition of the two composition parts, which means there are interaction between the two components.

Secondly, severe degeneration appeared in CNT-6Cu case, which is in consistent with the fact that the bandgap of CNT-6Cu is symmetric. No severe degeneration has been shown in all other cases. After examining the structure of CNT(10,0)-6Cu unit cell (Figure 26(e)), we found that
after relaxation, the Cu atoms have formed two pentagons interlocking and connecting to each other. the 5 sides and the CNT(10,0) structure are almost symmetric, instead of others’ obvious asymmetric structure, that caused the severe degeneration in CNT-6Cu.

Thirdly, the CNT-Cu system’s bandstructure shows much of the characteristic of the distorted CNT, rather than that of Cu chain. It means that Cu chain is only tuning the electronic structure on the base of CNT.
A better insight into the electronic interaction between the CNT and the Cu chain is the density of states (DOS). The density of states of the Cu chain, the CNT (10, 0) and the coupled Cu/CNT systems are presented in Figure 28. In each part of the Figure 28, the DOS of a Cu-CNT system has been presented: the DOS for a distorted CNT (10, 0), the DOS for a free-standing Cu chain, and the DOS for the hybrid Cu/CNT system. As a comparison, the DOS of the pristine CNT (10, 0) is also presented.
The copper chain has created some additional states around the Fermi level, which enhances the conductivity of the system. After the encapsulation of Cu chain, since the high DOS of Cu around the Fermi level, the DOS of the system has been enhanced close to the value of Cu. An increased value of DOS at the Fermi level is found in every CNT (10, 0)/Cu system, even 1 Cu chain would modulate the system’s electronic properties from semiconducting to metallic, which is different from the situation when Cu chain is placed outside the carbon nanotube[56]. On the other hand, the integration of Cu chain doesn’t change the DOS of the CNT(10,0) around the Fermi level, which is staying zero, but the gap of CNT’s DOS gets shrank. This means that there is interaction between the carbon nanotube and the copper chain and this interaction modifies each other’s electronic structure.

5.2.3. Charge Density

Figure 29. The charge density for (a) CNT-1Cu;(b)CNT-4Cu;(c)CNT-6Cu;(d)CNT-8Cu.

The charge density contour of the CNT-Cu systems is presented in the Figure 29. The CNT-6Cu’s charge density contour presented a symmetric pattern, while other cases showed asymmetric character more or less. Generally speaking, the carbon nanotube circle in all the cases showed deformation as a result of Cu-CNT interaction, which can be regarded as strong
force inferred from the obvious deformation. The deformation in CNT-8Cu case is the most severe, while the adding of more Cu chain would cause the carbon nanotube’s graphenic structure to be broken.

The Carbon-Cu interaction can also be interpreted from the charge density contour on each carbon atom. In some carbon atoms closest to Cu atoms, the charge density contour on these atoms has deformed from oval to triangle due to the interaction with nearby Cu atoms. This phenomenon exists in all the CNT-1Cu, CNT-4Cu, CNT-6Cu, CNT-8Cu cases.
The local density of states (LDOS) at Fermi level ($E_F=0$) has been calculated for each case. Figure 30 presented the 3D isosurface illustration of LDOS. These figures clearly show that the LDOS spreads on both carbon nanotube and Cu chain. At the place where the curvature is small and where the carbon nanotube is flat, the local density of states (LDOS) appeared of a low value, while at the place with a large curvature, the LDOS appeared of a high value. This trend
apparently showed that the curvature has a strong relation with the distribution of LDOS and thus the electron transport[57].

In another aspect, the more Cu chain has been added into the carbon nanotube, the larger value the LDOS shows. It can be easily explained by the fact that more copper chains have introduced more electrons.

5.3 Transmission Spectrum

Figure31  Transmission spectrum of (a) pristine CNT (10,0); (b)CNT-1Cu;(c) CNT-4 Cu; (d) CNT-6Cu;(e)CNT-8 Cu.
The calculated transmission coefficients $T(E)$ at zero bias for each system has been calculated and presented in Figure 31. As a comparison, the transmission spectrum of pristine CNT (10, 0) is also presented. In each diagram, the black line indicates for the transmission spectrum for CNT-Cu systems, the blue line indicates for the transmission spectrum of Cu chain, while the red line indicates for the spectrum of the distorted CNT without Cu chain.

Table 4 Transmission Coefficient $T(E_f)$ Value for each component part

<table>
<thead>
<tr>
<th>Case</th>
<th>$T(E_f)$ for total</th>
<th>$T(E_f)$ for Cu part</th>
<th>$T(E_f)$ for CNT part</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-1Cu</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CNT-4Cu</td>
<td>4</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>CNT-6Cu</td>
<td>8</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>CNT-8Cu</td>
<td>9</td>
<td>6</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4 shows the transmission coefficient at Fermi level for each component of each system. Since the transport is ballistic in all these systems, the transmission coefficient could also be achieved from the band structure[48]. According to Figure 31, all the transmission gap is existing in all the CNT-Cu systems, indicating that the distorted CNT in these systems are still semiconducting. However, only the encapsulation of one Cu chain would cause the system’s transition from semiconducting to metallic. Encapsulation of more Cu chains would cause the transmission coefficient at Fermi level goes up to a high value.

The conductance of the system could be calculated via Landauer formula. In nano dimensions where the nanowire’s size is comparable to the electron mean free path, the transport could be viewed as ballistic, and according to the Landauer formula[13], the conductance of a nanowire is understood as electronic transport through channels and is calculated as a function of transmission probability for each channel of the nanowire[9].
\[ G = G_0 \times T \]  \hspace{1cm} (5.11)

Where \( G_0 = \frac{2e^2}{h} = \frac{1}{12.9k\Omega} \), and \( T \) is the transmission coefficient of the system. Thus the total conductance of the above Cu-CNT nanowires are \( 2G_0, 4G_0, 8G_0 \), and \( 9G_0 \) respectively. The conductance of each part can similarly be calculated according to (5.11) using the data from Table 4. From which we know that \( G(\text{total}) = G(\text{Cu}) + G(\text{CNT}) \), and thus the interaction between Cu and CNT are positive in improving the system’s conductance.

5.4 Conclusion

In summary, we employed the density functional theory in conjunction with NEGF approach to studied the electronic and transport properties of the zigzag \((10, 0)\) carbon nanotube (CNT) clamped with 1, 4, 6, 8 of Cu chains. The following conclusions are included:

(1) the band structure and the DOS of the free standing Cu chain, distorted carbon nanotube, and the CNT-clamped Cu system indicates that there’s interaction between CNT and Cu chain, which modifies each other’s electronic structure.

(2) The charge density contour intuitionally presents the interaction, which deforms both the tube wall and the charge density contour on carbon atoms.

(3) The LDOS isosurface plot presented the specific distribution of the interaction, that is, in the place with larger curvature, the LDOS has a larger value, and there’s a stronger interaction.

(4) The conductance value from the transmission spectrum proves the interaction synergistic for the system’s electronic properties, and the system has been changed with metallic character.
The Cu chain clamped within the carbon nanotube showed better efficiency in tuning the semiconducting CNT/Cu system’s electronic properties. The curvature may have influence on the system’s conductance too, which needs further investigation. This result is meaningful in nanoelectronic applications.
CHAPTER SIX: ELECTRIC RESISTANCE AND TRANSPORT STUDY OF CARBON NANOTUBE WITH A CU CHAIN: A FIRST PRINCIPLE CALCULATION

This chapter has used previously published materials of:


6.1 Introduction

Metallic carbon nanotube has been proven with a large current density capacity and a large electron mean free path. As a result, it has long been regarded as replacement to Cu interconnects. However, due to the low density of states in CNTs near the Fermi level, a single carbon nanotube has an intrinsic resistance of about $6.5 \, k\Omega$ [22], which is greater than copper and could cause excessive $RC$ delays of signals. Bundles of carbon nanotubes, since the parallel channels contributing to the conduction, have been proposed and experimentally proved as better interconnect to solve this problem [58-60]. However, carbon nanotubes alone cannot be used in practical application as actual device[61]. Metal on the other hand, could give carbon nanotube both as support and link with their environment. Therefore metal/carbon nanotube hybrid system would be a most important system in nanotechnology[40].

The successful fabrication of a continuous Titanium chain on carbon nanotube has corroborated the hope for CNT/metal system[62]. Carbon nanotube with a Titanium chain has
been proved to change its electronic structure and the metallic properties. It has been reported that the incorporation of a metal chain modifies the electronic structure of carbon nanotube via the charge transfer and the orbital hybridization[63-65].

In comparison with the Ti, Cu is also a transition metal with 3$d$ electrons that could interact with carbon nanotube. Our assumption is that Cu could generate delocalized states that could be in use of the carbon nanotube’s long mean free path capability, and thus produce a much higher conductivity in the hybrid material. Instead of using the parallel channel in CNT bundles, free electrons from Cu could contribute to the density of states (DOS) at the Fermi level, therefore contributing to the conductivity. It may therefore break the intrinsic ballistic resistivity limit of CNT.

Our research has found that Cu/CNT hybrid material could improve the conductivity of CNT as expected, and have studied the possible underlying fundamentals.

6.2 Calculation and Simulation Model

In this chapter, we present the Cu chain’s effect on the transport properties and conductivity in Cu/CNT/Cu junctions. As shown in Figure 32(a), the Cu/CNT/Cu junction has a CNT in the center, and two Cu electrodes in end contact with the central part. The CNT presented here are all CNT (5, 5). The length of CNT is more than 1 nm with about six unit cells. The Cu electrode consists of 5×5×4 Cu atoms. The distance between the electrode and the central part has been optimized[57, 65] with the equilibrium value of 1.71 Å. Our aim is to investigate the effects of Cu chain on the properties of Cu/CNT/Cu. As a result, a pure Cu chain was added onto the central part of CNT to form the Cu/CNT+Cu/Cu system as presented in the Figure 32(b). The central Cu/CNT part is geometry optimized before calculation.
Density functional theory and the Non-equilibrium Green function are employed to calculate the transport properties of our systems. The current that passes through the center region can be calculated by using the Landauer-Büttiker formula [66]:

\[ I(V_b) = \frac{2e}{h} \int_{\mu_L}^{\mu_R} dE (f_L(E, V_b) - f_R(E, V_b)) T(E, V_b) \]  

(6.12)

Where \( \mu_L \) and \( \mu_R \) are the chemical potential of the left and right electrodes, \( f_L(E, V_b) \) and \( f_R(E, V_b) \) are the Fermi-Dirac functions at the energy \( E \) under the bias \( V_b \) in the left and the right electrodes. The \( T(E, V_b) \) is the transmission coefficient.

The general gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) pseudoatomic potentials with double zeta basis sets were used. A tolerance of \( 1 \times 10^{-5} \) has been used as the energetic convergence criterion. For the two systems (with/without Cu chain), the \( k \) point samplings are both set as \( 3 \times 3 \times 100 \). The commercial software QuantumWise [27] has been used to perform all our calculations.
6.3 Results and Discussion

6.3.1 Transport Properties at Equilibrium

6.3.1.1 Transmission Spectrum at Zero Bias

The equilibrium conductance is related to the transmission coefficients $T(E)$ under zero bias\[66\]. In order to compare the equilibrium conductance, the transmission coefficients at the zero bias for the two different systems have been calculated as is presented in Figure 33. The black line represents the transmission coefficient of the Cu/CNT/Cu system, while the red line represents the transmission coefficient of the Cu/CNT+Cu/Cu system. The result of the Cu/CNT(5,5)/Cu junction presented in Figure 33 agree well with the reported \[65\] by others, although there’s minor difference on the device setup.
Figure 33 Transmission spectrums of Cu/CNT/Cu junction and Cu/CNT + Cu/Cu junction.

Figure 33 shows that the Cu chain has brought significant effect on the transmission coefficient of the Cu/CNT/Cu junction. In the vicinity of Fermi level, the transmission coefficient of the Cu/CNT/Cu system has been increased, which indicates that the conductance of the Cu/CNT/Cu system is also increased by incorporating Cu chain.

The equilibrium conductance for the two systems could be calculated by the following equation[41, 66]:

\[
G = \frac{2e^2}{h} T(E_f, V_b = 0V)
\]  

(6.13)

So the conductance of the two systems could be evaluated by using the transmission coefficients \(T\) at the Fermi level at the zero bias voltage. The \(T(E_f)\) for Cu/CNT/Cu is about 1.66304 here, while the \(T(E_f)\) for the Cu/CNT+Cu/Cu junction is about 1.779245. According to Eq. 6.13, we
could get the conductance for each system: $128.9 \mu S$ for the Cu/CNT/Cu junction, and $137.908 \mu S$ for the Cu/CNT+Cu/Cu junction.

By assuming the Cu/central part contact area is the cross section area of the carbon nanotube (the Cu’s contribution in area is ignored since it’s relatively small), and that the CNT’s wall thickness is the atomic diameter of the carbon atoms, then we could calculate the contact resistivity[67]: which is $4.596 \Omega \cdot \mu m$ for Cu/CNT/Cu, and $4.27 \Omega \cdot \mu m$ for Cu/CNT+Cu/Cu. Therefore the adding of Cu atoms has enhanced the Cu/CNT/Cu system’s equilibrium conductance at around 7%.

6.3.2 Transport Properties at Non-equilibrium

6.3.2.1 Current-voltage (I-V) Curve of the Two Probe Systems

Figure 34 shows the current-voltage (I-V) curve as well as the slope of the $I-V$ curve for the two-probe systems. The Cu/CNT + Cu/Cu system shows a higher conductance than that of the Cu/CNT/Cu system.

The $I-V$ curves at low bias show a linear behavior (Figure 34(a)) from which we can use the Ohmic law to calculate the conductance of the system. By averaging the data below 0.1V, we could calculate the conductance for the Cu/Cu+ CNT/Cu as $134.73 \mu S$, while the conductance for the Cu/CNT/Cu is about $127.05 \mu S$. The respective resistivity can also be calculated according to the cross section area of the contact. They are $4.371 \Omega \cdot \mu m$ and $4.635 \Omega \cdot \mu m$ accordingly. The resistivity calculated from I-V curve didn’t deviate much from the resistivity we got from the equilibrium condition.
Figure 34 Current-voltage (I-V) curve of the two-probe systems. (a) I-V curve. (b) Slope of I-V curve as a function of bias voltage.

All the data we have achieved have been presented in Table 5. Comparing the data we have achieved, one could conclude that the CNT+Cu composite has a greater conductance than that of the pure CNT at both equilibrium and low bias voltage cases, and the conductivity has been enhanced by 7.1% and 5.7% respectively.

Table 5 The conductance of the two probe systems

<table>
<thead>
<tr>
<th>Equilibrium state</th>
<th>Conductance/µS</th>
<th>Cu/CNT(5,5)/Cu</th>
<th>Cu/CNT(5,5)+Cu/Cu</th>
<th>Increasement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resistivity ρ/Ω·µm</td>
<td>128.9</td>
<td>137.908</td>
<td>7.1%</td>
</tr>
<tr>
<td>Non-equilibrium state</td>
<td>Conductance/µS</td>
<td>127.05</td>
<td>134.73</td>
<td>5.7%</td>
</tr>
</tbody>
</table>
|                   | Resistivity ρ/Ω·µm | 4.635 | 4.371 | |}

From Figure 34 we could also see that the I-V curve has an obvious slope transition in both cases. The I-V curve can be divided into three regions according to the slope change: from 0V-
1V (region I); from 1V-1.5V (region II) and from 1.5V-2.0V (region III). This transition could be more clearly seen in Figure34 (b): When entering region II, there’s an obvious slope transition occurring, and they occur almost at the same position in Cu/CNT/Cu case and Cu/CNT+Cu/Cu case. Among the three regions, the region I has the steepest slope. The decreased slope at the region I may be caused by phonons. At higher bias voltages, electrons would emit optic and zone-boundary phonons to cause efficiently backscattering. This would largely reduce the conductance of the carbon nanotube that has been reported in the literature[48, 68]. The increased slope in region III would be explained in the following discussion.

6.3.2.2 Transmissions of Different Bias Voltage for Two Probe Systems

The voltage dependent transmission spectra $T(E,V_b)$ for the two systems have been presented in the Figure 35. The two dotted lines in each diagram indicate the integral region between $\mu_L$ and $\mu_R$, as showed in the Landauer-Büttiker formula (equation 6.12)[41]. The transmission spectrums at different bias voltages have shown similar pattern as the equilibrium but increased as the effect of external bias voltage applied.
Figure 35 Transmission spectrum at different bias voltage for two-probe systems. (a) Cu/CNT/Cu system. (b) Cu/CNT+Cu/Cu system.

As indicated in Figure 35 for the two systems the first transmission peak occurs when both sides of $E_f$ enters the integration area at about 1.5V, which would generate the rapid current rise in the region III of Figure 35. This may explain the increased slope in that region. While the backscattering phonons cause the reduction of the conductance, the rapid increased current coming from the transmission integral area would fling up the slope.

6.3.3 Transmission Eigenstates at the Fermi Level

Transmission eigenstates indicate the electronic states that contributes to the conductance[48]. By performing the eigenstates analysis, we found that there’re two main transmission eigenstates for the Cu/CNT/Cu system, and three transmission eigenstates for the Cu/CNT+Cu/Cu system. Since the whole central parts in both devices are metallic, we could just analysis the transmission eigenstates at the Fermi level. Figure 36a & Figure 36c present the
primary transmission eigenstate for the Cu/CNT/Cu in the form of isosurface and contour, while Figure 36b and Figure 36d present the primary transmission eigenstate for the Cu/CNT+Cu/Cu in corresponding forms. From Figure 36, we found that the eigenstate for the pure CNT were distributed evenly over the whole nanotube, while the eigenstate for the CNT/Cu case were mainly concentrated in the region consists of Cu and carbon nanotube. The interaction between Cu and CNT can be seen clearly from Figure 36b and Figure 36d. It is suggested that the electrons pass the system mainly via the interaction region between the Cu chain and the CNT. This interaction between Cu and CNT could be responsible for the increased conductance of the Cu/Cu+CNT/CNT system. Our analysis of all the other eigenstates denotes the similar pattern as the main eigenstate presented here.
6.4 Conclusion

Using the non-equilibrium Green’s function in conjunction with DFT, we have obtained the current-voltage characteristics for the Cu/CNT/Cu junction and the Cu/CNT+Cu/CNT junction. Our calculations have shown that by incorporating Cu atoms into Cu/CNT/Cu system, a system with an enhanced conductance under both equilibrium and non-equilibrium condition has been achieved. The interaction between the Cu and the CNT has enhanced the system’s conductance by around 7%. The features explored here may benefit the future NEMS systems such as to significantly increase the conductivity of interconnects in nanoscale.
CHAPTER SEVEN: THE EFFECT OF END GEOMETRY ON THE ELECTRICAL CONTACT RESISTANCE OF THE CARBON NANOTUBE (10, 0)/CU INTERFACES

7.1 Introduction

Carbon nanotubes (CNT) [37] have exhibited exceptional mechanical properties like ultra high strength, stiffness[16], and Young’s modulus [1] plus the extraordinary resilient properties. However, for the electric conduction it varies between metallic and semiconducting. Metallic carbon nanotube has shown excellent electrical properties like a large current carrying capacity[69], mainly due to its large mean free path and ballistic electronic transport properties[5]. Metallic CNT is thus a good building block for developing conductive composites or as conductors/interconnects in nanoelectronic applications[9].

Cu/CNT/Cu sandwiched structure is a popular structure ever since its built up. This structure is important because in reality, an individual semiconducting CNT is widely used either as a conventional metal-oxide-semiconductor field-effect (MOSFET) transistor, or as an unconventional Schottky barrier transistor where it forms a contact with a metal electrode[70]. The contact resistance between CNTs and metal electrodes is a key issue prevalent practical applications[71]. The interaction between the carbon nanotube and the metal electrodes is important for the performance of the potential electronic device.

The details of the interface geometry are believed to strongly affect the nature of the contact[57]. In our research, we found that by tailoring the end structure of a semiconducting carbon nanotube, the CNT/Cu’s contact resistance would be largely affected. The open ended geometry in a semiconducting CNT can enhance the system’s conductance even more beyond
that of the metallic CNT system. Tailoring the semiconducting CNT thus could be a possible way to get rid of separating different types of CNT, to break the conductivity limit of semiconducting CNT, and can even find its applications on nanoelectronic device since its good electronic properties. Similar results have been achieved on (8, 0) and (10, 0) SWCNTs, and thus could be generalized to all the semiconducting carbon nanotubes. Then we selected the CNT (10,0)/Cu system as a representative, and tried to find out the difference between the close and open ended semiconducting CNT/Cu systems. The CNT (5, 5)/Cu system has been examined all the way as a reference.
7.2 Geometry Configuration

Our calculations were conducted on a two-probe structure consisting of a center part sandwiched between two Cu electrodes. The center part is consisted of a semiconducting SWCNT adsorbed with a Cu chain. The Cu chain was added to ensure and enhance the systems’ conductivity as in accordance with our formal research. The CNT is approximately 1.1~1.2 nm in length and it has an end as generated, which we define as the “close end”. After tailoring the carbon atoms at the end, we get an end structure with dangling bonds, and we define this type of end as the “open end”. As an illustration, the open end and the close end are circled in red in Figure 37. We have examined two semiconducting groups: CNT (10, 0) and CNT (8, 0), with a Cu chain in the center part. In each group we studied both the open end and the close end cases.

A similar two probe device with a metallic CNT (5, 5) and a copper chain in the center is also calculated as the reference. CNT (5, 5) has an armchair chirality and because of the way the graphene sheet has been rolled, it doesn’t have the open/close ends difference as in semiconducting nanotube. All the Cu/CNT central parts are geometry optimized before calculations.

The Cu electrode consists of 5×5×4 atoms. The distance between the electrode and the central part has been optimized [57, 65] before the calculation. The general gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) pseudo atomic potentials with double zeta basis sets were used. A tolerance of 1×10⁻⁵ has been used as the energetic convergence criterion. For the two probe systems, the k point samplings are set to as 3×3×100. The commercial software QuantumWise [27, 41-43] has been used to perform all our calculations.
Figure 37 Typical structure of two-probe device with different CNT and Cu chain sandwiched between two Cu electrodes.
7.3 Results and Discussion

7.3.1 LDOS

To understand the interactions between the C and Cu atoms at the interface, the local density of states (LDOS) at the Fermi level was calculated. The color scales used in all the pictures in Figure 38 are the same. Overall, the LDOS are significantly increased at the end where CNT and Cu electrodes are close to each other. Due to the CNT-Cu interaction at the interface, the isosurface of LDOS showed different shape. As can be seen in Figure 38, the LDOS of the semiconducting tube with the open ends ((c) , (e)) have a larger LDOS than the semiconducting tube with the close ends((b), (d)). This larger LDOS value exists not only in the end contact but also in the carbon nanotube bulk, which implies a more active electron transport in the open ended two probe device[67].
CNT(5,5) system also has a different shape at the end contact similar to that of all semiconducting cases, however, CNT(5,5) doesn’t have the strong electron transport as semiconducting ones with the open ends, and the LDOS only concentrated at the contact interface, instead of spreading everywhere.

7.3.2 Transmission Spectrum

Figure 39 presented the transmission spectrum at zero bias voltage for the five different systems. It is found that, at the Fermi level, the \( T(E) \) fall into three groups: the \( T(E) \) of
semiconducting CNT with open ends are on the top, while the $T(E)$ of semiconducting CNT with
the close ends are at the bottom, as the reference, the metallic CNT system’s $T(E)$ lies in the
middle. For the two-probe system, the equilibrium conductance $G$ has a relation with the
transmission coefficients $T(E)$ at the Fermi level under zero bias voltage[66].

$$G = \frac{2e^2}{h} T(E_f)$$  \hspace{1cm} (7.14)

From Eq.(7.14), higher $T(E_f)$ indicates a higher conductance, so the open ended
semiconducting systems (CNT(10,0) and CNT(8,0)) have a top conductance, while there’s a
lowest conductance for the close ended systems (CNT(10,0) and CNT(8,0)). The CNT (5,5)’s
transmissibility and thus conductance lies in the middle, not on the top of all as commonly
expected. The open/close end geometry should play an important role in the system’s
conductance, even beyond the importance of the CNT’s chirality.
Since CNT (10, 0) and CNT (8,0) systems showed similar properties, we will focus on CNT(10,0) system representing all the semiconducting CNT systems. The electronic transport properties of CNT (10, 0) system with the open/close ends, and the CNT (5,5) system will be examined in the following part.

Further calculations of the transmission spectra at various bias voltages have showed the same trend as at the zero bias. It is seen in Figure 40 that the transmission spectrum has a relation with the applied bias voltage. On the other hand, overall, the CNT (10, 0) system with the open ends has a higher transmissibility, the CNT (5, 5) has a lower transmissibility, while the CNT (10,0)
system with the close ends has the lowest transmissibility among the three, which is in consistent with the results shown in Figure 39 at the zero bias.

(a) CNT \((10,0)\) with open end
(b) CNT \((10,0)\) with close ends
(c) CNT \((5,5)\)

Figure 40 Transmission Spectrum at different voltage bias
7.3.3 I-V Curve

In order to compute the Cu/CNT contact resistance, the I-V curve of the two probe system is needed. The current that passes through the center region can be calculated by using the Landauer-Büttiker formula[15]:

\[
I(V_b) = \frac{2e}{h} \int_{\mu_L}^{\mu_R} dE (f_L(E, V_b) - f_R(E, V_b)) \cdot T(E, V_b)
\]  

(7.15)

Where \(\mu_L\) and \(\mu_R\) are the chemical potential of the left and right electrodes, \(f_L(E, V_b)\) and \(f_R(E, V_b)\) are the Fermi-Dirac functions at the energy \(E\) under the bias \(V_b\) in the left and the right electrodes. The \(T(E, V_b)\) is the transmission coefficient. This equation relates the conductance to the transmission probability \(T(E, V_b)\) we have calculated in Figure 40.[57]

The corresponding I-V curves for CNT (10, 0) system with open the ends and the close ends, as well as the CNT (5, 5) system have been presented in Figure 41. From Figure 41, under the lower bias, all of the I-V curves are linear and obeying the Ohmic law. Under higher bias, the CNT (10, 0) system with the close end shows a semiconducting characteristic with a sharply increasing the slope after the point of 1.0V. The CNT (10, 0) system with the open ends shows a negative differential resistance after the transition point. The negative slope of I-V curve for CNT (10, 0) with the open ends may be explained from Figure 41(a), because the transmission spectrum moved downward at the higher voltage bias (1V), and the resonance peak entering the integration range is descending after 1V.
By averaging the data below 0.1V on the I-V curve[57, 65], we got the total conductance of the Cu/CNT(10,0)+Cu/Cu system as 342.47 µS for the open ended system, and 31.71 µS for the close ended system. The conductance of the Cu/CNT(5,5)+Cu/Cu system is 134.73 µS (Table 6).

By assuming the Cu/central part contact area is the cross section area of the carbon nanotube (the Cu’s contribution in the area is ignored since it’s relatively small), and that the CNT’s wall thickness is the atomic diameter of the carbon atoms, then we could calculate the contact resistivity[67]. The corresponding contact resistivity is 2.024 Ω·µm for the CNT(10,0) system with the open end, 23.208 Ω·µm for the CNT(10,0) system with the close end, and 4.371 Ω·µm.
for the CNT(5,5) system (Table 1). The results for CNT(5,5) system are in the similar as the transmission spectrum (equilibrium/non-equilibrium) calculated by other researchers.

Table 6 The conductance of the two probe systems

<table>
<thead>
<tr>
<th></th>
<th>CNT (10,0) with open end</th>
<th>CNT (10,0) with close end</th>
<th>CNT (5,5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductance/µS</td>
<td>342.47</td>
<td>31.71</td>
<td>134.73</td>
</tr>
<tr>
<td>Resistivity ρ/Ω·µm</td>
<td>2.024</td>
<td>23.208</td>
<td>4.371</td>
</tr>
</tbody>
</table>
7.3.4 MOP/Transmission Eigenvalues

To characterize the bonds between CNT and Cu electrode and fully understand the transmission spectrums presented, the Mulliken overlap population (MOP) and the transmission eigenvalues at the Fermi level have been calculated. The Mulliken population separates the electron density into atomic contributions, and the Mulliken overlap population (MOP) indicates the chemical bonds between each atoms qualitatively[72]. Figure 42 presented the MOP for all the three two probe systems. It is seen that the Cu-C bond is formed at the Cu/CNT interface in all three systems. The CNT(5,5) system shows a stronger bond than the other two cases at the interface. (Thicker lines mean the higher bond strength.) The chemical bonds between the dangling carbon atoms in CNT(10,0) with the open end formed a circle, which is different from that of CNT(10,0) with the close end. This loose bond circle may cause the electrons move more freely between the carbon atoms and the Cu electrodes, as well as between carbon atoms themselves.
The transmission eigenvalues and the corresponding transmission eigenstates have similar trend as MOP and LDOS. According to the transmission eigenvalue analysis, the transmission eigenstates at the Fermi level is 3 for the CNT(5,5) system, 7 for the CNT(10,0) with the open end, and 1 for the CNT(10,0) system with the close end, in correspondence to the value of order of $T(E_f)$ we calculated. Since the transmission eigenstates indicates the electronic states that contribute to the conductance[48], the more eigenstates may prove more active electron transport.
in the CNT(10,0) with the open ends, and thus causes a higher $T(E)$ either in equilibrium, or in non-equilibrium cases.

The typical transmission eigenstate for each case is shown in Figure43. As one can see, the eigenstate of CNT(5,5) is spreading over both CNT and Cu chain, which means that both Cu and CNT are contributing to the conductance, but a lot of electrons are concentrated on the Cu chain. The CNT(10,0) system with the close end also exhibits anti-symmetric $\pi$-orbitals as CNT(5,5) does, but the eigenstates shows a strong asymmetry on both ends, which means bad contact is formed at least in the one end. The eigenstates of CNT(10,0) with the open ends appeared as $\pi$-orbitals, but it shows strong coupling effect between the CNT/Cu interface, as well as between the carbon atoms in the end. On the other hand, the Cu chain doesn’t play the major role here as in the CNT(5,5) case. The transmission eigenstates spread more evenly at the CNT and Cu body part, and a little more concentration is formed at the Cu/CNT interface. This uniform eigenstate distribution and the good contact at the interface may account for the fact that the CNT(10,0) with the open ends has the highest conductivity.
Figure 43 Transmission eigenstates of Cu/CNT+Cu/Cu two-probe systems
7.4 Conclusion

Our simulations show that the end geometry significantly affects the resultant contact resistance. The open ended CNT(10,0)/Cu contact has a lowest resistivity of 2.024 $\Omega \cdot \mu$m, which is half of that of the CNT(5,5)/Cu contact. These results show the feasibility of semiconducting CNTs like CNT(10,0) or CNT (8,0) can replace or even outperform the metallic CNT in electronic devices, simply by tailoring its end geometry.
CHAPTER EIGHT: ELECTRONIC STRUCTURES AND THE TRANSPORT PROPERTIES OF CARBON NANOTUBES ADSORBED WITH AL CHAINS

8.1 Introduction

As one of the three traditional conducting material, Al has long been used as the interconnects metallization on integrated circuit (IC) in the semiconductor industry. However, since the late 1990s, Cu has replaced Al with its higher conductivity, improved electro migration performance and the reduced cost of manufacturing[7, 74]. As the feature size keeps shrinking, the copper interconnects are also suffered from its relatively low electro migration resistance, and Cu/CNT composite nanowires have been proposed as a replacement of Cu.

Our previous calculation shows that copper could tune CNT from semiconducting to metallic, so that the distinguishing/separation metallic CNTs from semiconducting ones could be unnecessary. Cu/CNT composite has thus become a more feasible alternative as a novel interconnects building blocks which will benefit the VLSI.

However, when happens with the case of Al/CNT? Our results have shown that Al has an unexpected better ability in tailoring the electronic structure of CNT than Cu, disregard of its relatively lower conductivity. Our research proves that when the same amount of metal atoms is adsorbed on to a semiconducting CNT, the Al/CNT composite has showed superior conductivity.

We choose a single wall carbon nanotube (10, 0) for this study, and adsorb it with two, four and six aluminum chains and to determine how many aluminum atoms will bring about the transition of the CNT from the semiconducting to metallic.
The electronic structure and the transport properties of the Al/CNT hybrid structures were calculated by using the QuantumWise 2012/ (ATK12.2.0) package[27, 41-43]. Figure 44 shows the relaxed unit cells and the two probe models of hybrid CNT (10, 0) and adsorbed aluminum chain (2, 4 and 6 chains respectively) used in our calculations. The unit cells consist of four, eight and twelve aluminum atoms and a primitive tube cell, respectively. The initial distance between Al atoms and its nearest carbon atoms were kept at around 1.5 Å. All unit cells were then fully relaxed until the maximum force was less than 0.05eV/Å. The two probe models are constructed by using the relaxed unit cell geometries. For convenience, we denote each case as CNT-2Al, CNT-4Al, and CNT-6Al, respectively.

In the geometry optimization process, the local density approximation (LDA) with the Perdew-Zunger(PZ) exchange-correlation functional[44]was employed. 1×1×30 k points sampling and the double-zeta polarized (DZP) basis set were used for both the carbon atoms and the aluminum atoms.

The electronic structure and the transport properties were then calculated in using the two probe model shown in Figure 44. In this part of work the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional[45], and a Monkhorst-Pack grid of 1×1×100 were used. A tolerance of $1\times10^{-5}$ of the total energy was used as the convergence criterion.
Figure 44. The optimized unit cells of the zigzag CNT(10,0) adsorbed with different number of aluminum chains, and the two probe models constructed by the optimized unit cell. (a)(c)(e) are the optimized unit cells of CNT(10,0) with 2,4,6 Al chain(s), (b)(d)(f) are the two probe models constructed by corresponding unit cell.

8.2 Electronic Structure

Figure 45 shows the band structure of CNT (10, 0) adsorbed with 2, 4 and 6 Al-chains. The band structure for the pristine CNT(10,0) is also presented for the comparison purpose. Band gaps are observed for both the pristine CNT and the CNT-2Al cases. However, after two Al chains have been absorbed, the band gap has been shrank from [-0.44eV, 0.44eV] in the pristine CNT (10, 0) to [-0.26eV, 0.16eV] in the CNT-2Al system. More adsorption of Al chains (4 chains) has eventually closed the band gaps, and has transformed the CNT-Al system from the semiconducting to metallic. Three bands are going across the Fermi level in CNT-4Al, while seven bands are going across the Fermi level in CNT-6Al. As can be seen from Figure 45(d), the
6 Al chains have generated denser bands and therefore more bands are going across the Fermi level.

Figure 45. Band structures of (a) pristine CNT (10,0); (b) CNT(10,0) adsorbed with 2 Al-chains; (c) CNT(10,0) adsorbed with 4 Al-chains; (d) CNT(10,0) adsorbed with 6 Al-chains.

8.3 Transmission Spectrum

Figure 46 shows the transmission spectrum at the zero bias for the two-probe CNT-2Al, CNT-4Al, CNT-6Al systems, respectively. As a comparison, the transmission spectrum of the pristine CNT(10,0) is also provided. The Fermi levels were set to zero in all cases. According to Figure 46, a transmission gap exists for both the pristine CNT (10, 0) and the CNT-2Al system, which indicates that the two systems remain as semiconducting. However, after two aluminum chains are absorbed, the transmission gap has been significantly shrank from [-4.4eV, 4.4eV] to [-
0.08eV, 0.08eV]. The transmission gap closed up for the CNT-4Al, meanwhile whose transmission coefficient at the Fermi level has been increased to 3. As for the CNT-6Al case, the transmission coefficient has been raised to 7. Since the transport in our systems can be considered as ballistic, the transmission coefficient at the Fermi level can be also obtained by the band structures[48]. The transmission coefficient at the Fermi level is corresponding to the number of bands going across the Fermi level in each case.

![Transmission spectrum of CNT](image)

Figure 46  Transmission spectrum of (a)pristine CNT (10,0);(b)CNT(10,0) adsorbed with 2 Al-chains;(c) CNT(10,0) adsorbed with 4 Al-chains; (d) CNT(10,0) adsorbed with 6 Al-chains.
8.4 Conductivity of Al/CNT Compared with Cu/CNT at Fermi Level

According to the Landauer Büttiker formalism[13], since the CNT/Al hybrid nanowires could be regarded as ballistic, the conductance of a CNT/Al hybrid nanowires can be calculated according to the equation shown below:

\[
G = G_0 * T
\]

(8.16)

Where \(G_0 = \frac{2e^2}{h}\), and \(T\) is the transmission coefficient of the system. From the value we get in Figure 46, we could calculate the resistivity for each system and the results are listed in the following table:

<table>
<thead>
<tr>
<th>System</th>
<th>Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT+4Al</td>
<td>1.058 (\mu\Omega\cdot m)</td>
</tr>
<tr>
<td>CNT+6Al</td>
<td>0.4537 (\mu\Omega\cdot m)</td>
</tr>
<tr>
<td>CNT+6Cu</td>
<td>3.176 (\mu\Omega\cdot m)</td>
</tr>
</tbody>
</table>

From the table above we could see that the CNT/Al systems have a much lower resistivity than that of the CNT/Cu system. Among all three systems, the CNT (10,0) with 6 Al chains has the lowest resistivity of 0.4537 \(\mu\Omega\cdot m\); while the system of CNT (10,0) with 6 Cu chains has the highest resistivity of 3.176 \(\mu\Omega\cdot m\), which is about 7 times larger than that of the CNT-6Al system. The CNT-4Al system, even less Al atoms are adsorbed, still has about 2 times lower resistivity than that of the CNT-6Cu case. These results have proven that Al has a higher efficiency than copper in increasing the conductivity of the semiconducting CNTs. On the other hand, more Al atoms played a better role in the conductivity enhancement, as can be seen from results shown in Figure 46 and Table 7.
8.5 Transmission Eigenstates

The transmission eigenstates provide a direct picture of the electronic states that contribute to the conductance[38, 75]. From this point of view we are going to analyze what has caused the increase in the conductivity of the CNT-Al systems.

Considering the system has been transformed from the semiconducting to metallic after absorbing 4 Al chains, we only analyze the transmission eigenstates at the Fermi level for the two metallic systems: CNT-4Al, and CNT-6Al. By performing the transmission eigenvalue analysis at the Fermi level, we have found that the number of eigenstates of the CNT-4Al is 3, while the number of eigenstates of the CNT-6Al is 7, which are the same as the transmission coefficient of each system at the Fermi level, as well as the respective number of bands crossing the Fermi level.

The transmission eigenstates at the Fermi level for both systems are presented in Figure 47. The Figure 47(a)(b)(c) are the eigenstates for the CNT+2Al system. In the first two of them((a)(b)), the electron states are focused on two of the four Al chains, which are closer to each other in all the four chains. While in the last one((c)), the electron states spread on both the carbon nanotube and the Al chains. Thus, the CNT (10, 0) is typically metallic when four Al chains are absorbed.

For the CNT-6Al, we have found that all the seven transmission eigenstates spreading on both the CNT and Al chains: they are not only localized on Al chains. That implies the electronic states of the CNT also contribute to the system’s conductivity. The CNT-6Al system is definitely more metallic too.
Figure 47. Transmission eigenstates of (a)(b)(c)CNT(10,0) adsorbed with 4 Al-chain;(d)-(j)CNT(10,0) adsorbed with 6 Al-chains.

8.6 Charge Density

Figure 48 shows the contour plots of the electron density distribution of a slice through carbon atoms and the adsorbed Al atoms. As a reference, the electron density distribution of the pristine CNT (10,0) is also presented. As can be found from Figure 48, the electron density is delocalized and distributed on both the aluminum and the carbon atoms. In some carbon atoms nearest the Al
atoms, the charge density contour on these atoms has deformed from the oval to the triangle in shape due to the interaction with the nearby Al atoms. The contour view shows that Al atoms are also deformed, but due to the low electron density of Al atoms, it doesn’t appear as clearly as that of the carbon atoms.

Figure 48 Electron density distribution of CNT/Al systems. (a) CNT(10,0) adsorbed with 2 Al-chains; (b) CNT(10,0) adsorbed with 4 Al-chains; (c) CNT(10,0) adsorbed with 6 Al-chains; (d) pristine CNT (10,0).

8.7 Mulliken Overlap Population

To characterize the bond between the metal and the carbon nanotube, the Mulliken Overlap Population has been computed. The Mulliken overlap population is to separate the electron density among atomic contributions[57]. The MOP was then plotted with an open-source Java viewer Jmol[73]. To compare with our former research, we have also plotted the MOP for Cu/CNT systems. The MOP results are presented in Figure 49. Thicker lines represent the higher bond strength[67].

As can be seen from Figure 49, the Al atoms have formed chemical bonds with the CNT in all the cases, while the Cu atoms only show a very weak bond with the CNT in the CNT-6Cu case. This is reasonable considering the fact that Al has a better chemical reactivity with C than Cu. Al
can form an aluminum carbide with carbon when heated to 1000°C[76] while no copper carbide has been observed in the scientific community.

Figure 49 Mulliken Overlap population of CNT/Cu and CNT/Al systems. (a)(b)(c) are CNT/Al system, and (d)-(g) are CNT/Cu system. (h) is the pristine CNT as a reference.

8.8 Conclusion

In summary, our research has investigated the electronic and transport properties of CNT adsorbed with different number of Al chains in using the DFT in conjunction with the NEGF. The following conclusions are obtained:
(1) With 4 Al chains adsorbed onto the carbon nanotube (10, 0), the CNT/Al system could be transformed from the semiconducting to metallic. In comparison to the case of Cu atoms, Al atoms show more efficiency (7 times) in tuning the system’s conductivity. More Al atoms would cause more increase in the system’s conductivity too.

(2) The analysis results about the transmission eigenstates have proved the typical metallic structure in CNT/Al systems, while the MOP and the charge density analysis have also proved that Al could not only interact but also form bonds with C, which is a unique character of Al. This may be accountable for its better improvement in the system’s conductivity than that of Cu case.
CHAPTER NINE: CONCLUSION

Carbon nanotube, although it has excellent electrical and mechanical properties, itself has inherent limitations for practical applications as we have illustrated in the introduction: 1) an individual carbon nanotube has a low density of states at the Fermi level, and thus its resistivity is only comparable to that of copper. 2) Metallic and semiconducting tubes are usually mixed together as received from synthesis, and the selection/separation is very difficult with a low efficiency. 3) For most cases carbon nanotubes alone cannot be used in practical applications as the actual devices.

In recent researches metal/carbon nanotube hybrid materials have been proposed as an alternative solution. In our idea, Cu could generate delocalized states that could be in use of the carbon nanotube’s long mean free path. By doing this it may therefore break the intrinsic ballistic resistance limit of CNT and produce a much higher conductive material.

In this dissertation we basically provide a feasible solution to overcome carbon nanotube’s intrinsic limitations by either encapsulate copper atomic chains into it, or by adsorbing copper atomic chains peripherally on it. Both methods are able to effectively transit the semiconducting carbon nanotubes into metallic, or enhance the metallic carbon nanotube’s conductance to a higher level. Further study shows that Al has a better efficiency in tailoring carbon nanotube’s electronic structure: the same amount of Al atoms would cause a larger content of the increase in the conductance.

Considering the actual situation in applications, we have done a research on the Cu/CNT/Cu junction that is modeling the metal in contact with a carbon nanotube in mimic a realistic
electronic device. On this junction, we have modulated its conductance by adding a copper atomic chain onto the conducting carbon nanotube. The result is ideal and the system’s conductance has been enhanced. Copper atoms have the ability to improve the CNT system’s conductance, which verifies our idea from the result: If copper can utilize carbon nanotube’s long mean free path, then a high conductive material would be possible. Now we get a higher conductive material, but why is that? Is it coming from the copper’s free electrons or something else? Further analysis is therefore conducted to figure it out.

The copper-carbon atoms’ interaction is obvious and strong in each case. The electrons can pass through the structure not only via the copper chain, but also through the carbon nanotube itself, no matter it is semiconducting or metallic. These interactions may be accountable for the increased conductance. In this term it may also explain why Al has a better efficiency because Al has freer electron density than copper and it is also more reactive with carbon. Further analysis of the current density may give a more explicit proof, which is still ongoing.

Through the way of research, an interesting phenomenon is found accidently, which gives rise in conductance as discussed in chapter 7. The end geometry can give such a profound effect that it enables the semiconducting CNT group exceed the metallic CNT group in terms of conductance. This is indeed possible, since the only difference between the semiconducting and the metallic CNTs is their way of rolling.

In a summary, our research results provide solutions to skip the difficult CNT selection process, either by encapsulation or adsorption, or even by tailoring CNT’s end geometry, to use CNTs wisely with the enhanced conductance. The performance of CNTs under various
conditions has been examined. Metal atoms especially copper should be very useful in tailoring CNT based hybrid nanomaterials’ electronic properties, via the effective interaction between the CNT and the interacted metal layer or matrix.

Carbon nanotube and graphene have been the hottest new material in the last 20 years. However, there’re still a lot of fundamental things that haven’t been clarified. Due to the limitation in experimental approaches, computational material research provides an intuitive way to understand those deep rules, but one should have a clear direction in mind. In our research, generally speaking, the next step should go deeper and more fundamental:

(1) Besides the current density we are still working on, we need to find out better ways to present the actual picture between Cu-C interactions.

(2) To prove if electrons from Cu are actually moving in the conduction channels of carbon nanotube, and how are they exactly moving.

(3) Explore other ways to see if CNT-Cu hybrid structure’s conductance can be increased further.

(4) Explore other metals than Cu, like Al and Ag, and study the resultant conductance of metal-CNT hybrid structures.

(5) Expand our work to graphene related devices.

The work on Carbon nanotube and graphene has a lot of space for one to explore, observe and discover. As a low dimensional material, they should bring us unexpected new properties which can be observed beforehand on computer. The interaction with other materials, its own structure
change due to the interactions, etc, any of them will give rise to exciting results. In the future, I hope someone who has interests either in carbon based materials with computational and experimental studies, could get more findings soon in these areas
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